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Numerical Investigation of Chaotic Dynamics in Multidimensional Transition States

by

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in the

Faculty of Science Department of Mathematical Sciences

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"Geometry is not true, it is advantageous."

Henri Poincaré

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Abstract

Faculty of Science, Department of Mathematical Sciences

by Ali Ibraheem Allahem

Many chemical reactions can be described as the crossing of an energetic barrier. This process is mediated by an invariant object in phase space. One can construct a normally hyperbolic invariant manifold (NHIM) of the reactive dynamical system which is an invariant sphere that can be considered as the geometric representation of the transition state itself. The NHIM has invariant cylinders (reaction channels) attached to it. This invariant geometric structure survives as long as the invariant sphere is normally hyperbolic. We applied this theory to the hydrogen exchange reaction in three degrees of freedom in order to figure out the reason of the transition state theory (TST) failure. Energies high above the reaction threshold, the dynamics within the transition state becomes partially chaotic. We have found that the invariant sphere first ceases to be normally hyperbolic at fairly low energies. Surprisingly normal hyperbolicity is then restored and the invariant sphere remains normally hyperbolic even at very high energies. This observation shows two different energy values for the breakdown of the TST and the breakdown of the NHIM.

This leads to seek another phase space object that is related to the breakdown of the TST. Using theory of the dividing surface including reactive islands (RIs), we can investigate such an object. We found out that the first nonreactive trajectory has been found at the same energy values for both collinear and full systems, and coincides with the first bifurcation of periodic orbit dividing surface (PODS) at the collinear configuration. The bifurcation creates the unstable periodic orbit (UPO). Indeed, the new PODS (UPO) is the reason for the TST failure. The manifolds (stable and centre-stable) of the UPO clarify these expectations by intersecting the dividing surface at the boundary of the reactive island (on the collinear and the three (full) systems, respectively).

Keywords:

Transition state theory, Hamiltonian, dividing surface, NHIM, centre manifold, Lyapunov exponents, reactive island, stable and unstable cylindrical manifolds.

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Abbreviations

| \mathbf{TST} | Transition State Theory |
|----------------|---|
| PODS | $\mathbf{P}\mathrm{eriodic}\ \mathbf{O}\mathrm{rbit}\ \mathbf{D}\mathrm{ividing}\ \mathbf{S}\mathrm{urface}$ |
| NHIM | Normally Hyperbolic Invariant Manifold |
| dof | degree of freedom |
| SSPO | $\mathbf{S} \mathbf{y} \mathbf{m} \mathbf{m} \mathbf{t} \mathbf{r} \mathbf{c} \mathbf{c} \mathbf{h} \mathbf{P} \mathbf{e} \mathbf{r} \mathbf{i} \mathbf{o} \mathbf{c} \mathbf{O} \mathbf{r} \mathbf{b} \mathbf{i} \mathbf{t}$ |
| BPO | $\mathbf{B} \mathbf{ending} \ \mathbf{P} \mathbf{eriodic} \ \mathbf{O} \mathbf{r} \mathbf{bit}$ |
| ScPO | ${\bf Sec} {\bf ondary}$ symmetric stretch ${\bf P} {\bf eriodic}$ ${\bf O} {\bf r} {\bf bit}$ |
| RI | \mathbf{R} eactive \mathbf{I} sland |
| UPO | Collinear Unstable Periodic Orbit |
| H1, H2, H3 | refer to three Hydrogen atoms |

To my family...

Chapter 1

Introduction

Transition state theory [1–5] (TST) is over 80 years old, and it is the basis of reaction rate theory. It assumes that reactant and product areas can be divided by a dividing surface. The transition state of chemical reaction is defined with a "dividing surface" separating reactant and product regions of configuration space (more generally, of phase space). Transition state theory represents a fundamental framework for calculating the total flux of trajectories from reactant to product, through the dividing surface (determining the chemical reaction rate). The main notion of TST started in works of Marcelin [6], Polanyi and Eyring [7] and Wigner [8] and is still an active topic in many works for different purposes such as reaction probabilities. Recently, TST has been not only used for chemical reaction rate problems but it also appeared in many other applications (e.g. atomic physics [9], rearrangements of clusters [10], cosmology [11] and celestial mechanics [12]).

TST is exact if and only if there is no trajectory crossing the dividing surface more than once. This is the fundamental assumption of TST. However, if there are recrossing trajectories on the dividing surface, then TST provides upper bound of the exact rate. The exact rate will depend on the choice of dividing surface. This leads to a so-called the variational approach. In the variational problem, the TST is not exact and results in an overestimation for the chemical reaction rate. One can solve the variational problem by choosing the dividing surface with minimum flux through it.

If the reaction is mediated by crossing of an energetic barrier, the dividing surface is chosen close to the saddle point located between reactant and product. This object is often determined by normal coordinate analysis close to the saddle point. Other dividing surfaces generalize the definition of the transition state. An appropriate choice of the dividing surface at small enough energy above the threshold allows the reactive trajectory to pass through a tiny bottleneck close to the saddle point. At high energies, the bottleneck around the saddle point becomes wider and hence there is a possibility for recrossing.

For two degrees of freedom (2 dof), the problem of determining the optimal dividing surface for TST of collinear reactions was solved during 1970's by Pechukas, Pollak and McLafferty [13–15]. At low energies just above the threshold of reaction, they considered a dividing surface in configuration space that is given by the projection of an unstable periodic orbit. For symmetric molecules, this is the symmetric stretch vibration. This curve is the so-called "periodic orbit dividing surface" (PODS). The unstable PODS is an optimal solution for the recrossing problem as no projected trajectory moving from reactant to product (or vice versa) is tangent to it. Once a reactive trajectory crosses the unstable PODS, then it must leave the neighbourhood of the PODS before possibly recrossing it. If there is only one PODS at a certain energy E, then it is the best dividing surface to choose because it yields the exact reaction rate. Pechukas et al [16-18] discuss that if there is more than one PODS at a certain energy E, then TST breaks down and one PODS with minimum flux is the best among the others. As a result, the reason for the breakdown of TST in the reaction with two degrees of freedom is well-known which is the emerging of the additional PODS from the bifurcation of the original PODS. The dynamical behaviour close to the PODS has been explained in several references, e.g. [5, 17–20]. Quite recently, the numerical continuation and the bifurcation of PODS has been studied by Iñarea et al [21] for the collinear $H + H_2$ reaction. Burghardt and Gaspard [22] examined the bifurcation of the PODS on semiclassical quantization and quantum resonance states in the collinear reaction of $HgI_2 \rightarrow HgI + I$. They were able to characterize a series of resonances at low energy where the dynamics is regular as well as at high energies where the dynamics transit to chaos.

For many degrees of freedom (n dof), it is easy to guess that the generalized transition state (the dividing surface) is an unstable manifold of a suitable dimension [1]. Recently, the construction of the dividing surface in phase space has been shown firstly by Uzer *et al* [23] and Komatsuzaki *et al* [24] for linear and nonlinear Hamiltonian systems with (finitely) many degrees of freedom. The basis is to generate a sequence of canonical transformations in the area of rank-one saddle that transform the Hamiltonian into a normal form using Lie transformation method. The construction provides as a new fundamental geometrical object a normally hyperbolic invariant manifold (NHIM), which is the generalization of the PODS in systems with many degrees of freedom.

In this thesis, we use the $H + H_2$ reaction as an example because it has many advantages. For instance, the collinear configuration of the system is widely studied in the literature. Moreover, the reaction probability has been calculated for both collinear and three (full) dimensional systems. Also, the potential energy function of the $H + H_2$ reaction has been calculated several times (see e.g. [25, 26]). In addition, the reaction itself has many features (e.g. the geometrical symmetry and it involves three identical atoms) which allow us to calculate the centre manifold of the saddle point and derive a Hamiltonian function with appropriate coordinates for collinear (2 dof) and three dimensional (full 3 dof) systems.

Knowledge of the $H + H_2$ reaction from previous other works helps us to find the shortcomings and gaps of TST rate. We know that the dynamics is simple and TST is exact at small enough energies above the threshold for the collinear system as well as the three (full) dimensional system. As energy increases, the dynamics surely undergoes a sequence of bifurcations, chaos and hence the TST is not exact. For the collinear system of the $H + H_2$ reaction, Pechukas and McLafferty [13] found that TST is exact at sufficiently low energies (about 0.2 eV above the threshold). In addition, Miller *et al* [27, 28] have calculated the reaction probability of the collinear $H + H_2$ reaction as well as the reaction probability in the three dimensional system. In both cases, TST is exact to over 0.2 eV above the threshold. Quite recently, the reaction probability of the collinear $H + H_2$ reaction has been calculated more accurately by Iñarrea *et al* [21]; they found out that the TST fails at about 0.2 eV above the potential energy barrier. These results used the Porter-Karplus potential energy [25] which is the same potential energy function used in this thesis. Other than TST calculations, the bifurcation of the PODS [21] and the bifurcation of the NHIM [29, 30] have been investigated for collinear and three dimensional systems, respectively. The reason for the breakdown of TST in the collinear case is well-known: It is caused by the additional PODS that emerge from bifurcations. New periodic orbit of this bifurcation fails the TST which provides an overestimate in chemical reaction rate. The shortcoming is that the reason for the TST failure in the three (full 3dof) dimensional system is unknown. Figure 1.1 shows a sketch of the previous knowledge and points out the shortcoming.

The main purpose of this thesis is to seek the phase space object that causes the TST failure in the system with three degrees of freedom. Our attempts to find such an object are divided into two main parts. First of all, we examine the persistence of the NHIM under perturbation (by increasing the energy parameter). In other words, we need to show at which energies the NHIM ceases to be normally hyperbolic. Then we compare the output with the energy at which the TST breaks down and find out if there is any agreement. Secondly, if the breakdown of the NHIM is not the reason (which indeed it is not), we seek another phase space object by investigating the reactivity on the dividing surface. In this part, we want to determine the first nonreactive trajectory that appears on the dividing



FIGURE 1.1: A sketch outlining the previous knowledge and pointing out the shortcoming.

surface. We follow this trajectory until it hits the phase space object before it returns to the dividing surface. This procedure allows us to figure out the target.

The contents of this thesis are as follows. In Chapter 2, we give an overview of some important background material that is used in the thesis. We start by giving some history in transition state theory. Chapter 2 also includes the fundamental basis such as Hamiltonian vector fields, canonical transformations, the transition state rate formula and the comparison between phase space and configuration space, including the stability of the stationary point. In addition, we describe the phase space structure close to the saddle point for n degrees of freedom which contains many objects (for instance the energy shell, the NHIM and its stable and unstable manifolds and the dividing surface). The structure of the cylindrical manifolds and the conditions for their persistence under perturbation are stated at the end. In Chapter 3, we provide our example which is the $H + H_2$ reaction as a Hamiltonian system with two degrees of freedom as well as three degrees of freedom. In this chapter, we state the Porter-Karplus potential energy [25] and derive the kinetic energy function in appropriate coordinates. Also, we represent the features of the $H + H_2$ reaction, including the symmetry, calculating the centre manifold of the saddle point and the analytical solution of the harmonic Hamiltonian. In Chapter 4, we study the persistence of the NHIM. It is done by firstly investigating the dynamics in the centre manifold using the Poincaré surface of section. The investigations include the dynamical behaviour (regular and chaotic motions) and the bifurcation of periodic orbits. At the end of Chapter 4, we calculate the Lyapunov exponents for an arbitrary trajectory in directions parallel and transverse to the NHIM for both periodic and non-periodic orbits which allow us to figure out the breakdown of the NHIM. In Chapter 5, we seek another phase space object that causes the TST failure by studying the reactivity on the dividing surface in the collinear and the three (full 3 dof) systems. The study includes the phase space structure of the reactive islands and determines at which energy level nonreactive island appeared. These attempts show the reason of the breakdown of TST. The reason has been stated at the end. Chapters 3, 4 and 5 are the main body of the thesis. Finally, we draw the conclusion of our results and discuss possible future work in Chapter 6.

Chapter 2

Theoretical Background

2.1 Introduction

The idea of the transition state (TS) early appeared in the work of Marcelin [6] in 1915. Sixteen years later, Eyring and Polanyi [7] started to reconsider the idea of TS by calculating the absolute reaction rate of the collinear $H_2 + H$ reaction. Eyring and Polanyi's potential energy surface is calculated by a mixture of experiment and theory. In their paper, they defined the potential energy surface as two valleys associated with reactant and product which are separated by the saddle point. The dividing surface is determined as the path of steepest ascent from the saddle point in configuration space. I was assumed to be a surface of no return. However, it was soon recognised that recrossing is possible due to the dynamical effects from coupling terms in the kinetic energy. The difficulty of finding a recrossing surface was a stumbling block to apply TST in multidimensional system as well as in the strongly coupled case. Important contributions have been made by Evans, Farkas, Szilard, Horiuti, Pelzer and Marcelin, and these are explained for example in Refs [5, 31]. Transition state theory (TST) is used to determine the absolute chemical reaction rate. It makes three assumptions: the motion of the nuclei take places on the Born-Oppenheimer potential energy surface, the motion of the nuclei is described by the classical (Hamiltonian) mechanics and the dividing surface separates the reactant and product and has no classical trajectory goes through it more than once. Wigner [8] noticed if the latter assumption fails, then the reaction rate is overestimated. Wigner's formulation leads to the recognition that the transition state is a general property of all dynamical systems in which a transition from "reactant" to "product" states takes place. Thus, the TS is not confined to the chemical reaction dynamics, but also plays an important feature in many interesting systems, including, for instance, the rearrangements of clusters [24], the ionisation of atoms [9, 32] and diffusion jumps in solids [33].

The recognition that recrossing-free dividing surfaces are difficult or impossible to construct. This led to the variational TST approach. The main idea of the variational TST is to consider the set of all possible dividing surfaces that divide the configuration space into two parts, namely reactant and product. Then one chooses the dividing surface with minimum flux. Even though, the minimum flux dividing surface has been selected, there will usually still be recrossings of the dividing surface and the chemical reaction rate will not be exact.

Pechukas and Pollak [1, 20, 34] solved the problem of variational TST for systems with two degrees for freedom. They found that the projections of periodic orbits into the configuration space, which are called periodic orbit dividing surfaces (PODS), are surfaces of stationary flux. Their solution is very important and considerable, regardless of the shortcoming because of the formulation of the variational principle in configuration space. The shortcoming of Pechukas and Pollak solution affects the problem with the formulation of variational principle. Consequently, new problem arises in the variational TST which is, the work must be extended to higher dimensional system which is not easy to generated to higher dimensions, and indeed recrossing-free dividing surface exist only in phase space, not in configuration space. In order to achieve this generalization, we need two developments: (1) advanced theory in the study of multidimensional dynamical system (provided in Section 2.6), and (2) high computing power. We will now show a brief history of transition state theory.

In the 1970's, Pechukas and Pollak [1, 5, 13, 15–18, 20, 34] made a good contribution in the development of TST. During 1970's, the research get improved from the advance computer power which encouraged the scientist to investigate the dynamics of realistic model systems. The numerical investigation was not only achievement in the dynamics of reactive systems, but also perform many significant tools such as the Poincaré surface of section. Such development can be seen in many references, for instance, MacKay, Meiss and Percival [35, 36] who are interesting in the existence of cantori acting as space barriers in the neighbourhood of the last surviving torus.

In the 1980's, number of the dynamics reactive systems have been studied in the phase space by Davis and co-workers [37-39]. They used the manifolds of the PODS to show the partitioning of the phase space. Similarly, Tiyapan and Jaffé [40-42] have developed the idea of the manifolds of the PODS to form the invariant fractal of the phase space and the formation of complexes (unimolecular reactions) have described the structure of the fractal. Unfortunately, these developments on techniques are only applied on the dynamics reactive systems with two degrees of freedom, except for the classical transition state theory simulation [27, 43]. Thus efforts must rely on the extended systems with more than two degrees of freedom.

Komatsuzaki and co-workers have recently studied the dynamics in the neighbourhood of the TS in many-body system [10, 44–49]. They used Lie transformations to calculate the normal form. Moreover, Li et al [29] have used partial normal forms for the three degrees of freedom $H_2 + H$ reaction. In this thesis, we will avoid the use of normal form by taking advantage of the symmetry of our reactive system. Using this advantage, we can compute the centre manifold easily. This manifold involves all classical trajectories that remain trapped in the neighbourhood of the saddle point for all time. The centre manifold is an important tool to formulate TST in phase space.

Nowadays, problems with two degrees of freedom are now well understood, and many examples have been worked out in detail. In higher dimension, recent investigations of the geometry near saddle point in phase space by Wiggins [50] have shown that a Normal Hyperbolic Invariant Manifold (NHIM) is existed in the neighbourhood of the saddle point. The classical theory of chemical reactions [51] can now be established accurately in nonlinear dynamics. Invariant manifolds form impenetrable barriers in phase space. "Invariant" means all trajectories within manifold will remain on manifold for future as well as in the past. Therefore, no trajectory can intersect the invariant manifold, which make us able to reformulate the definition of the dividing surface in term of geometrical object in phase space. Thus, the NHIM is the cornerstone in the research development.

The content of this chapter is organized as follows: We will review important background material that will be used in this thesis, starting from fundamental concepts. Hamiltonian vector field represents in the Section 2.2. The review includes canonical transformations and the properties of symplectic matrix. In Section 2.3, we state the transition state theory rate formula. The definitions of the phase space and the configuration space and the declaration the difference between them present in the Section 2.4. The stability of the stationary points in both spaces is explored in Section 2.5. In Section 2.6, we give an overview of the general formations of the phase space structures close to a saddle point. It is a theory for a class of linear Hamiltonian systems. The linear systems involve the abstract of the geometrical structures contained in nonlinear systems and also represent the substantial advantage of being able to show all the relevant objects (e.g. the NHIM, its stable and unstable manifolds, and the dividing surface) as explicit formulae. The theory regarding cylindrical manifolds is represented in Section 2.7. In the end, we state the mathematical theory of the persistence of the normally hyperbolic invariant manifolds in Section 2.8.

2.2 Hamiltonian vector fields

Literature reviews on Hamiltonian vector fields appear in several books on classical mechanics (see, e.g. Goldstein [52] and Wiggins [53]). Recent research concerns the dynamical behaviour of the flow that is generated by Hamilton's equations of motion. We focus on molecular motions moving from the reactants to the products through the transition state and observe the dynamical properties of the flow.

A C^r Hamiltonian vector field with $r \ge 2$, is given by

$$\dot{q}_i = \frac{\partial H}{\partial p_i},\tag{2.1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i},\tag{2.2}$$

for i = 1, ..., n. Here $q \in \mathbb{R}^n$ represent coordinates of configuration variables (position of component parts) and their canonically conjugate momenta are denoted by $p \in \mathbb{R}^n$. The function H = H(q, p, t) is so-called Hamiltonian function. We may write a Hamiltonian vector field as a phase space vector x = $(q_1, ..., q_n, p_1, ..., p_n) \in \mathbb{R}^{2n}$ which is defined by

$$\dot{x} = -J \cdot \nabla H, \tag{2.3}$$

where

$$J = \begin{pmatrix} 0_n & -I_n \\ I_n & 0_n \end{pmatrix}, \tag{2.4}$$

is the $2n\times 2n$ Poisson (antisymmetric) matrix, I_n denotes the $n\times n$ identity matrix, and

$$\nabla H = \left(\frac{\partial H}{\partial q_1}, \dots, \frac{\partial H}{\partial q_n}, \frac{\partial H}{\partial p_1}, \dots, \frac{\partial H}{\partial p_n}\right)$$

For many mechanical systems, the Hamiltonian H represents the total energy of the system and takes the form

$$H(q, p) = T(q, p) + V(q),$$

where T is the kinetic energy, while V is the potential energy depending only on q. If a Hamiltonian does not depend explicitly on time t, then the energy is constant:

$$\frac{d}{dt}H(q(t),p(t)) = \frac{\partial H}{\partial q}\frac{dq}{dt} + \frac{\partial H}{\partial p}\frac{dp}{dt} = 0,$$

by (2.1) and (2.2). Thus H(q(t), p(t)) = H(q(0), p(0)) = E. This is called conservation of energy. If the Hamiltonian H(q, p, t) depends on time t, then the energy is not conserved.

Hamiltonian principle

The phase space path $(q(t), p(t)), t \in [t_0, t_1]$ is a solution of Hamilton's equations (2.1) and (2.2), if and only if it is an extremal of the functional:

$$\delta \int_{t_0}^{t_1} \sum_{i=1}^n p_i dq_i - H(q(t), p(t)) dt = 0$$

The boundary conditions each have a factor of δq and δp at the initial or final point which vanish,

$$\delta q(t_0) = \delta q(t_1) = \delta p(t_0) = \delta p(t_1) = 0.$$

2.2.1 Canonical transformation

A canonical transformation transfers the phase space coordinates q and momenta p to new coordinates Q and new momenta P which satisfy Hamilton's equations of motion with a new Hamiltonian K(Q, P, t).

Let the transformation of coordinates be Q = Q(q, p, t), P = P(q, p, t). We need to derive the condition on transformation such that

$$\dot{Q} = \frac{\partial K}{\partial P},$$

$$\dot{P} = -\frac{\partial K}{\partial Q}$$

are satisfied in the new coordinates Q and P with a new Hamiltonian K. Hamilton's principle of least action in phase space for the new Hamiltonian reads

$$\delta \int_{t_0}^{t_1} \sum_{i=1}^n P_i dQ_i - K dt = 0,$$

and thus

$$\delta \int_{t_0}^{t_1} \sum_{i=1}^n p_i dq_i - H dt = \delta \int_{t_0}^{t_1} \sum_{i=1}^n P_i dQ_i - K dt = 0,$$

which is

$$\delta \int_{t_0}^{t_1} \sum_{i=1}^n p_i dq_i - P_i dQ_i - (H - K) dt = 0.$$

This can be satisfied if the integrant is a total differential

$$dW(q, P, t) = \sum_{i=1}^{n} p_i dq_i - \sum_{i=1}^{n} P_i dQ_i - (H - K) dt$$
(2.5)

where W(q, P, t) is called the generating function (one of four generating functions type), expressed in terms of the old coordinates and new momenta. Writing out the terms of the differential of the left hand side of (2.5) gives

$$\sum_{i=1}^{n} \frac{\partial W}{\partial q_i} dq_i + \sum_{i=1}^{n} \frac{\partial W}{\partial P_i} dP_i + \frac{\partial W}{\partial t} dt = \sum_{i=1}^{n} p_i dq_i - \sum_{i=1}^{n} P_i dQ_i - (H - K) dt,$$

from which it follows that

$$p_{i} = \frac{\partial W}{\partial p_{i}},$$

$$Q_{i} = \frac{\partial W}{\partial P_{i}},$$

$$K(Q_{i}, P_{i}, t) = H(q_{i}, p_{i}, t) + \frac{\partial W}{\partial t}$$

It is clear that if the system does not depend explicitly on time t then the new Hamiltonian function (K) is the same as the old Hamiltonian function (H).

2.2.2 Symplectic forms

A symplectic vector space is a vector space that is equipped with a symplectic form. For the phase space \mathbb{R}^{2n} a symplectic form is given by

$$\Omega(u,v) \equiv \langle u, Jv \rangle, \qquad u, v \in \mathbb{R}^{2n}, \tag{2.6}$$

where $\langle \cdot, \cdot \rangle$ denotes the standard inner product on \mathbb{R}^{2n} . Hamilton's equations of motion can be derived from the symplectic structure $\Omega(\cdot, \cdot)$ by the following formula

$$\Omega(X_H(x), v) = \langle DH(x), v \rangle, \qquad x = (q, p) \in \mathbb{R}^{2n}, v \in \mathbb{R}^{2n}.$$
(2.7)

Let $X = (\dot{q}, \dot{p})$ be an arbitrary vector field on \mathbb{R}^{2n} and $DH = (\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p})$. Thus, equation (2.7) becomes

$$\Omega((\dot{q},\dot{p}),v) = \langle (\dot{q},\dot{p}), Jv \rangle = \langle \left(\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p}\right), v \rangle.$$

Thus,

$$\begin{aligned} \langle -J(\dot{q},\dot{p}),v\rangle &= \langle \left(\frac{\partial H}{\partial q},\frac{\partial H}{\partial p}\right),v\rangle, \quad \text{since } J^T = -J, \\ \langle (-\dot{p},\dot{q}),v\rangle &= \langle \left(\frac{\partial H}{\partial q},\frac{\partial H}{\partial p}\right),v\rangle. \end{aligned}$$

For any $v \in \mathbb{R}^{2n}$,

$$\langle (-\dot{p}, \dot{q}) - \left(\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p}\right), v \rangle = 0.$$

Hence,

$$(-\dot{p},\dot{q}) - \left(\frac{\partial H}{\partial q},\frac{\partial H}{\partial p}\right) = 0,$$

which are Hamilton's equations (2.1) and (2.2).

2.2.3 Eigenvalues of symplectic matrices

The symplectic (canonical) transformation (say f) can be written as

$$f: (q, p) \mapsto (Q(q, p), P(q, p)).$$

The Jacobian of f is given by a $2n \times 2n$ matrix (A)

$$A = \begin{pmatrix} \frac{\partial Q}{\partial q} & \frac{\partial Q}{\partial p} \\ \frac{\partial P}{\partial q} & \frac{\partial P}{\partial p} \end{pmatrix}$$
(2.8)

which is with matrix (2.4) satisfies

$$A^T J A = J, \quad (JA)^T = JA \quad \text{and} \quad A^{-1} = J^{-1} A^T J,$$

is so-called symplectic matrix. Also, the Poisson matrix J satisfies

$$J^{-1} = J^T = -J$$
 and $J^2 = -I_{2n}$

The eigenvalues of the symplectic matrix (A) can be determined by finding the roots of the characteristic polynomial

$$p(\lambda) = \det(A - \lambda I_{2n}),$$

Since the matrix A is symplectic and its coefficients are real, the eigenvalues of A have the following properties: if λ is eigenvalue then λ^{-1} is also an eigenvalue. Moreover, since the coefficients of the characteristic polynomial are real (A is real), if λ is a complex eigenvalue, its complex conjugate $\overline{\lambda}$ is also an eigenvalue. Hence, if $\lambda = 1$ or $\lambda = -1$, then they must be double eigenvalues.

Proposition 2.1. Wiggins [53] Let A to be a symplectic matrix and $\lambda \in \mathbb{C}$ be an eigenvalue of A. Then λ^{-1} , $\overline{\lambda}$ and $\overline{\lambda}^{-1}$ are also eigenvalues of A. If λ is an eigenvalue of multiplicity k, then λ^{-1} is an eigenvalue of multiplicity k too. Also, the multiplicities of the eigenvalues +1 and -1, if they occur, are even.

Note that because we study the Hamiltonian system, this fixes one eigenvalue is equal to 1, and hence by the symplectic condition another eigenvalue is equal to 1. Thus there are only 2n - 2 eigenvalues need to calculate in order to see the type of the stability of n degrees of freedom Hamiltonian system.

2.3 The transition state theory rate formula

Transition state theory provides a good method to describe the rate of the chemical reactions. TST is based on the observation that large energy barriers hindering reactive events lead to a bottleneck in phase space. The rate constant of reaction is determined by the flux of reactive trajectories through a dividing surface that is chosen close to the bottleneck.

To set up the rate formula, consider the Hamiltonian H(p,q) of the collinear system with two degrees of freedom where p and q are two momentum and coordinate vectors. The characteristic function χ_a of the reactive phase space is defined by

$$\chi_a = \begin{cases} 1, & \text{reactive trajectory,} \\ 0, & \text{otherwise.} \end{cases}$$
(2.9)

Choose a dividing surface that is given by a curve in configuration space. The flux integral through the dividing surface for the exact rate in phase space is given by

$$K_{exact} = \int \int dp ds (p \cdot n_s) \delta(E - H(p, q_s)) \chi_a(p, q_s), \qquad (2.10)$$

where the function $\delta(E - H(p, q))$ is the density of phase point at fixed energy E, q_s is a point on the dividing surface parametrized by arc length s; and n_s is the normal to this line in the product direction. Equation (2.10) gives the exact reaction rate, but it requires a detailed knowledge of the dynamics because it contain the characteristic function χ_a .

By contrast, the TST rate is easier to calculate than the exact rate. In TST, we consider a trajectory as reactive if it crosses the dividing surface from the reactant to product side and nonreactive otherwise. The characteristic function for the TST rate approximation is given by

$$\chi_b = \begin{cases} 1, & (p \cdot n_s) > 0, \\ 0, & \text{otherwise,} \end{cases}$$
(2.11)

Thus, the integration of the flux in (2.10) becomes

$$K_{TST} = \int \int dp ds (p \cdot n_s) \delta(E - H(p, q_s)) \chi_b(p, q_s).$$
(2.12)

Thus the transition state theory rate is exact if $\chi_a = \chi_b$. This condition is the norecrossing assumption: It is satisfied if no trajectory crosses the dividing surface more than once. Otherwise, TST will overestimate the reaction rate.

The momentum integral in (2.12) can be carried out to give

$$K_{TST} = 2^{3/2} \int ds (E - V(q_s))^{1/2}, \qquad (2.13)$$

where V is the potential energy. This is an action integral. The principle of least action therefore means that q_s should be the configuration space path of a trajectory of energy E [17].

In fact, the recrossing-free assumption is strictly dependent on the choice of the dividing surface. We want to choose the dividing surface q_s with minimum flux. Most possible dividing surfaces lead to many recrossings and lose the accuracy of the rate [54]. For example, if we choose the dividing surface far on the reactant side, then it would result in many recrossings, most of which have enough energy to cross the barrier and soon recross it [34].

2.4 Phase space and configuration space

In this section, we clarify the difference between configuration space and phase space. Dimensionally, the potential energy surface is defined in n-dimensional configuration space while the total energy in the phase space is defined in 2ndimensions. Consequently, finding the stationary points and calculating their linear stabilities in the phase space is hard, but we have essentially the same analysis method for both spaces. The main difference between phase and coordinate space is that phase space is a state space. Each point in the phase space represents a unique state of the system while each point in configuration space represents only the physical position of the system. In the configuration space, the minima on the energy surface are called potential wells that are separated by a saddle point. The motion from one potential well to another one must pass over the saddle. In the phase space, we are concerned with the total energy surface and determine its stationary points and their linear stabilities. The saddles work as barriers in the phase space. Once the saddle points are found and characterized, the machinery of geometrical mechanics can be applied to get the invariant manifolds and their stable and unstable manifolds associated with the stationary points. Using these geometrical structure of the stable and unstable manifolds in phase space can be separated the reactive and nonreactive regions. However, finding the stationary states of the systems with more than two degrees of freedom is an unsolved problem, the isolated stationary points are the most familiar in such manifolds.

There are two assumptions that have to be considered for the formulation of the Hamiltonian system when we deal with the configuration space. Firstly, the Hamiltonian can be separated into a sum of two terms, kinetic energy function and potential energy function. Secondly, the kinetic energy function has to be positive definite and quadratic in the momenta. Under these assumptions, a stationary point of the potential energy surface in configuration space gives rise to a stationary point of the Hamiltonian flow in phase space. That means, the momenta at the stationary point are zero, and hence, the configuration space of this point balances the various forces (i.e. the extremum of the potential energy).

We will face many critical problems when using the configuration space approach to TST. The most important one is the transition state or the dividing surface which must be defined in the phase space. The problem is that the dividing surface that is recrossing-free in phase space does not project to a recrossingfree dividing surface in configuration space. Of course, these difficulties will arise when we attempt to extend the study of the system with more than two degrees of freedom [55].

2.5 Stability of stationary points

In configuration space, the negative gradient of the potential energy function represents the forces exerted on the system. The eigenvalues of the matrix of the second derivative of the potential energy function evaluated at the state point characterize the linear stability of the potential energy function. Suppose the system possesses n degrees of freedom, then the stability of the saddle point is characterized by the number of negative and positive eigenvalues. The extremum is a minimum, if all eigenvalues are positive and moreover it is stable. On the other hand, the extremum is a maximum, if all eigenvalues are negative and moreover it is called a rank-m saddle which it is unstable in m degrees of freedom and stable in the remaining n - m degrees of freedom.

In the phase space, the treatment is different due to the momenta. The stability of the stationary point is examined by the stability matrix

$$\begin{pmatrix} \frac{\partial \dot{q}}{\partial q} & \frac{\partial \dot{q}}{\partial p} \\ \frac{\partial \dot{p}}{\partial q} & \frac{\partial \dot{p}}{\partial p} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 H}{\partial q \partial p} & \frac{\partial^2 H}{\partial^2 p} \\ -\frac{\partial^2 H}{\partial^2 q} & -\frac{\partial^2 H}{\partial q \partial p} \end{pmatrix}$$
(2.14)

evaluated at the stationary point of the flow. For systems with n degrees of freedom, the eigenvalues of the stability matrix (2.14) are n pairs which are either complex numbers and their conjugates or real numbers and their inverses. A pair of complex conjugate eigenvalues corresponds to a stable degree of freedom (elliptical) and a pair of real eigenvalues corresponds to an unstable degree of freedom (hyperbolic) [55]. There is a rare case in which the eigenvalues are equal to zero. In this case, the manifolds of the stationary point need not be isolated points. For more details about this case, the reader is referred to [56].

2.6 Phase space structure close to the saddle point

In this section we will show the phase space structure for a class of *n*-dof linear Hamiltonian systems that are appropriate for the study of reaction dynamics [23]. For such a class of systems we will show some important phase space objects that are used to describe the reaction dynamics, including the energy surface, a higher-dimensional object of a saddle denoted by NHIM [50], its stable and unstable manifolds and the dividing surface. In an area close to the NHIM, we can construct the dividing surface which is a dynamical surface with recrossingfree trajectories. The aim of this Section is to distinguish the NHIM, its stable and unstable manifolds, the dividing surface, together with study all possible trajectories close to the saddle point. We will begin by stating a class of *n*-dof linear Hamiltonian systems.

2.6.1 The *n* degrees of freedom Hamiltonian

We now present the phase space structure of a linear Hamiltonian system near an equilibrium point associated with a centre \times centre $\times \cdots \times$ saddle type (a rankone saddle) in the phase space flow [23]. Close to the saddle point, the dynamics is well described by the harmonic Hamiltonian

$$H = \frac{1}{2} \sum_{j=1}^{n} p_j^2 + \frac{1}{2} \sum_{j=1}^{n-1} \omega_j^2 q_j^2 - \frac{\lambda^2}{2} q_n^2.$$
(2.15)

The corresponding equations of motion are given by

$$\dot{q}_j = \frac{\partial H}{\partial p_j}, \qquad \dot{p}_j = -\frac{\partial H}{\partial q_j}.$$
 (2.16)
.

They read explicitly

$$q_{j} = p_{j},$$

$$\dot{p}_{j} = -\omega_{j}^{2}q_{j} \quad \text{for } j = 1, \dots, n-1,$$

$$\dot{q}_{n} = p_{n},$$

$$\dot{p}_{n} = \lambda^{2}q_{n}.$$
(2.17)

The eigenvalues of the matrix associated to the linearized Hamiltonian vector field around the saddle point are $\pm \lambda$ and $\pm i\omega_j$ where j = 1, ..., n - 1. The pair of real eigenvalues $\pm \lambda$ describe the hyperbolic direction of the saddle point which are referred to as the reaction coordinates. The complex eigenvalues describe the elliptic directions of the saddle point, i.e., oscillations transverse to the reaction coordinate.

The dynamics described by the Hamiltonian (2.15) has a stationary point (saddle point) at $p_i = q_i = 0$ at energy zero. We will study the dynamics at a fixed energy h > 0 above the reaction threshold. The energy surface is (2n - 1) dimensional and is given by

$$\frac{1}{2}\sum_{j=1}^{n}p_{j}^{2} + \frac{1}{2}\sum_{j=1}^{n-1}\omega_{j}^{2}q_{j}^{2} - \frac{\lambda^{2}}{2}q_{n}^{2} = \text{constant} = h > 0.$$
(2.18)

We can split the energy for each degree of freedom individually as follows

$$\frac{1}{2}(p_j^2 + \omega_j^2 q_j^2) = E_j \quad \text{for } j = 1, \dots, n-1,$$

$$\frac{1}{2}(p_n^2 - \lambda^2 q_n^2) = E_n, \quad (2.19)$$

where $E_1 + E_2 + \dots + E_n = h$ and also h > 0, $\omega_j > 0$ for $j = 1, \dots, n-1$ and $\lambda > 0$.



FIGURE 2.1: Phase portrait for the hyperbolic and elliptic directions. The positive and negative energy are indicated in phase portrait of the saddle region. The separatrices have zero energy. (Adapted from reference [23]).

In the $q_n - p_n$ phase portrait the trajectories that go from $q_n > 0$ to $q_n < 0$ (or vice versa) are said to be the trajectories that undergo reaction, see Figure 2.1. Such trajectories can be seen with $E_n > 0$ in Figure 2.1. This Figure explains the phase space structure of the hyperbolic direction and the elliptic directions of systems. More precisely, it shows that there are two types of reactive trajectories. Those with $p_n > 0$, which are referred to as the forward reactive trajectories, and those with $p_n < 0$, which are referred to as the backward reactive trajectories. Notice that the p_n component of a reactive trajectory cannot change sign during its evolution. The trajectories with $E_n < 0$ are referred to as nonreactive trajectories.

2.6.2 The energy surface

The (2n-1)-dimensional energy surface can be visualised if we rewrite (2.18) as follows

$$\frac{1}{2}\sum_{j=1}^{n}p_{j}^{2} + \frac{1}{2}\sum_{j=1}^{n-1}\omega_{j}^{2}q_{j}^{2} = \frac{\lambda^{2}}{2}q_{n}^{2} + h.$$
(2.20)

From (2.20), we can see the that the section through the energy surface at fixed q_n is a (2n-2) sphere with radius $\sqrt{h + \frac{\lambda^2}{2}q_n^2}$. Thus the energy surface is a hyper-cylinder $S^{2n-2} \times \mathbb{R}$. The explicit map from the energy surface in \mathbb{R}^{2n} into $S^{2n-2} \times \mathbb{R}$ is clear from the formula. For each $q_n \in \mathbb{R}$, we have a map of

 $(q_1, p_1, \ldots, q_{n-1}, p_{n-1}, p_n)$ into S^{2n-2} defined by

$$(q_1, p_1, \dots, q_{n-1}, p_{n-1}, p_n) \\ \mapsto \left\{ (q_1, \dots, q_n, p_1, \dots, p_n) \middle| \frac{1}{2} \sum_{j=1}^n p_j^2 + \frac{1}{2} \sum_{j=1}^{n-1} \omega_j^2 q_j^2 = \frac{\lambda^2}{2} q_n^2 + h \right\}.$$
(2.21)

2.6.3 The NHIM and its stable and unstable manifolds

The centre manifold of the equilibrium point is given by $q_n = p_n = 0$. It contains all trajectories that remain trapped close to the equilibrium for all time in the infinite future and the infinite past. This surface is invariant because the equations of motion (2.17) imply $\dot{q}_n = \dot{p}_n = 0$. It has dimension 2n - 2. For a fixed energy h > 0, the intersection of the centre manifold with the energy shell is in a surface that satisfies

$$\frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h.$$
(2.22)

This equation describes an (2n - 3) dimensional hyper-sphere S^{2n-3} . This is the NHIM (used in Chapter 3 and called the central sphere) that forms the bottleneck for phase space transport from reactants to products. The term NHIM means that the dynamical expansion and contraction rates transverse to the hyper-sphere are larger then those in directions tangent to it. This sphere has stable and unstable manifolds attached to it. These are (2n - 2) dimensional manifolds, denoted by $W^s(S_h^{2n-3})$ and $W^u(S_h^{2n-3})$, respectively which are of one dimension less than the energy surface. These manifolds separate reactive from non-reactive trajectories in phase space. They act as reaction channels that guide the system from the reactant configuration towards the transition state and on into the product region. They

are given by

$$W^{s}(S_{h}^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_{j}^{2} + \frac{1}{2}\sum_{j=1}^{n-1}\omega_{j}^{2}q_{j}^{2} = h, \quad p_{n} = -\lambda q_{n},$$

$$W^{u}(S_{h}^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_{j}^{2} + \frac{1}{2}\sum_{j=1}^{n-1}\omega_{j}^{2}q_{j}^{2} = h, \quad p_{n} = \lambda q_{n}.$$
(2.23)

These manifolds are referred to as reaction cylinders. Their structure is $S^{2n-3} \times \mathbb{R}$, which we refer to as spherical cylinders. Note that the stable and unstable manifolds of the NHIM have the same energy value as energy of the NHIM since the two lines $p_n = -\lambda q_n$ and $p_n = \lambda q_n$ have zero energy value. The stable and unstable cylinders have two branches each that are referred to as the forward and backward reaction cylinders. The reaction direction depends on the sign of p_n . The following definitions clarify the forward and backward reaction in stable and unstable cylinders.

The forward stable cylinder:

$$W_f^s(S_h^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h, \quad p_n = -\lambda q_n > 0, \tag{2.24}$$

The backward stable cylinder:

$$W_b^s(S_h^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h, \quad p_n = -\lambda q_n < 0.$$
(2.25)

The forward unstable cylinder:

$$W_f^u(S_h^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h, \quad p_n = \lambda q_n > 0.$$
(2.26)

The backward unstable cylinder:

$$W_b^u(S_h^{2n-3}): \quad \frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h, \quad p_n = \lambda q_n < 0.$$
(2.27)

2.6.4 The relation of the normally hyperbolic invariant spheres to the centre manifold of the saddle

We have the saddle point of the Hamiltonian vector field (2.19). This saddle point has a (2n-2)-dimensional centre manifold given by $p_n = q_n = 0$, a one-dimensional stable manifold given by $q_j = p_j = 0, j = 1, ..., n - 1, p_n = -\lambda q_n$, and a onedimensional unstable manifold given by $q_j = p_j = 0, j = 1, ..., n - 1, p_n = \lambda q_n$. It is easy to verify that the stable and unstable manifolds of the saddle point have the same energy as the saddle point, i.e. h = 0. The relation is, the intersection of the centre manifold of the saddle point with the energy surface gives the definition of the NHIM (2.28), (2n - 3)-dimensional sphere.

$$\frac{1}{2}\sum_{j=1}^{n-1}p_j^2 + \frac{1}{2}\sum_{j=1}^{n-1}\omega_j^2 q_j^2 = h = \text{constant.}$$
(2.28)

Thus we see that the centre manifold of the saddle point is filled out by a oneparameter (normally the energy) family of normally hyperbolic invariant (2n-3)dimensional spheres.

2.6.5 The dividing surface

Trajectories that cross the dividing surface correspond to reactive trajectories. A recrossing-free dividing surface is a (2n - 2) dimensional hyper-sphere that is defined by setting $q_n = 0$.

$$\frac{1}{2}\sum_{j=1}^{n}p_{j}^{2} + \frac{1}{2}\sum_{j=1}^{n-1}\omega_{j}^{2}q_{j}^{2} = h = \text{constant.}$$
(2.29)

It has codimension-one in the energy shell and separates reactant from product regions. Each trajectory that crosses the dividing surfaces crosses only once, going from reactants to products if $p_n > 0$ or from products to reactants if $p_n < 0$. The only exceptions are trajectories within the NHIM (central sphere), which have $p_n = 0$ and remain in the dividing surface for all times. The NHIM (central sphere) is an equator of the dividing surface and splits the dividing surface into two hemispheres with $p_n > 0$ and $p_n < 0$ that mediate forward and backward reactions, respectively. The forward dividing surface has $p_n > 0$, and the backward dividing surface has $p_n < 0$. The forward and backward dividing surfaces have the structure of (2n - 2)-dimensional balls, which are denoted by $B_f^{2n-2}(h)$ and $B_b^{2n-2}(h)$, respectively. All forward reactive trajectories pass through $B_f^{2n-2}(h)$; all backward reactive trajectories pass through $B_b^{2n-2}(h)$. Thus all reactive trajectories have to leave the neighbourhood of the dividing surface except for the boundary of the dividing surface (NHIM), which is an invariant manifold.

In summary, the dividing surface will have the following properties:

- It will be of dimension 2n-2 in the (2n-1)-dimensional energy surface;
- Trajectories that cross the dividing surface are referred to as reactive trajectories;
- The (2n-3)-dimensional invariant hyper-sphere plays an important role in the construction of the dividing surface;
- In the linear Hamiltonian system, the dividing surface is truly recrossing-free.

2.6.6 The relation of the reactive trajectories and the stable and unstable spherical cylinders

The stable and unstable spherical cylinders play an important role in determining the trajectories that do or do not react. To that end, rewrite the equation of the energy surface as

$$\frac{1}{2}\sum_{j=1}^{n-1} (p_j^2 + \omega_j^2 q_j^2) + \frac{1}{2} (p_n - \lambda q_n)(p_n + \lambda q_n) = h$$

The trajectories that undergo reaction satisfy

$$0 < \frac{1}{2}(p_j^2 + \omega_j^2 q_j^2) = E_j < h, \qquad j = 1, \dots, n-1,$$

$$\frac{1}{2}(p_n - \lambda q_n)(p_n + \lambda q_n) = E_n > 0, \qquad (2.30)$$

where

$$\sum_{j=1}^{n} E_j = h.$$

The forward and backward reactive region are determined using the relation in (2.30). We have $(p_n - \lambda q_n)(p_n + \lambda q_n) > 0$. Thus we get either

$$(p_n - \lambda q_n) > 0, \quad (p_n + \lambda q_n) > 0 \quad (\text{forward reactive region}, p_n > 0).$$
 (2.31)

or

$$(p_n - \lambda q_n) < 0, \quad (p_n + \lambda q_n) < 0 \quad (\text{backward reactive region}, p_n < 0).$$
 (2.32)

The equation (2.31) defines the boundary of the forward reactive region which is given by

$$p_n = -\lambda q_n, \quad p_n = \lambda q_n, \quad p_n > 0,$$



FIGURE 2.2: Phase portrait for the forward and backward reactive regions with total energy h as well as their boundaries. (Adapted from reference [23]).

and bounded by $W_f^s(S_h^{2n-3})$ and $W_f^u(S_h^{2n-3})$. Similarly, the equation (2.32) defines the boundary of the forward reactive region which is given by

$$p_n = -\lambda q_n, \quad p_n = \lambda q_n, \quad p_n < 0$$

and bounded by $W_b^s(S_h^{2n-3})$ and $W_b^u(S_h^{2n-3})$. These regions and their boundaries are sketched and explained in Figure 2.2.

2.6.7 The reactive trajectories in the reactant and product sections

In order to explain the reactive trajectories in more detail, we need to clarify their behaviour in reactant and product sections. Let us consider the forward reactive trajectories. Likewise the backward reactive trajectories with opposite signs of q_n and p_n .

Starting with initial condition of the forward reactive trajectory $p_n > 0$ and $q_n < 0$, the trajectory is shown as green dashed curves in Figure 2.3. This trajectory propagates in time until it reaches $q_n = 0$ where the dividing surface is located. Then q_n continues to grow as the trajectory moves into the product region $(q_n > 0)$. The section of the trajectory with $q_n < 0$ is referred to as the reactant section (shown in Figure 2.3(b)) and the section of the trajectory with $q_n > 0$ is referred to as the product section (shown in Figure 2.3(c)).

Figure 2.4 shows the pieces of the reactive region corresponding to forward and reverse reactant sections of trajectories. Likewise, Figure 2.5 shows the piece of the reactive region corresponding to forward and reverse reactive trajectories.

The interior of the stable and unstable spherical cylinders are identical. To see this, we know that the stable and unstable spherical cylinder are $S^{2n-3} \times \mathbb{R}$. As energy decrease in the $(q_1, p_1), \ldots, (q_{n-1}, p_{n-1})$ components, the radius of S^{2n-3} contracts, until we have only \mathbb{R} . This means

$$0 < \frac{1}{2} \sum_{j=1}^{n-1} (p_j^2 + \omega_j^2 q_j^2) = \sum_{j=1}^{n-1} E_j < h.$$

Thus the energy of the (q_n, p_n) component has to be increased $(\sum_{j=1}^n E_j = h)$. As results, the (q_n, p_n) component of trajectories in the interior of the spherical cylinders must satisfy

$$\frac{1}{2}(p_n^2-\lambda^2 q_n^2)=E_n>0$$

The same procedure can be applied in the stable or unstable spherical cylinders. Consequently, they have the same trajectories for different directions.

The following theorem summarizes the dynamics close to the saddle point.

Theorem 2.2. Uzer et al [23] The stable and unstable spherical cylinders bound a region in the energy surface that is divided into two disconnected components by the dividing surface. All reactive trajectories start inside one connected component, cross the dividing surface and leave the dividing surface passing into the other connected component.



FIGURE 2.3: (a) forward reactive trajectory in a dashed green curves. (b) The reactant section of the forward reactive trajectory. (c) The product section of the forward reactive trajectory. (Adapted from reference [23]).

2.7 Cylindrical manifolds in phase space

In this Section, we will illustrate the configuration of the invariant manifold for a system with two degrees of freedom. The cylindrical manifolds of the bimolecular reaction (e.g. $H_2 + H \leftrightarrow H + H_2$) in phase space can be classified with respect to the total energy (E_{tot} , kinetic energy plus potential energy). The following



FIGURE 2.4: Phase portrait for the piece of the reactive region corresponding to forward and reverse reactant sections of trajectories. (Adapted from reference [23]).



FIGURE 2.5: Phase portrait for the piece of the reactive region corresponding to backward and reverse reactant sections of trajectories. (Adapted from reference [23]).

theory is applicable to a harmonic approximation for systems with two degrees of freedom by De Leon *et al* [57]. Consider a Hamiltonian $H(q_1, q_2, p_1, p_2)$ and $q_1 = 0$ is the dividing surface. Trajectories with energy less than saddle point energy $E_{\rm sp}$ will be reflected off the barrier. Thus, all trajectories with $E_{\rm tot} < E_{\rm sp}$ will return back to the reactants and never reach the products. Trajectories lie on two dimensional invariant cylinders whose geometry is the product of S^1 and \mathbb{R}^1 . The motion on $S^1 \times \mathbb{R}^1$ forms an invariant cylinder denoted by $\Omega^{\rm rec}(E)$ which is shown in Figure 2.6. Similarly, the motion from the products lies on an invariant cylinder, denoted by $\Omega^{\rm pro}(E)$ which is also shown in Figure 2.6.



FIGURE 2.6: Below the energy of saddle point, the trajectories are nonreactive which their motion forms invariant cylinders $\Omega^{rec}(E)$ and $\Omega^{pro}(E)$.

For energies above the threshold $(E_{tot} \ge E_{sp})$, some trajectories cross. The boundary between the two type of trajectory is formed ny the cylindrical manifolds $(W_f^{s,u}, W_b^{s,u})$. On the reactant side, a trajectory on the invariant cylinder W_f^s approaches the barrier and never crosses the barrier in the infinite future. Also, a trajectory on the invariant cylinder W_b^u departs from the barrier and never crosses the barrier in the infinite past. A similar pair of cylinders in the product side do the same action and will be denoted by W_f^u, W_b^s . A sketch of these manifolds is shown in Figure 2.7(a). These four cylinders approach and emerge from the PODS in the collinear system with two degrees of freedom.

In case of $E_{\text{tot}} > E_{\text{sp}}$, the reactive trajectory will cross the dividing surface and never come back. They lie inside the cylindrical invariant manifolds, as shown in Figure 2.7(b). In the linear system, they form a family $\Omega^{\text{rec}\to\text{pro}}(E)$ of invariant cylinders that lie inside the cylindrical manifold, W_f^s and W_f^u . Similarly, trajectories moving from product to reactant form a family $\Omega^{\text{rec}\leftarrow\text{pro}}(E)$ of invariant cylinders that lie inside the other pair of cylindrical manifold, W_b^s and W_b^u . The nonreactive trajectories that stay on the reactant side or the product side lie on cylindrical invariant manifolds, outside $W_f^{s,u}$ and $W_b^{s,u}$. Trajectories in these cylindrical manifolds approach the bottleneck area from the reactants or the products side and then return back deeper into the reactants or products region. A sketch of these manifolds is shown in Figure 2.7(c).



FIGURE 2.7: Cylinders above the energy of saddle point are: (a) stable and unstable cylindrical manifolds. (b) forward and backward reaction paths. (c) nonreactive trajectories.

The set of invariant cylinders in phase space is

$$\{\Omega^{\rm rec}(E), \quad \Omega^{\rm pro}(E), \quad W_f^{s,u}, \quad W_b^{s,u}, \quad \Omega^{\rm rec \to pro}(E), \quad \Omega^{\rm rec \leftarrow pro}(E)\}$$

The four cylinders, $W_f^{s,u}$ and $W_b^{s,u}$, meet at the NHIM. The reactive trajectories are enclosed in these cylinders, go through the dividing surface and never return. Thus, these cylinders provide the phase space boundary between reactive and nonreactive trajectories. Thus, the stable and unstable cylindrical manifolds represent the separatrix to reaction for the system.

As discussed in more detail below, among these invariant manifolds only the NHIM and its stable and unstable manifolds $W_f^{s,u}$ and $W_b^{s,u}$ will persist in the full nonlinear system. The cylinders $\{\Omega^{\rm rec}(E), \Omega^{\rm pro}(E), W_f^{s,u}, W_b^{s,u}, \Omega^{\rm rec \to pro}(E), \Omega^{\rm rec \leftarrow pro}(E)\}$ will in general break up in the presence of anharmonic coupling between the degrees of freedom. As energy increases, the cylinders, $W_{f}^{s,u}$ and $W_{b}^{s,u}$ will then extend into the phase space and overlap one another. The dynamical behaviour of cylinders in the phase space has an interesting property. One can focus on the reactant side, namely W_f^s and W_b^u . These two cylinders intersect at so-called homoclinic trajectories. These trajectories will asymptotically reach the NHIM along the cylinders in both forward and backward in time. The overall structure in phase space is often called the homoclinic tangle. Consequently, an obvious phase space structure appears on the dividing surface as infinitely many layers. The manner in which the invariant cylinders overlap one another in phase space explains that stable and unstable manifold do not extend in the reactants or products in the infinite time but they go back again to the dividing surface (bound motion). In higher energies, the chaotic motion is involved in the overall motion which will essentially recross the dividing surface. The recrossing trajectories intersect the dividing surface in points. We will indicated the intersections with dividing surface as the reactive and nonreactive islands (RIs) which will be studied in details in Chapter 5.

2.8 Persistence of normally hyperbolic invariant manifolds

The concept of the normally hyperbolic invariant manifolds (NHIMs) is a generalization of fixed points and periodic orbits to higher dimensional manifolds which the dynamical expansion and contraction rates transverse to the NHIM are larger than those in direction parallel to it. The dynamics on the invariant manifold is approximately neutral and the dynamics in the transverse directions is hyperbolic; hence it is called normally hyperbolic.

The theory of the NHIM developed over many years. In 1970s, Fenichel [58] and Hirsch, Pugh and Shub [59] established the theoretical framework. Wiggins [50] describes Fenichel's theory regarding the NHIM and provides a discussion of some possible applications in the theory of dynamical system. This theory is more general than we will need in this study. We will here state the general result in a special case that will be sufficient for our purposes.

An invariant manifold is called normally hyperbolic if the dynamical expansion and contraction rates transverse to the manifold are larger than for the internal dynamics within the manifold. Two properties of a NHIM are relevant to our study: These are persistence of the invariant manifold under perturbation and the existence of stable and unstable manifolds of the NHIM.

Lyapunov exponents provide a precise formulation for the concept of transverse and internal dynamical expansion rate.

To compute a Lyapunov exponent for an arbitrary trajectory, consider a trajectory x(t) and a neighboring trajectory $x(t) + \sigma(t)$. Both trajectories must satisfy the equations of motion (2.3). If the variation σ is assumed to be infinitesimally small and the equations of motion are linearized in σ , we obtain the variational equations

$$\dot{\sigma} = -J \cdot \mathcal{P} \cdot \sigma, \quad \sigma(t_0) = \sigma_0,$$
(2.33)

where \mathcal{P} is the Hessian matrix of the Hamiltonian,

$$\mathcal{P}_{ij} = \frac{\partial^2 H}{\partial x_i \partial x_j}$$

We integrate the combined systems (2.3) and (2.33) with arbitrary initial conditions x_0 and σ_0 , and we ask how fast the length of the tangent vector $\sigma(t)$ will grow. The Lyapunov exponent of the trajectory starting at x_0 is defined by

$$\lambda(x_0, \sigma_0) = \limsup_{t \to \infty} \frac{1}{t} \ln \frac{\|\sigma(t)\|}{\|\sigma_0\|}, \qquad (2.34)$$

where $\|\sigma\|$ denotes the length of the vector σ . This definition corresponds to an exponential growth $\|\sigma(t)\| \propto e^{\lambda t}$. In general, the tangent vector σ will quickly align itself with the direction in which the expansion rate is largest. The resulting Lyapunov exponent does then not depend on the arbitrarily chosen initial vector σ_0 . There is an exception, however, for a trajectory in an invariant manifold: if the vector σ is initially chosen tangent to the invariant manifold, it will remain tangent to it at all times. In this situation, we can meaningfully compute a Lyapunov exponent parallel to the invariant manifold and a Lyapunov exponent in the full phase space. The invariant manifold is normally hyperbolic if the latter is larger than the former.

The Lyapunov exponents are particularly easy to compute for a periodic orbit [60]. Because the evolution equation (2.33) is linear in the variation vector σ , its solution can be written as $\sigma(t) = Y(t) \cdot \sigma_0$ with a matrix Y(t) that does not depend on σ . The matrix Y(T) is called the monodromy matrix of the corresponding periodic orbit with period T, its eigenvalues m_1, \ldots, m_{2n} are the Floquet multipliers. For a periodic orbit with period T, we have $Y(\mu T) = (Y(T))^{\mu}$ for $\mu = 1, 2, \ldots$. Therefore

$$\sigma(\mu T) = (Y(T))^{\mu} \cdot \sigma_0. \tag{2.35}$$

So, $m_1^{\mu}, ..., m_{2n}^{\mu}$ are the eigenvalues of $Y(\mu T)$. The spectrum of Lyapunov exponents of the particular periodic orbit is then

$$\lambda_i = \lim_{\mu \to \infty} \frac{1}{\mu T} \ln |m_i^{\mu}| = \frac{1}{T} \ln |m_i|, \qquad (2.36)$$

and the largest of the Floquet multipliers m_i will give the Lyapunov exponent (2.34). For a periodic orbit in an invariant manifold we can use the eigenvectors of Y(T) to distinguish whether eigenvalues correspond to variations parallel or transverse to the invariant manifold, and we can then choose the largest Lyapunov exponents in the parallel and transverse directions.

In a Hamiltonian dynamical system, the eigenvalues of the stability matrix Y(T) will always occur in pairs $e^{\pm\lambda T}$ or $e^{\pm i\varphi T}$ with real numbers λ and φ . These types of eigenvalues correspond to variations in unstable and marginally stable directions, and yield Lyapunov exponents λ and 0, respectively. A third possibility arises in Hamiltonian systems with three or more degrees of freedom: Eigenvalues can occur in quartets $e^{(\pm\lambda\pm i\varphi)T}$. In Chapter 4, this case is not relevant for our situation because the periodic orbits we are study lie within the centre manifold, which is a subsystem with only two degrees of freedom.

The parallel and perpendicular Lyapunov exponents will in general be different for different trajectories in the invariant manifold, though they will be equal for trajectories on the same invariant torus or in the same chaotic sea. To verify normal hyperbolicity numerically, we must therefore calculate Lyapunov exponents for a large number of representative trajectories and check that the perpendicular Lyapunov exponent is larger than the parallel exponent in all cases.

Chapter 3

The $H_2 + H$ exchange reaction

3.1 Introduction

The example we consider in this work is the simplest chemical reaction,

$$H + H_2 \longrightarrow H_2 + H.$$

The simplicity of this reaction is that the molecule consists of three hydrogen atoms which involve three electrons and three protons. This reaction played an important role in the development of theoretical and experimental investigations in reaction dynamics. In 1927, Born and Oppenheimer [61] derived a good approximation of the nuclei in a molecule with respect to the electrons. The Born-Oppenheimer approximation is based on the assumption that the electronic motion in molecules take place on much short time scales than the nuclear motion because the nuclear mass is much larger (about 2000 times) than the electron mass. This approximation implies that the total molecular wavefunction is defined as a product of an electronic wavefunction and a nuclear wavefunction. Born-Oppenheimer approximation is determined by fixing the nuclei at some chosen configuration and solve the Schrödinger equation for the motion of the electrons. The energy of the electronic ground state is regarded as potential energy for the this nuclear configuration. The effective interaction of the nuclei is described by the potential energy surface. An early fundamental investigations of chemical reaction dynamics have been done by London (1929) [62]. Using the framework of Born-Oppenheimer approximation, he provided a semi-empirical formula for the potential energy surface which describes the nuclear motions for the $H_2 + H$ system.

Eyring and Polanyi (1930) [7] extended London's approach and numerically computed the collinear potential energy surface for the $H_2 + H$ system. Hirschfelder, Eyring and Topley (1936) [63] calculated the first classical trajectories of the dynamics of the $H_2 + H$ reaction, using the potential energy surface of Eyring and Polanyi.

Truhlar and Wyatt [64] reviewed the improvements concerning calculations of an accurate potential energy surface which were worked out during the 1960's. Porter and Karplus [25] have essentially improved the semi-empirical potential energy function, which is applied in this thesis and also been used in some recent works in the dynamics studies [21]. The analytic expression of this surface is presented in section 3.2. The theoretical investigations concern the nuclei are dynamics which is considered as a mass, moving in the potential energy surface. For development on the experimental investigations, the reader is referred to the literature [65–69].

In this Chapter, we present a Hamiltonian that is applied to the hydrogen exchange molecular reaction. We derive a Hamiltonian for the system with three degrees of freedom, called *full system*, and its two sub-systems with two degrees of freedom, namely *collinear and reduced centre manifold systems*. The Hamiltonians derived in this Chapter will be used in the following two Chapters. Results in Chapter 4 are based on the Hamiltonian of full system and the reduced centre manifold system while results in Chapter 5 are based on the Hamiltonian of full system.

3.2 Potential energy function

The Porter-Karplus potential energy function [25] is given by

$$V = (1/C_1) \left[-C_2 - (C_2^2 - C_1 C_3)^{1/2} \right]$$
(3.1)

where the quantities C_1, C_2 and C_3 are given as follows

$$\begin{split} C_1 &= (1 - S_1 S_2 S_3)^2 - \frac{1}{2} \left[(S_1^2 - S_2^2)^2 + (S_2^2 - S_3^2)^2 + (S_1^2 - S_3^2)^2 \right], \\ C_2 &= -(Q - J_{123})(1 - S_1 S_2 S_3) \\ &\quad + \frac{1}{2} \left[(J_1 - J_2)(S_1^2 - S_2^2) + (J_2 - J_3)(S_2^2 - S_3^2) + (J_1 - J_3)(S_1^2 - S_3^2) \right], \\ C_3 &= (Q - J_{123})^2 - \frac{1}{2} \left[(J_1 - J_2)^2 + (J_2 - J_3)^2 + (J_1 - J_3)^2 \right], \\ Q &= Q_1^d + Q_2^d + Q_3^d, \\ Q_k^d &= \frac{1}{2} \left[{}^1 E_k + {}^3 E_k + S_k^2 ({}^1 E_k - {}^3 E_k) \right], \end{split}$$

$$J_{k} = \frac{1}{2} ({}^{1}E_{k} - {}^{3}E_{k}) + S_{k}^{2} \{\frac{1}{2} ({}^{1}E_{k} + {}^{3}E_{k}) + \delta [(1 + R_{l}^{-1}) \exp(-2R_{l}) + (1 + R_{m}^{-1}) \exp(-2R_{m})]\},$$

$${}^{1}E_{k} = D_{1} \{ \exp [-2\alpha (R_{k} - R_{e})] - 2 \exp [-\alpha (R_{k} - R_{e})]\},$$

$${}^{3}E_{k} = D_{3} \{ \exp [-2\beta (R_{k} - R_{e})] + 2 \exp [-\beta (R_{k} - R_{e})]\},$$

$$S_{k} = (1 + \zeta_{k}R_{k} + \frac{1}{3}\zeta_{k}^{2}R_{k}^{2}) \exp(-\zeta_{k}R_{k}),$$

$$\zeta_{k} = 1 + \kappa \exp(-\lambda R_{k}),$$

$$J_{123} = \epsilon S_{1}S_{2}S_{3},$$



FIGURE 3.1: The contour plot of the potential energy function $V(R_1, R_2)$. sp refers to the saddle point.

where k, l, m = 1, 2, 3 with $m \neq l \neq k$. The potential energy expression depends on three variables, namely R_1, R_2 and R_3 (distances between three atoms) and contains nine parameters which are $D_1, D_3, R_e, \alpha, \beta, \kappa, \lambda, \delta$ and ϵ . These parameters are shown in Table 3.1. The saddle point configuration is linear and symmetric and satisfies

$$R_1 = R_2 = \frac{1}{2}R_3. \tag{3.2}$$

Thus, the saddle point configuration is collinear. Figure 3.1 shows the collinear potential energy surface of (3.2). It appears like an L-shaped valley, located between two 'knolls'. The saddle point (sp) lies on the highest point on the valley path and between two cliffs. The saddle point has coordinates $R_1 = R_2 = 1.70083$ a.u. and energy value -4.3504 eV. TABLE 3.1: The $H_2 + H$ potential energy parameters. Taken from [25].

| $D_1 = 4.7466 \text{ eV}$ | $\beta = 28.2 \text{ eV}$ |
|---------------------------|-----------------------------|
| $D_3 = 1.9668 \text{ eV}$ | $\epsilon = -17.5~{\rm eV}$ |
| $R_e = 1.40083$ a.u. | $\kappa = 0.60$ |
| $\alpha = 1.04435$ a.u. | $\lambda = 0.65$ |
| $\beta = 1.000122$ a.u. | |
| | |



FIGURE 3.2: The coordinates for $H + H_2$ exchange reaction.

3.3 Kinetic energy function

Kinetic energy is the energy of motion. The kinetic energy of an object is the energy which it possesses due to its motion.

In our example the hydrogen exchange reaction, the kinetic energy is derived from that given, for example, by Waalkens *et al* [70]. They study the HCN/CNH isomerization reaction in Jacobi coordinates: r the distance between C and N, Rthe distance between H and the centre of mass of CN and γ the angle between H, the centre of mass of CN and C (i.e.: Here the atoms C, N and H take the places of H1, H2 and H3, respectively in Figure 3.2). The corresponding kinetic energy expression is

$$T = \frac{1}{2\mu}p_r^2 + \frac{1}{2m}p_R^2 + \frac{1}{2}\left(\frac{1}{\mu r^2} + \frac{1}{mR^2}\right)p_{\gamma}^2,$$
(3.3)

where $\mu = m_C m_N / (m_C + m_N)$ is the reduced mass of CN and $m = m_H (m_C + m_N) / (m_H + m_C + m_N)$ is the reduced mass of the full system. In the exchange hydrogen reaction, we have three identical atoms (all atoms have same mass). Thus μ and m become $\frac{1}{2}m_H$ and $\frac{2}{3}m_H$, respectively. As a result, the kinetic energy function (3.3) has the following form

$$T = \frac{1}{m_H} p_r^2 + \frac{3}{4m_H} p_R^2 + \left(\frac{1}{m_H r^2} + \frac{3}{4m_H R^2}\right) p_\gamma^2.$$
 (3.4)

It is singular when R = 0. This is the case for symmetric collinear configurations such as the saddle point that is of central importance in our study. To avoid this singularity, we replace the polar coordinates R and γ by Cartesian coordinates xand y, as shown in Figure. 3.2. The coordinate systems are related by

$$x = R \cos \gamma,$$
 $y = R \sin \gamma,$
 $R^2 = x^2 + y^2,$ $\gamma = \arctan\left(\frac{y}{x}\right).$

We use r as the third coordinate as before.

The generating function W associated with this transformation is

$$W = p_r r + p_x R \cos \gamma + p_y R \sin \gamma.$$

It yields the following transformation of momenta:

$$p_{R} = \frac{\partial W}{\partial R} = p_{x} \cos \gamma + p_{y} \sin \gamma$$
$$= \frac{x p_{x} + y p_{y}}{R},$$
$$p_{\gamma} = \frac{\partial W}{\partial \gamma} = -p_{x} R \sin \gamma + p_{y} R \cos \gamma$$
$$= -y p_{x} + x p_{y}.$$

Substituting these results into (3.4), we get

$$T = \frac{1}{m_H} \left[p_r^2 + \frac{3}{4} (p_x^2 + p_y^2) + \frac{(xp_y - yp_x)^2}{r^2} \right], \qquad (3.5)$$

which is the result that will be used in the Hamiltonian systems with two and three degrees of freedom (the collinear system, the reduced centre manifold system and the full-dimensional system). The singularity where r = 0 is not relevant to our study because it represents the distance between H1 and H2 which cannot be zero during the reaction neither in the reactants, the products or the transition state.

3.4 Hamiltonian function and its subsystems

The hydrogen exchange reaction $H + H_2 \rightarrow H_2 + H$ involves three atoms. Consequently, if the atoms are assumed to move in three-dimensional space, the reaction is described by nine degrees of freedom. Three of these, which represent the centre of mass motion, can be separated directly. Of the remaining six degrees of freedom, three describe spatial rotations of the complex and three describe vibrations. They can be separated only if the total engulf momentum of the molecule is zero, with we will assume. Even then, the attempt to separate the rotational degrees of freedom leads to a vibrational phase space that is singular for all collinear configurations, which are invariant under rotations around the axis on which the atoms lie [71, 72].

The origin of this singularity can be illustrated with the help of Figure. 3.2. To obtain the configuration space of the vibrational dynamics, we have to identify all configurations of the reactive complex that can be transformed into each other by translations or rigid rotations. The shape of the complex can then be described by the three coordinates r, x and y, where r is the distance between H1 and H2, y is the perpendicular distance from H3 to the distance r, and x is the distance from the midpoint of H1 and H2 to the end of the line through H3 perpendicular

to r. There are some configurations are not different, namely (r, x, y) can be transformed (r, x, -y) by a rotation around the axis through H1 and H2. To resolve this ambiguity, the configuration space must be restricted to the half space $(r, x, y \ge 0)$. It has a boundary that is formed by the collinear configurations with y = 0. The dynamics must necessarily be singular at these configurations.

We are mainly interested in studying the dynamics in the vicinity of the saddle point that marks the transition region for the exchange reaction. Unfortunately, the activated complex is collinear at the saddle point, and the ensuing singularity makes it difficult to analyze the dynamics. To circumvent this difficulty, we regard configurations with positive and negative values of y as different. This convention, which has also been employed in previous studies [55, 70], can physically be interpreted as constraining the three atoms to move in a plane. The full system then has six degrees of freedom, two of which correspond to the centre of mass motion and one to planar rotations. Again, we assume vanishing angular momentum. The remaining three degrees of freedom, which can be described, for example, by the three coordinates r, x and y of Figure. 3.2, describe the vibrational dynamics of the complex. Because the collinear configurations are not invariant under rotations in the plane, or equivalently, because configurations with positive and negative y cannot be transformed into each other through planar rotations, the symmetry-reduced phase space does not have singularities. It is well suited to an investigation of the dynamics near the saddle point.

We will study the vibrational dynamics of the complex at zero angular momentum. The Hamiltonian is then given by

$$H = \frac{1}{m_H} \left[p_r^2 + \frac{3}{4} (p_x^2 + p_y^2) + \frac{(xp_y - yp_x)^2}{r^2} \right] + V(r, x, y),$$
(3.6)

where m_H is the mass of the hydrogen atom ($m_H = 1.00794$ u). The expression for the kinetic energy is already derived from that given, for example, by Waalkens *et al* [73]. The transformation to our reaction was shown earlier. We use the potential energy surface V(r, x, y) derived by Porter and Karplus [25] (see Section 3.2). Distances will be measured in atomic units (a.u.) and energies in electron volts (eV), with the potential energy of three isolated hydrogen atoms chosen as zero.

The potential energy V(r, x, y) has two reflection symmetries: $x \mapsto -x$ and $y \mapsto -y$. That these transformations must leave the potential invariant is clear from Figure. 3.2 because the three atoms are identical. The two reflections of configuration space are extended to phase space by the canonical transformations

$$P_{x}: (r, x, y, p_{r}, p_{x}, p_{y}) \mapsto (r, -x, y, p_{r}, -p_{x}, p_{y}),$$

$$P_{y}: (r, x, y, p_{r}, p_{x}, p_{y}) \mapsto (r, x, -y, p_{r}, p_{x}, -p_{y}).$$
(3.7)

Both of these are symmetries of the Hamiltonian (3.6), as is their composition

$$P_x \circ P_y: \quad (r, x, y, p_r, p_x, p_y) \mapsto (r, -x, -y, p_r, -p_x, -p_y).$$

Corresponding to the two reflection symmetries (3.7) there are two subsystems with two degrees of freedom. They contain all configurations that are invariant under one of the reflections.

The reactive complex is invariant under P_y if $y = p_y = 0$. These are precisely the collinear configurations. The Hamiltonian of the collinear case is given by

$$H = \frac{1}{m_H} \left[p_r^2 + \frac{3}{4} p_x^2 \right] + V(r, x).$$
(3.8)

Numerous researchers including Pollak and co-workers [17–19, 74] and most recently Iñarrea *et al* [21] have studied the collinear hydrogen exchange reaction.

The subsystem invariant under the reflection P_x contains all axially symmetric configurations with $x = p_x = 0$ (triangle with two equal angles). The dynamics within this subsystem is described by the Hamiltonian

$$H = \frac{1}{m_H} \left[p_r^2 + \frac{3}{4} p_y^2 \right] + V(r, y).$$
(3.9)

The saddle point of the Porter-Karplus potential energy surface is located at the symmetric collinear configuration $(r, x, y) = (r_S, 0, 0)$ with $r_S = 3.40166$ a.u. To obtain a harmonic approximation of the dynamics close to the saddle point, we expand the Hamiltonian (3.6) in a Taylor series up to second order. The last term in the kinetic energy (the fourth order) will not contribute because x and y are zero. Due to its symmetries the expansion of the potential energy cannot contain any terms of odd order in either x or y. Up to an additive constant the harmonic Hamiltonian must therefore be of the form

$$H_2 = \frac{1}{m_H} \left[p_r^2 + \frac{3}{4} (p_x^2 + p_y^2) \right] + a_1 (r - r_{\rm S})^2 + b_1 x^2 + c_1 y^2 \tag{3.10}$$

with constants a_1 , b_1 , c_1 that cannot be determined from symmetry considerations. Thus, the dynamics in r, x and y will decouple in the harmonic approximation. Because the expansion point is a saddle, the dynamics must be unstable in one of the three coordinates, namely the reaction coordinate. In the reactant and product states the middle atom H3 is bound to either H1 or H2, whereas the third atom is far away. It is therefore plausible to identify the reaction coordinate with the coordinate x that brings H3 closer to one or the other atom. Indeed, the expansion of the Porter-Karplus potential shows that the coefficient b_1 is negative whereas a_1 and c_1 are positive.

As a consequence, the symmetric subsystem $x = p_x = 0$ in which the motion in the reaction coordinate is suppressed forms the centre manifold of the transition state, i.e. it contains all configurations in which the system oscillates around the unstable equilibrium point. The symmetry of the system makes it easy to identify the centre manifold without laborious calculations. It allows us to avoid the normal form calculations that are required in reactive systems without this symmetry [23, 75, 76].

Furthermore, we can demonstrate the analytical solution of the harmonic Hamiltonian. In the full system with three degrees of freedom, the harmonic Hamiltonian equations of motion are as follow

$$\dot{r} = \frac{\partial H_2}{\partial p_r} = \frac{2}{m_H} p_r = a_2 p_r,$$

$$\dot{x} = \frac{\partial H_2}{\partial p_x} = \frac{3}{2m_H} p_x = b_2 p_x,$$

$$\dot{y} = \frac{\partial H_2}{\partial p_y} = \frac{3}{2m_H} p_y = c_2 p_y,$$

$$\dot{p}_r = \frac{-\partial H_2}{\partial r} = -a_1 r,$$

$$\dot{p}_x = \frac{-\partial H_2}{\partial x} = -b_1 x,$$

$$\dot{p}_y = \frac{-\partial H_2}{\partial y} = -c_1 y.$$

where a_1, b_1, c_1 are obtained by Taylor series and denoted in (3.10). The coefficients a_1, b_1, c_1 with their units are 2.47328 $\frac{eV}{a_0^2}$, -3.31467 $\frac{eV}{a_0^2}$ and 0.664463 $\frac{eV}{a_0^2}$, respectively where a_0 is the Bohr radius. The eigenvalues of the Hamiltonian Hessian matrix are

$$(\pm\lambda, \pm\omega_1 i, \pm\omega_2 i) = (\pm 2.221, \pm 2.21531i, \pm 0.994401i)$$

where $\omega_1 = \sqrt{a_1 a_2}$, $\lambda = \sqrt{b_1 b_2}$ and $\omega_2 = \sqrt{c_1 c_2}$. With the following constants

(Bohr Radius)
$$1a_0 = 0.52917 \times 10^{-10} \text{m},$$

(Atomic Mass Constant) $1u = 1.6605 \times 10^{-27} \text{kg},$
(Electron Volt) $1eV = 1.602 \times 10^{-19} \text{J},$

the frequency unit is given by

$$\sqrt{\frac{eV}{u \cdot a_0^2}} = 1.85617 \times 10^{14} s^{-1}.$$

Thus the frequencies (ω_1, ω_2) are

$$\omega_1 = \pm 4.1121 \times 10^{14} \mathrm{s}^{-1}, \qquad (3.11)$$

$$\omega_2 = \pm 1.84583 \times 10^{14} \mathrm{s}^{-1}. \tag{3.12}$$

Moreover we can simplify the corresponding solution in terms of the initial conditions, hydrogen mass and the eigenvalues as

$$r(t) = r_0 \cos \omega_1 t + \frac{a_2}{\omega_1} p_{r_0} \sin \omega_1 t,$$

$$p_r(t) = p_{r_0} \cos \omega_1 t - \frac{\omega_1}{a_2} r_0 \sin \omega_1 t,$$

$$x(t) = x_0 \cosh \lambda t + \frac{b_2}{\lambda} p_{x_0} \sinh \lambda t,$$

$$p_x(t) = p_{x_0} \cosh \lambda t + \frac{\lambda}{b_2} x_0 \sinh \lambda t,$$

$$y(t) = y_0 \cos \omega_2 t + \frac{c_2}{\omega_2} p_{y_0} \sin \omega_2 t,$$

$$p_y(t) = p_{y_0} \cos \omega_2 t - \frac{\omega_2}{c_2} y_0 \sin \omega_2 t,$$

(3.13)

where $r_0, x_0, y_0, p_{r_0}, p_{x_0}$ and p_{y_0} are the initial conditions.

Chapter 4

Chaotic dynamics in multidimensional transition states

4.1 Introduction

As described in Chapter 2, the important structures that determine the dynamics in the transition region of a system with three degrees of freedom, include a three-dimensional sphere, the NHIM, and it stable and unstable manifolds. These structures were found in the harmonic approximation, and the question remains under what condition they survive in the realistic anharmonic system.

In general, the persistence of these manifolds can be guaranteed as long as the three-sphere that embodies the transition state and that we will call the central sphere, is normally hyperbolic, i.e., the dynamical expansion and contraction rates transverse to the central sphere are larger than those within it. For the hydrogen exchange reaction, we will see that the existence of the central sphere itself can be assured up to high energies even if it is not normally hyperbolic. Its stable and unstable manifolds, the reaction cylinders, will, however, break up if normal hyperbolicity fails. It is therefore important to study whether, and at what energies, that happens.

The central sphere is normally hyperbolic for energies just above the reaction threshold. The reaction dynamics within the transition state region is then accurately described by a harmonic approximation (see e.g. Section 3.4). The dynamics within the invariant hyper-sphere is therefore completely regular, and the condition of normal hyperbolicity is satisfied. At higher energies, the dynamics within the sphere will become partially chaotic, and a breakdown of normal hyperbolicity may result. Such a scenario has indeed been described in [29, 75, 76] for a model reaction. The authors analyse the dynamics with the help of normal form transformations. Because this procedure does not in general converge, it can become difficult, in particular at higher energies, to distinguish the properties of the underlying dynamical system from artefacts of the normal form. In this chapter, we will investigate the dynamics within the transition state of a physical system and present a detailed description of those features that lead to a breakdown and, surprisingly, to a subsequent reestablishment of normal hyperbolicity.

The central sphere has customarily [23, 70, 77–80] been called "the NHIM". Because we are interested in situations in which the invariant hyper-sphere fails to be normally hyperbolic, we will avoid that term.

There are two fundamental periodic orbits within the centre manifold: a symmetric stretch periodic orbit (SSPO) and a bending periodic orbit (BPO). In addition, a secondary symmetric stretch periodic orbit (ScPO), that is generated by a bifurcation, plays an important role because it gives rise to a large regular island. These periodic orbits undergo a sequence of bifurcations in which they successively lose and regain stability.

To decide at what energies the central sphere is normally hyperbolic, we compute Lyapunov exponents in directions parallel and perpendicular to the sphere for both periodic and non-periodic orbits. We find that the SSPO is the only orbit that violates the condition of normal hyperbolicity, and that only in a small energy interval. Nevertheless, the dynamics of the exchange becomes more and more complex as the energy is increased, as is evident already in the collinear subsystem. The results in this chapter have been published in the Journal of Chemical Physics with co-author Thomas Bartsch [81].

4.2 Dynamics within the centre manifold

The Hamiltonian vector field of (3.6) has an equilibrium point (saddle point) which is (r, x, y) = (3.40166 a.u., 0, 0). As we are interested in the transition state, we seek the centre manifold of the saddle point. The reduction to the centre manifold for the Hamiltonian system (3.9) gets rid of one degree of freedom. Hence, the centre manifold forms a subsystem with two degrees of freedom. Specifically, it is the space of all symmetric configurations, where $x = p_x = 0$. Since the hydrogen exchange reaction has three identical atoms, if any arbitrary trajectory starts with a symmetric state, it will remain in a symmetric configuration. Thus, the symmetry makes it easy to identify the centre manifold.

The central sphere that controls transport through the transition state at low energies can be identified with the energy shell within the centre manifold, as described in Chapter. 2. As we aim to investigate the breakdown of the lowenergy phase space structures, we will start by studying the dynamics within the centre manifold.

Figure 4.1 shows a contour plot of the potential energy for symmetric configurations (i.e. within the centre manifold, with x = 0). The saddle point (sp) of the three-dimensional system appears as a minimum. It lies at (3.40166 a.u., 0) in r, ycoordinates and has energy value -4.3504 eV. The second prominent feature of the potential is a conical intersection ridge. It occurs at equilateral configurations,



FIGURE 4.1: The contour plot of the potential energy surface of the centre manifold (x = 0) of the equilibrium saddle point of the Hamiltonian flow. (sp) refers to saddle point and (c.i.) refers to the conical intersection.

where $y = \frac{\sqrt{3}}{2}r$. For these configurations the two lowest electronic states are degenerate. As a consequence, the potential energy surface, which gives the energy of the lowest state, is not smooth at the intersection. The lowest point on the ridge occurs at r = 1.90352 a.u., $y = \pm 1.64849$ a.u. with energy $E_{c.i.} = -1.9514$ eV. Above this energy, a new reaction channel opens in which the central atom (H3 in Figure 3.1) can escape across the ridge, leaving the two outer atoms bound as a molecule. The transition across the conical intersection cannot be described by classical mechanics. We will restrict our following investigations to energies below $E_{c.i.}$. As we will see, complicated dynamics develop well below this threshold.

For energies between the saddle point and the conical intersection, the contour line of the potential energy is topologically a circle. The energy shell in phase space (within the centre manifold) has therefore the same topology as it has in the harmonic approximation, i.e., it is a three-dimensional hyper-sphere that we have called the central sphere. At low energies, it is normally hyperbolic. As the energy increases, normal hyperbolicity might, and indeed will, be destroyed. We know from these simple considerations, however, that the central sphere will persist even at energies where it is not normally hyperbolic.

4.2.1 Bifurcation of periodic orbits

The internal dynamics of the central sphere, can be described by two bath modes [82]. The first bath mode resulting in a symmetric stretch periodic orbit (SSPO). The second in a bending periodic orbit (BPO). At energies close to the saddle point, where the harmonic approximation is accurate, the dynamics within the central manifold can be described by two normal mode vibrations, a symmetric stretch and a bend of the activated complex. Their frequencies can be obtained from a second-order Taylor series expansion of the potential, i.e., from the constants *a* and *c* in equation (3.10), as $\omega_{SSPO} = 4.1121 \times 10^{14} \text{ s}^{-1}$ and $\omega_{BPO} = 1.8458 \times 10^{14} \text{ s}^{-1}$, indicated in more details in (3.11), (3.12) respectively. Both normal mode periodic orbits are stable with respect to a perturbation of initial conditions within the centre manifold. As the energy increases, they undergo a sequence of bifurcations in which they lose their stability and give rise to further stable periodic orbits, as illustrated schematically in Figure 4.2.

Figure 4.2 shows the bifurcation diagram of the two fundamental periodic orbits, the symmetric stretch (SSPO) and the bend (BPO) within the centre manifold. The first bifurcation occurs in the SSPO at $E \approx -4.32547$ eV, just above the saddle point energy. The SSPO undergoes a period doubling bifurcation: It becomes unstable and a new stable periodic orbit with twice the period appears. We will see that this periodic orbit plays an important role in structuring the dynamics within the centre manifold. We will call it the secondary symmetric stretch periodic orbit (ScPO).

The configuration space projections of the fundamental periodic orbits are shown in Figure 4.3 for energies E = -4.3 eV and E = -4.0 eV. It can be clearly seen that even though the ScPO is generated by a bifurcation from the SSPO, it takes on pronounced bending character at higher energies. All three periodic orbits are invariant under the reflection P_y . The SSPO is located within the collinear subsystem, which means that each point on the SSPO is invariant under



FIGURE 4.2: Schematic Bifurcation diagram for the system within centre manifold. The solid and dashed black lines denote stable and unstable periodic orbits, respectively. PD refers to periodic doubling bifurcation and SB refers to symmetry breaking bifurcation.

reflection. This is not true for the ScPO and BPO. These periodic orbits are invariant in the sense that any point on one of these orbits is mapped under reflection to a different point on the same orbit. Periodic orbits of this type can undergo symmetry breaking bifurcations that do not exist in systems without reflection symmetries [83, 84]: A stable periodic orbit (ScPO) that is invariant under reflection turns unstable and gives rise to two stable periodic orbits that are not invariant, but are mirror images of each other. The asymmetric periodic orbits have roughly the same period as the symmetric one.

A symmetry breaking bifurcation of the ScPO occurs at the energy $E \approx -2.5$ eV. Figure 4.4 shows the configuration space projections of the ScPO and the two new periodic orbits for energy E = -2.3 eV. It is obvious from the figure that the



FIGURE 4.3: Periodic orbits on the potential energy of centre manifold at energies (a) E = -4.3 eV, (b) E = -4.0 eV.

satellite orbits have lost their reflection symmetry. At a higher energy $E \approx -2.2$ eV the asymmetric periodic orbits collapse onto the ScPO again and the ScPO regains stability in an inverse symmetry breaking bifurcation.

In a similar scenario, the BPO undergoes a symmetry breaking bifurcation at $E \approx -3.8$ eV, and the two asymmetric periodic orbits thus generated collapse onto the BPO again and disappear at $E \approx -2.4$ eV in an inverse symmetry breaking bifurcation. These three periodic orbits are shown in Figure 4.5 for energy $E \approx -3.3$ eV. The two asymmetric orbits have the same projection into


FIGURE 4.4: The ScPO (black) and its branches (green and brown) at E = -2.3 eV.

configuration space, but, as the phase space figures show, they are traversed in different directions.

4.2.2 Poincaré surface of section

In order to investigate the dynamics within the centre manifold in more detail, we choose a suitable Poincaré surface of section. Since the centre manifold is four dimensional, the surface of section will have two dimensions and will be easy to visualize. A standard approach is to look at a Poincaré surface of section.

For our example (3.9), we fix the energy E and pick the surface of section y = 0. The surface of section is two-dimensional, with coordinates r and p_r . The remaining phase space coordinates p_y is determined from the condition

$$H(p_r, p_y, r, y = 0) = E.$$
(4.1)

This is a quadratic equation for p_y . We choose the positive value of p_y to define a two-dimension surface of section in the three-dimensional energy shell. A given trajectory starting on the surface of section will in general intersect this surface



FIGURE 4.5: The BPO and its branches at $E = -3.3 \,\text{eV}$.

several times. A Poincaré surface of section plot is obtained by making successive intersection of a single trajectory with the surface of section.

The SSPO lies within the surface of section. Indeed, it bounds the area that is energetically accessible at a given energy. In contrast, the BPO appears as the central point in the low energy surface of section. For various energies, the surface of section is shown in Figure 4.6.

In phase space, the Poincaré surface of sections determine the dynamical behaviour. If the plotted points on the Poincaré surface of sections appear as closed curve in the two dimensional (r, p_r) plane, then the motion is regular and not a chaotic motion. This is because we have a regular orbit (quasiperiodic orbit) that moves on a torus in the phase space and the curve appears in the intersection of y = 0. In a non-chaotic (integrable) Hamiltonian system, the regular motion (quasiperiodic) has more than one dependent frequency. This orbit moves on



-0.15

0.6

0.4

0.2

0.0

-0.2

-0.4

-0.6

3.0

(f)

1.0

0.5

0.0

-0.5

-1.0

-1.5

p_r(a.u.)

p_r (a.u.)

3.30

(d) E=-4.0 eV

0

3.2

E=-2.3 eV

3.35

3.45

^{3.6} r (a.u.)

r (a.u.)

3.40

r (a.u.)

3.50

3.55

-0.02

0.2

0.1

0.0

-0.1

0.6

0.4

0.2

0.0

-0.2

-0.4

-0.6 ScPC

2.8

3.0

3.2

p_r (a.u.)

-0.2 - ScPC

(e) E=-3.9 eV

SSPO

p_r (a.u.)

(c) E=-4.3 eV

SSPO

r (a.u.)

BPQ

r (a.u.)

BPO

3.6

r (a.u.)

3.4

4.0

3.8

4.2

FIGURE 4.6: Poincaré surface of section $y = 0, p_y > 0$ for dynamics within the centre manifold at the energies (a) -4.35 eV, (b) -4.32547 eV, (c) -4.3 eV, (d) -4.0 eV, (e) -3.9 eV (BPO is unstable) and (f) -2.3 eV (ScPO is unstable). The main periodic orbits are labeled in (a), (c) and (e).



FIGURE 4.7: Poincaré surface of section r = 3.40166 a.u., $p_r > 0$ for dynamics within the centre manifold at the energies (a) -4.35 eV, (b) -4.3 eV, (c) -4.0 eV and (d) -3.5 eV. The main periodic orbits are labeled in (c).

an invariant torus. However, most quasiperiodic motion is preserved under weak perturbations in accordance with the Kolmogorov Arnold and Moser KAM Theorem [85]. In contrast, the chaotic motion occurs, if those KAM tori are destroyed. The points in Poincaré section appear as randomly distributed points in the area of chaos. In Figure 4.6(c) the energy is -4.25 eV, the chaotic region starts to appear in a very small area. As the energy value gets higher, the chaotic region grows up and the Poincaré section preserves also two islands where the chaos is in between. The energy -2.3 eV has a largest chaos region in Figure 4.6 series.

Some of the bifurcations of the fundamental periodic orbits, such as the loss and return of stability of the BPO, can also be seen in Figure 4.6. The bifurcation of the SSPO has an unusual appearance because the SSPO forms the boundary of the surface of section. As a consequence, the ScPO appears at the boundary and moves toward the centre of the surface of section. The Poincaré plots show only a single periodic point corresponding to the ScPO, as the chosen surface of section is $p_y > 0$. A second periodic point is located in the surface $p_y < 0$. Both periodic points can be seen in Figure 4.7, which shows the Poincaré surface of section $r = r_{\rm S} = 3.40166$ a.u for some selected energies, namely (a) -4.35 eV, (b) -4.3 eV, (c) $-4.0 \,\mathrm{eV}$ and (d) $-3.5 \,\mathrm{eV}$. In details, the SSPO in Figure 4.7(b) intersects this surface transversely, and its bifurcations are therefore shown more clearly. The neighborhood of the SSPO in Figure 4.7(c) has the appearance one would expect close to a period doubling bifurcation. Note, however, that the situation is different from that shown in Figure. 4.6(e) in the neighbourhood of the BPO. As indicated by the colors, the two periodic points appearing there belong to two different periodic orbits, each of which has approximately the same period as the BPO. The two periodic points close to the SSPO in Figure 4.7(c) lie on a single periodic orbit of twice the period.

In Figure 4.8, we show the two periodic orbits, SSPO and BPO, are located in the boundary of the Poincaré section and the central point, respectively where the section is y = 0 in the centre manifold of the saddle point. At low energies, the intersections of a single trajectory with the surface of section lies on closed curve, indicating quasi-periodic motion. The BPO moves along the perpendicular circle that crosses the Poincaré section in the centre. If we move slightly away from the BPO bath mode, the motion takes place on a small 2-torus. Any initial condition on 2-torus corresponds to a quasi-periodic trajectory which remains on the 2-torus. As we move from the BPO bath mode, the 2-torus becomes thicker,



FIGURE 4.8: Symmetric stretch periodic orbit and Bending periodic orbit at low energy.

and then thiner until we reach to the SSPO bath mode. The motion at SSPO is along a horizontal circle. This procedure shows the internal dynamics of the NHIM which is foliated by a numbers of 2-torus. Thus trajectory on the 2-torus moves in both bath modes [82].

In addition to the fundamental periodic orbits, the surface of section plots show many other, longer periodic orbits that are not included in Figure 4.2. Of these there are, of course, infinitely many. Most important for our purposes is the observation that regions of chaotic dynamics appear and grow as the energy is increased. If the dynamics within the central sphere is chaotic, the central sphere might fail to be normally hyperbolic. We will investigate this question in the following section.

| Energy | Within centre manifold | | Off centre manifold | |
|----------|------------------------|-------------------|---------------------|-------------------|
| -4.35 | -0.949855 | $0 \pm 0.312691i$ | 543.591 | 0.00183962 |
| -4.32547 | $-1 \pm 0.000746992i$ | | 513.284 | 0.00194824 |
| -4.02482 | -2.80253 | -0.35682 | 2.80224 | 0.35685751 |
| -4.02425 | -2.8049 | -0.356519 | 0.950972 | $2 \pm 0.309275i$ |
| -4.02251 | -2.81218 | -0.355595 | -0.9855 | $57 \pm 0.16925i$ |
| -4.02195 | -2.81447 | -0.355306 | -2.83866 | -0.35227832 |
| -4.0 | -2.9049 | -0.344246 | -52.8575 | -0.0189188 |
| -3.5 | -4.63902 | -0.215563 | -1922.55 | -0.000520141 |
| -3.0 | -5.8626 | -0.170573 | -6579.25 | -0.000151993 |
| -2.5 | -6.54368 | -0.152819 | -19026.1 | -0.000052559 |
| -2.0 | -6.53349 | -0.153057 | -57321.7 | -0.000017445 |

TABLE 4.1: Floquet multipliers of the Symmetric Stretch Periodic Orbit (SSPO).

4.3 Breakdown of normal hyperbolicity

For the hydrogen exchange reaction, we have seen that we can guarantee the existence of the central sphere for energies up to the conical intersection ridge without having to rely on its normal hyperbolicity. The full geometric structure of TST, however, also requires the existence of the reaction tubes, i.e., the stable and unstable manifolds of the central sphere. This can only be guaranteed if the central sphere is normally hyperbolic. We need to investigate the energy range in which this is the case. To do this, we compute Lyapunov exponents for our fundamental periodic orbits and for arbitrary initial conditions.

Earlier studies of the dynamics in the collinear subsystem [19, 86] found an energy interval in which the SSPO is stable against variations within that subsystem, which is transverse to the centre manifold. Also the narrow energy interval coincides with those values found recently by Iñarrea *et al* [21] in the collinear case for the Porter-Karplus potential energy surface. For these energies, the transverse

| Energy | Within centre manifold | Off centre manifold | |
|----------|------------------------|---------------------|--|
| -4.35 | 0 | 2.220474458259545 | |
| -4.32547 | 0.001595724796612 | 2.193684182205109 | |
| -4.02482 | 0.348776954066669 | 0.348741930492273 | |
| -4.02425 | 0.349037205882743 | 0 | |
| -4.02251 | 0.349834777590742 | 0 | |
| -4.02195 | 0.350085127667877 | 0.352980521930331 | |
| -4.0 | 0.359752944464669 | 1.338481833206746 | |
| -3.5 | 0.482967609340161 | 2.379868060383772 | |
| -3.0 | 0.514280646841623 | 2.556488886847313 | |
| -2.5 | 0.497885535004521 | 2.611631229788495 | |
| -2.0 | 0.444521028240257 | 2.594841756256228 | |

TABLE 4.2: Lyapunov Exponents of SSPO

Lyapunov exponent of the SSPO is zero, and it is clear that this situation must violate the condition of normal hyperbolicity as soon as the transverse Lyapunov exponent decreases below that within the centre manifold. Table 4.1 shows the Floquet multipliers of the SSPO within and transverse to the centre manifold. The SSPO is unstable within the centre manifold for those energies where it is stable in the collinear direction. As the energy increases further, the SSPO is unstable in both directions, but the instability in the collinear direction grows faster than that within the centre manifold, so that soon the SSPO does not violate the normal hyperbolicity of the central sphere any more. The corresponding Lyapunov exponents of SSPO are shown in the Table 4.2, within and transverse to the centre manifold, respectively.

On its own, this observation does not allow us to conclude that the centre manifold returns to being normally hyperbolic. It remains possible that normal hyperbolicity could be broken by any orbit other than the SSPO. To check this, we have calculated the Lyapunov exponents for a variety of orbits in the centre manifold over a range of energies up to the conical intersection ridge. It turns out that



FIGURE 4.9: The Lyapunov exponents within centre manifold (blue) and off centre manifold (red) through the section $p_r = 0.0$ in the Poincaré surface for energy E = -4.023 eV in the middle of the stable interval of SSPO.

across the entire range of energies no orbit apart from the SSPO violates normal hyperbolicity.

As an example of these calculations, Figure 4.9(a) shows the Lyapunov exponents within and off the centre manifold for the energy -4.023 eV, at which the SSPO is stable in the transverse direction, and for orbits on the line $p_r = 0$ in the Poincaré surface of section. This section includes the SSPO, ScPO, BPO and both regular and chaotic nonperiodic orbits. Because the SSPO forms the boundary of the surface of section, the two points with the highest and lowest admissible values of r correspond to the SSPO. The figure shows that normal hyperbolicity fails for these points, but not for any other orbits. The enlargement in Figure 4.9(b) confirms this conclusion. Note that even for orbits arbitrarily close to the SSPO the transverse Lyapunov exponent is nonzero. Because the SSPO is unstable under variations within the centre manifold, an orbit that starts arbitrarily close to the SSPO will quickly move away from it, and its long term behaviour will be entirely different from that of the SSPO. For this reason, the Lyapunov exponents can be discontinuous at the SSPO.

Figure 4.9(c) focuses on the Lyapunov exponents within the centre manifold. They are much smaller than the transverse Lyapunov exponents, and the difference between trajectories on regular islands or in a chaotic sea can clearly be seen. For regular trajectories, we would expect these Lyapunov exponents to be zero. The numerical results show small, but finite values instead because the Lyapunov exponents were obtained by solving the equations of motion for a finite time only, whereas the definition (2.34) requires the limit of infinitely long simulation time. If the actual simulation time in is increased, the resulting Lyapunov exponents to zero.

We have so far focused only on the question whether the central sphere is normally hyperbolic, i.e., whether the ratio k of the transverse to the parallel Lyapunov exponents is larger than one. In fact, the precise value of this ratio is also relevant because the fundamental theorems [50, 58] about normally hyperbolic invariant manifolds [50, 58] guarantee that the stable and unstable manifolds of a NHIM exist and are differentiable at least k times. This result is important if normal form transformations are used to compute these manifolds, as they often have been [23, 70, 75, 76, 78]. The normal form will effectively represent the invariant manifolds by Taylor series, which requires the existence of sufficiently high derivatives. Because derivatives of order higher than k are not known to exist, the use of high order normal forms is questionable if the ratio k is low.

Figure 4.10 shows the ratio k of Lyapunov exponents for the SSPO, which is the orbit that potentially violates normal hyperbolicity, for energies from the saddle point up to the conical intersection ridge. The ratio is infinite just above the



FIGURE 4.10: The ratio k of two Lyapunov exponents within and off the centre manifold for SSPO.

saddle point because the Lyapunov exponent within the centre manifold is zero. It decreases from there and reaches zero when the SSPO is stable. It then rises again and reaches a nearly constant value of $k \approx 5$. As a consequence, we can expect the central sphere and its stable and unstable manifolds to be at least four times differentiable at all energies, except in a narrow range around the interval in which the SSPO is stable in the transverse direction.

4.4 Summary

We have shown that in the hydrogen exchange reaction the central sphere exists for all energies below the conical intersection ridge and that it will possess stable and unstable manifolds for all energies outside a small interval. The surprising fact that the normal hyperbolicity of the central sphere is restored after it has been lost implies that the phase space structure fundamental to TST, which consists of the central sphere and its associated reaction tubes, will be in place even at energies high above the reaction threshold. Unfortunately, this result does not imply that the dynamics in the transition region will be simple. There will be homoclinic and heteroclinic tangles that lead to complex phase space geometry and consequently to complex dynamics. In the collinear subsystem of the full system, this complex behaviour has been shown by Davis [38] and the most recently by Iñarrea *et al* [21].

In the collinear subsystem, it is known that dynamics is as simple as assumed by TST only if the PODS is unique [19]. However, additional periodic orbits arise at energies even lower than the energy at which the SSPO becomes stable, and trajectories that violate the no-recrossing assumption of TST appear at the same energy.

Non-TST behavior in the full three-dimensional system must be at least as prevalent as in the two-dimensional subsystem. This means that even at energies at which the central sphere is normally hyperbolic, non-TST behavior must be present. These energies are both below and above the range in which normal hyperbolicity is broken. Thus, while the results of the current chapter demonstrate that the normal hyperbolicity of the central sphere is more robust than one might have anticipated, this robustness also implies that there is no direct link between the failure of TST and the violation of normal hyperbolicity. It now becomes a separate question to determine what dynamical effects, and what phase space structures, cause the failure of TST. We will address this question in the following Chapter.

Chapter 5

Reactivity on the dividing surface in multidimensional systems

5.1 Introduction

Transition state theory [28] provides a very good approximation for the rate of chemical reaction. Pechukas *et al* [13, 14] have found the TST is exact for the collinear case of the hydrogen exchange reaction at lower energies. One year later, Miller *et al* [27] on TST has also addressed the reaction probabilities for the collinear version of the hydrogen exchange reaction and additionally the three dimensional space. They ended up with TST for both cases is essentially exact up to $E \approx 0.3$ eV. This energy value is equivalent to $E \approx -4.0$ eV in our selected energy unit because they choose the energy unit as zero at the saddle point (barrier). Miller *et al* calculated the reaction rate and determined the energy at which TST fails.

At such energies, there are regions of the dividing surface that according to TST should be reactive, but are not. The reactive and nonreactive part have boundaries. Their shapes (geometric structures of nonreactive part) have been early examined

by De Leon and Marston in the study of isomerization reactions [87, 88] which they called "reactive islands". Also, Pollak and Child [15] and Davis [37] have discussed this shape in the collinear hydrogen exchange reaction which Davis called "droplets". The denotation "reactive islands" (RIs) is selected as reactive and nonreactive part in the dividing surface in this work. Note that we mean by reactive islands (RIs) the islands of reactive and nonreactive which will be shown in the dividing surface later.

The reactive islands are enclosed on the dividing surface. A reactive trajectory either forward or backward must pass through one of these islands. The structure of the reactive islands in phase space can be examined by the invariant phase space manifolds that form their boundaries. They are cylindrical manifolds in phase space. Tubes $(S^1 \times \mathbb{R})$ in the collinear system (two degrees of freedom) and n a higher dimensional cylinders for more than two degrees of freedom. The cylindrical manifolds have a complex structure, in particular at high energies. We get advantage of the theory of cylindrical manifolds in phase space that has been presented in the Section 2.7.

The purpose of this Chapter is to study the reactivity on the dividing surface that is bounded by the central sphere. This kind of study allows us to figure out when the first nonreactive island starts to appear and what the reason of TST failure is. In addition, it shows the dynamical behaviour of the first nonreactive trajectories in the neighbourhood of the dividing surface. Furthermore, we want to determine the geometric structure of reactive and nonreactive islands on the dividing surface not only for the collinear subsystem case but also full dimensional case of the hydrogen exchange reaction. We will focus on nonreactive islands at the lower energies where they appear in order to discover the phase space object that causes the breakdown of the TST.

5.2Collinear subsystem case

The H_2+H reaction is collinear if $(y, p_y) = (0, 0)$ which is given by the Hamiltonian function (3.8). We set x = 0 as dividing surface. The dividing surface is a two dimensional sphere S^2 . The PODS divides it into two hemisphere, $p_x > 0$ and $p_x < 0$ that at low energies mediate the forward and backward reactions, respectively. We will investigate reactivity on the hemisphere with $p_x > 0$. The hemisphere $p_x < 0$ is its mirror image. Now we start analyzing the reactivity on the dividing surface, the geometric structure of the reactive islands and then find out at which energy level the transition state theory is not exact at the end.

5.2.1The geometric structure of RIs

In order to show the shape of the reactive islands, we pick the energy E = -4.0eV as an example. This is definitely above the violation of TST. Figure 5.1(a)shows for $p_x > 0$ a big green island representing the reactive trajectories and a small red island representing the nonreactive trajectories. One can observe that the nonreactive islands surround a big green reactive island but does not lie on the boundary of the dividing surface. On the boundary of these layers, the cylindrical manifolds (tubes) are connected with the NHIM (PODS).

As described in Chapter 2, the NHIM generates four cylinders, two stable manifolds $W_f^s(E)$, $W_b^s(E)$ and two unstable manifolds $W_f^u(E)$, $W_b^u(E)$ each on $S^1 \times$ $(0,\infty)$. The cylinders $W_f^{s,u}(E)$ and $W_b^{s,u}(E)$ intersect the dividing surface, extend into the phase space and then partly overlap one another. The resulting geometric structure is often called a homoclinic tangle. In Figure 5.1(b), the layers between reactive and nonreactive islands are caused by the homoclinic tangle from the intersection of two cylinders. Davis [38] has previously calculated such homoclinic tangle and found a homoclinic point of collinear $H_2 + H$ reaction. For energy above the first bifurcation, there are more than one PODSs. Davis's work was done by



FIGURE 5.1: Reactivity on the dividing surface for collinear subsystem for energy E = -4.0. Details in the text.

propagating the trajectory in the unstable manifold of one unstable PODS and the stable manifold of another trajectory in unstable PODS forward and backward in time, respectively, to find the homoclinic trajectory (the intersection of these two manifolds). He found that there are many homoclinic trajectories because there are many periodic orbits (PODSs) above the first bifurcation. This number of periodic orbits has been reported by the recent paper Iñarrea *et al* [21]. The layered structure of the reactive islands results from the multiplicity of periodic orbits.

The trajectories close to the boundary of layers give a first indication of what causes the failure of TST. More precisely, the trajectories located close to the first exterior layer of nonreactive island provide the image of an unstable periodic orbit on the product side. Such trajectories and periodic orbits will be examined in more detail in Section 5.4. Similarly, the trajectories located close to the first interior layer of the nonreactive island provide the image of an unstable periodic orbit in reactant side. These images are shown in Figure 5.1(c) and 5.1(d) as extra loops on the unstable periodic orbits before the trajectory leave the transition state. These two special trajectories show the geometric structure of unstable periodic orbits in phase space. Furthermore, the trajectories on the boundary of the middle layers also oscillate between the two images of unstable periodic orbits before they decide to go either to the reactant or the product side. Such a trajectory doing this procedure can be seen in Figure 5.1(c).

5.2.2 Breakdown of TST

Throughout the numerical experiments, we find that TST above the threshold is exact up to energy $E \approx -4.14676$ eV, where the dividing surface is fully covered by the initial conditions of reactive trajectories. Above this energy, the first nonreactive trajectories are observed and the nonreactive islands start to grow on the dividing surface. This observation agrees well with Iñarrea *et al* [21] who recently found the first bifurcation of periodic orbit in the collinear subsystem at $E \approx -4.14676$ eV. In this bifurcation, a stable and an unstable periodic orbits are



FIGURE 5.2: The reactive and nonreactive islands on the dividing surface in the collinear case are indicated by green and red colour, respectively. Calculations made for energies -4.15 (before the first bifurcation of PODS), -4.1, -4.0 and -3.9 eV, respectively.

generated on each side of the dividing surface. Thus, TST breaks down as soon as more than one PODS appears. Figure 5.2 shows a series of the reactive and nonreactive islands on the dividing surface for different energy levels.

The outcome shows good agreement with results of Refs [13, 14, 18, 19, 27]. For energies less than -4.14676 eV, we find that TST is exact and only one PODS

exists in phase space, namely the symmetric stretch periodic orbit. For energies greater than -4.14676 eV, we find out that TST is overestimates the rate.

5.3 Full (3 dof) system case

The Hamiltonian function of the full three-dimensional system is given by (3.6). The dimensionality of the geometrical phase space objects is as follows: The phase space is six-dimensional and energy shell five dimensional. The dividing surface is a four-dimensional sphere of which by the three-dimensional central sphere forms the equator. Our aim in this section is to clarify the structure of the geometrical structure of the reactive islands (RIs) on its dividing surface and hence figure out the TST implementations.

5.3.1 The geometric structure of RIs

The geometric structure of the phase space in the full system with three degrees of freedom is not easy to visualize. The difficulty is due to the entire dividing surface being a four dimensional sphere and the NHIM is a three dimensional sphere. Therefore, to simplify that, we pick a family of sections that fills the NHIM on the dividing surface. In our full system with three degrees of freedom, we set x = 0 as dividing surface, which satisfies the symmetry in our system. At fixed energy E, the coordinates r and y on the dividing surface can only take values that satisfy

$$V(r, x = 0, y) < E.$$

Thus, the condition V(r, x = 0, y) = E limits the permissible region of r, y. Some selected energies show in Figure 5.3. We choose three-dimensional sections y =constant, through the dividing surface. Each section has reactive and nonreactive trajectories. Comparable to the collinear subsystem case, we want to show the



FIGURE 5.3: The contour plot for energies -4.0 eV (blue), -4.05 eV (red), -4.1 eV (green) and -4.14676 eV (dashed black).

reactive islands structure in the full system and finally find out at which energy level transition state theory fails.

We pick the same example as in the collinear case, namely the energy E = -4.0 eV. We find out that y is limited between almost $\pm 0.95 \text{ a.u.}$ Figure 5.3 shows the contours of three selected energies, namely E = -4.0 eV, -4.05 eV and -4.14676 eV(our example is the blue contour in Figure 5.3). Due to the reflection symmetry $y \mapsto -y$, a number of sections have been selected and computed in an interval [0.0, 0.95]. Figure 5.4 shows the construction of the nonreactive part for different y sections, namely y = 0.0 a.u., 0.1 a.u., 0.2 a.u., 0.3 a.u., 0.4 a.u. and 0.5 a.u. in the dividing surface for energy E = -4.0 eV. The nonreactive parts of these sections are shown in Figure 5.4. We find out that y = 0.0 section has the largest nonreactive part among. The structure of the nonreactive part resembles a cylinder with tip, and width of the cylinder shrinks close to the boundary of the dividing



FIGURE 5.4: Nonreactive part for energy E = -4.0 eV with sections y = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5.



FIGURE 5.5: The subsection r = 3.63 a.u. through the section y = 0.0 for energy E = -4.0 eV.

surface. Compared with the previous case, the layers in the collinear case come as envelopes covering the cylinder in the full system case. The thickness of the envelopes varies as the magnitude of layers in the collinear version varies. Figure 5.5 shows the sub-subsection at r = 3.63 a.u. through the section y = 0.0 and presents the thickness of the envelopes. This subsection now is two dimensions because r, x, y and p_x are already fixed. In the Figure 5.5, we see two separate nonreactive pieces, one on the left and another tiny on the right, enlarged in Figures 5.6 and 5.7, respectively. The one on the left is a section close to the tip of the cylinder while the layer on the right represents a section in the tail of the cylinder and does not surround the whole green reactive island. Compared with the collinear system, the important dynamical observation in Figure 5.6 is the envelopes which are caused by the homoclinic tangle in the full system. One can observe the symmetry around the p_y axis in Figure 5.6. Of course, the simple observation shows that if the sub-subsection $p_y = 0.0$ is fixed in Figure 5.4(a) then the result will give exactly Figure 5.1(a) which represents the collinear subsystem case.



FIGURE 5.6: Zoom in the left part of the Figure 5.5.



FIGURE 5.7: Zoom in the right part of the Figure 5.5.

5.3.2 Breakdown of TST

To illustrate the global structure of the nonreactive islands, we compute the percentage of nonreactive phase space volume in different sections y = constant. Results are shown in Figure 5.8. We have seen that at E = -4.0 eV, the limits of y are ± 0.95 a.u.. Figure 5.8 shows the relation of y-value with the nonreactive percentage for some energies E = -4.0 eV, E = -4.05 eV and E = -4.1 eV. One can observe, the nonreactive part on the dividing surface has 3.168% out of the total dividing surface size at y = 0.0 section. As the y-value increases, the nonreactive trajectories decrease until they vanish at $y \approx 0.8$ a.u. and hence the percentage decreases. Furthermore, p_y is limited between ± 0.6 a.u. in the section y = 0.0 and the subsection $p_y = 0.0$ has the largest number of nonreactive trajectories among the p_y limitation. We have enlarged the lower percentage of nonreactive in Figure 5.9 to show how they end and at which y section they vanish. There is a sharp end to the nonreactive island well before the end of the dividing surface, i.e., the largest percentage value of y, is reached.

Consequently, the collinear case where $y = p_y = 0.0$ consists of the largest number of the recrossing trajectories in the full system at any energy level above the non-reactivity threshold. As we move from the collinear case (by increasing y), the nonreactive percentage clearly decreases. Therefore, we expect that the collinear configuration plays an important role in the TST failure in the full three-dimensional system.

Figure 5.11 compares the maximum value of y in the dividing surface with the maximum value in the nonreactive island, from the saddle point energy level ($E \approx -4.3504 \,\mathrm{eV}$) up to the conical intersection ($E \approx -1.9514 \,\mathrm{eV}$). There are two important observations in Figure 5.11. Firstly, the nonreactive island appears, i.e., TST fails at energy $E \approx -4.14676 \,\mathrm{eV}$, which is same value as in the collinear case. Secondly, the energy interval from $E = -4.0 \,\mathrm{eV}$ to the TST failure energy, the y-curve of the nonreactive trajectories drops down when it passes near the instability interval of SSPO [81] ($\approx [-4.02425, -4.02251]$). Above the instability interval, the TST curve asymptotically converges to the curve of y limit and it is shown in Figure 5.10. Thus, the breakdown of TST in the full three-dimensional system has a direct link with the breakdown of TST in the collinear system. We will discuss this relationship in the following section.



FIGURE 5.8: Three individual energies curves, namely E = -4.0 eV, E = -4.05 eV and E = -4.1 eV are showing the percentage of nonreactive trajectories in the dividing surface versus the *y*-value.



FIGURE 5.9: Zoom in close to the vanishing of nonreactive percentage in figure 5.8. Also the y-limit for each energy show as vertical lines.



FIGURE 5.10: An overview of the *y*-limit and the *y*-value where nonreactive trajectories vanish, denoted by solid and dashed lines, respectively.



FIGURE 5.11: Enlarge the critical interval of the breakdown of TST in full system.

5.4 The reason of TST failure

According to the former results about the reactivity on the dividing surface in the full system, there is an object in the phase space which lies in the collinear configuration and causes the breakdown of TST. The first nonreactive trajectories start to appear at the first bifurcation. In the collinear case, a saddle node bifurcation occurs symmetrically on both sides of the saddle point and creates a stable and an unstable periodic orbits on each side. This bifurcation was described in [29, 38]. In the recent work by Iñarrea *et al* [21], the unstable and stable periodic orbits are called F_1 and F_2 , respectively. Our hypothesis is that in the full three dimensional system as well as in collinear subsystem with two degrees of freedom, trajectories that violate the no-recrossing assumption of TST are separated from those that obey it by invariant manifolds associated with the unstable periodic orbit F_1 , which we will call UPO. For the collinear subsystem with two degrees of freedom, this invariant manifold is the stable manifold of UPO. For the full three dimensional system, the invariant manifold is the centre-stable manifold of UPO, described below. These manifolds have the appropriate dimensions for partition the energy shell into reactive and nonreactive regions. If we follow the manifolds of UPO to the dividing surface, we expect them to intersect the dividing surface in the boundary of a nonreactive island.

In order to investigate this hypothesis, we need to study the stability of this collinear periodic orbit not only in the collinear system but in the full system and hence determine the type of the manifolds. The stability type of a periodic orbit is determined by the eigenvalues of its monodromy matrix. Since the full system has three degrees of freedom, there will be six eigenvalues. Two eigenvalues will be equal to 1: one eigenvector is tangent to the periodic orbit, the other transverse to the energy shell [89]. For the UPO orbit, two of the remaining four eigenvalues are real positive and inverse to each other: λ and $1/\lambda$ with $\lambda < 1$. They represent the stable and unstable manifolds, respectively. The final two eigenvalues form a complex conjugate pair which represent the centre manifold. The eigenvectors in the stable and unstable directions lie in the collinear subsystem. The central eigenvectors describe variation transverse to the collinear subsystem. They have nonzero components only in the y and p_y directions.



FIGURE 5.12: 100 trajectories in the stable manifold and also 100 trajectories in the unstable manifold of the unstable periodic orbit (UPO) cross the dividing surface (The DS).

To calculate the initial conditions in the stable and unstable manifolds of the linearized system, assume x_* is a point on the UPO. Denote the eigenvectors in the direction of the stable manifold and the unstable manifold by v_S and v_U , respectively. The initial conditions in the stable manifold (Sm) are given by

$$Sm = x_* + \alpha_S v_S,$$

where $\alpha_S \in \mathbb{R}$ is the variation along the stable manifold. Similarly, the initial conditions in the unstable manifold (USm) are given by

$$USm = x_* + \alpha_U v_U,$$

where $\alpha_U \in \mathbb{R}$ is the variation along the unstable manifold. The dimension of the stable and unstable manifolds of the UPO is two, its centre manifold is three-dimensional.



FIGURE 5.13: The stable intersection (blue) lies on the boundary of the main non-reactive island (red) in the collinear system with two degrees of freedom.

Figure 5.12 shows some trajectories in the stable and unstable manifold of the unstable periodic orbit (UPO). The stable manifold is two dimensional. It will intersect the dividing surface in a curve, called stable intersection. The intersection is shown in Figure 5.13 for energy E = -4.141 eV, just above the saddle node bifurcation energy. It forms the boundary of the main nonreactive island. Thus, our expectation is correct.

In Figure 5.13, we see that there are infinitely many layers for energy E = -4.141 eV. As seen in Figure 5.13, the stable intersection (blue) lies in the boundary of the main layer (island) in the collinear system. Trajectories on boundaries of other layers oscillate between the two unstable periodic orbits on both sides of the dividing surface, and then leave the transition state, which this procedure has been explained in Section 5.2.1. Thus, the stable intersection lies on the boundary of the first layer (main layer).

The centre-stable manifold defined as that the directions of centre and stable manifolds span in phase space in which the centre-stable manifold is tangent to their directions. In three degrees of freedom, the periodic orbit (UPO) has a fourdimensional centre-stable manifold. The intersection of this manifold with the dividing surface at the same energy, which is called centre-stable intersection, is three dimensional. It partitions the dividing surface into distinct regions, and we claim that it forms the boundary of the main nonreactive island.

Apart from the difficulty of visualization, we have the problem in computing the centre-stable manifold very well because the centre manifold is only known in linear approximation. The stable direction is less of a problem because every orbit in the stable manifold will come arbitrarily close to the periodic orbit (UPO), so that we can pick an initial condition where the linear approximation is good and then propagate backwards to the dividing surface. Trajectory on the centre manifold by contrast, do not approach the UPO. Those that are not close to the UPO cannot be described accurately by the linear approximation

The initial conditions in the centre-stable manifold (CSm) is given by

$$CSm = x_* + \alpha_S v_S + (\alpha_{C1} + \alpha_{C2} i) v_{C1} + (\alpha_{C1} - \alpha_{C2} i) v_{C2}$$

where α_{C1}, α_{C2} are the real and the imaginary parts of the complex conjugate pair which are the variation along the centre manifold. Also, v_{C1} and v_{C2} are the eigenvectors corresponding to the centre manifold directions.

Figure 5.14 (a) shows some initial conditions that lie on the centre-stable manifold close to the periodic orbit (UPO) for energy E = -4.141 eV. If we extend a choice of initial conditions further away from the UPO, the linear approximation of the centre-stable manifold is not valid any more for two reasons. Firstly, each trajectory will lie in different energy levels as shown in Figure 5.15, which indicates that the linear approximation breaks down as we move away from the UPO. Secondly, some trajectories away from the UPO do not go to the dividing surface (see the disconnection in Figure 5.14 (a)). Thus we pick initial conditions where the linear approximation is good. We propagate trajectories on the centre-stable



FIGURE 5.14: (a) Some initial conditions in the centre-stable manifold that intersect the dividing surface. (b) and (c) show this intersection in (r, p_r) and (y, p_y) , respectively. Three specific trajectories $(\beta_1, \beta_2 \text{ and } \beta_3)$ are pointed to be used in the next figure.

manifold, chosen as in Figure 5.14(a), backward in time toward the dividing surface. The centre-stable intersection is shown in Figure 5.14 (b), (c) in projection onto (r, p_r) and (y, p_y) , respectively. Three sample trajectories denoted by β_1, β_2 and β_3 are selected in the centre-stable manifold. We will show that they lie on the boundary of the nonreactive island on the dividing surface. In Figure 5.16, the intersection of β_1, β_2 and β_3 are clearly located on the boundary of reactive island in Figure 5.16 (a), (b) and (c), respectively. We expect other initial conditions in the centre-stable manifold will do the same procedure and hence have the same conclusion. Thus, the centre-stable intersection forms the boundary of the first (main) non-reactive island off the collinear configuration. The work can be extended by computing a good approximated centre-stable manifold rather than our linear approximation. Also, we expect the stable and unstable manifolds of the



FIGURE 5.15: The variation along the centre manifold direction versus the energy.

central sphere form the boundary of other islands which is again worth to extend the work on it.

5.5 Summary

On the dividing surface, we described the reactive and nonreactive islands for both the collinear subsystem and the full system. The reactivity on the dividing surface in the collinear case has been earlier studied and well explained. Thus, it is easy compared to the full system case as well as easy to visualize. We have observed at which energy level the nonreactive island appears and starts to grow on the dividing surface. Moreover, the analysis showed the geometric structure of the reactive islands. We have seen that the layers and envelopes between the reactive and nonreactive islands were caused by the homoclinic and hetroclinic tangle.

The progress has essentially been made in the capability to discover the phase space object that causes the failure of TST in the hydrogen exchange reaction for the cases: the full three dimensional system and the collinear subsystem. We have illustrated the failure of TST by observing the reactivity on the dividing surface



FIGURE 5.16: Locations of the intersection of β_1, β_2 and β_3 on the reactive island.

at various energy levels above threshold. The crucial observation is that TST is exact up to the same energy level in both cases, specifically $E \approx -4.14676 \,\mathrm{eV}$. Thus, it raises the question what the relationship between the full system and the collinear subsystem is in terms of TST.

In a nutshell, the collinear unstable periodic orbit (UPO) is the phase space object that causes the first non-reactive trajectories to appear not only in the collinear case but also in the full system case. We have given evidence to support the conclusion that the manifolds (stable and centre-stable manifold) of UPO intersect the dividing surface on the boundary of the nonreactive island. The stable manifold lies on the boundary of the collinear nonreactive island. By the three sample trajectories in the centre-stable manifold, the intersection lies off the collinear configuration on the boundary of the nonreactive island in the full system. The beauty of these results is that the full and collinear cases are linked by the TST failure and hence they have the same reason for the breakdown of TST.

Chapter 6

Conclusion

We have chosen the H_2+H exchange reaction for several reasons (e.g. the molecule is symmetric and has three identical atoms). In this example, we figured out the phase space object which causes the TST failure. All attempts to find this object were explained separately in Chapter 4 and Chapter 5, respectively. We first examined the breakdown of normal hyperbolicity of the central sphere which could lead to a breakdown of TST. This attempt led to study of the reactivity on the dividing surface in the three-dimensional system and in the collinear subsystem. In this chapter, we will present a summary of the outcome of the attempts.

In the $H_2 + H$ exchange reaction, we have shown that the central sphere exists for all energies up to the conical intersection energy level which limited our study. The central sphere and its stable and unstable manifolds persist for all energies below the conical intersection ridge except for a tiny range. We examined the normal hyperbolicity of the central sphere by computing the Lyapunov exponents within the central sphere and transverse to it. The main outcome was that the normal hyperbolicity breaks down in a narrow energy range and then gets restored. This means that the reaction tubes (stable and unstable manifolds) exist even at high energy values below the conical intersection ridge. Of course, due to homoclinic
and heteroclinic tangles, the dynamics close to the dividing surface will be complex. Thus, we have a complex geometrical phase space structure at high energies.

In the result of Chapter 4, we have seen that the main energy range represents the interval where the normal hyperbolicity is broken down and restored, respectively. We also knew that recrossing trajectories appear at energies below the failure of normal hyperbolicity. As a result, the breakdown of the normal hyperbolicity can not be the reason for the failure of the TST. Thus, the object in phase space that is causing the violation of TST was still questionable. Our research led to study the reactivity on the dividing surface in both systems, collinear and full cases, respectively.

Focusing on the dividing surface enables us not only to seek our purpose (the phase space object), but also allow us to describe the reactive islands (RIs) in the collinear case as well as in the full system case. The collinear subsystem case was much easier than full system case due to dimensionality.

In both cases, we showed the geometrical structure of the reactive islands and their complexity due to homoclinic and heteroclinic tangles. The crucial outcome is that nonreactive trajectories started to appear in both cases at the same energy level, namely $E \approx -4.14676$ eV, which is also the energy at which multiple PODSs appear. This suggests that the failure of TST in the full system is caused by the same mechanism that operates in the collinear subsystem. In particular, the collinear unstable periodic orbit (UPO) that arises from the first bifurcation of the PODS is the phase space object that causes the TST to fail and that its centre-stable manifold separates reactive and nonreactive trajectories. We have shown that trajectories on the stable manifold of the UPO intersected the dividing surface at the boundary of the main non-reactive island of the collinear subsystem. Furthermore, we have also shown that three sample trajectories on the centre-stable manifold of the UPO intersect the boundary of the nonreactive island in a non-collinear configuration.

To conclude, the failure of TST was not caused by the breakdown of normal hyperbolicity of the central sphere at least for our example, the $H_2 + H$ reaction. We have seen that it is caused by the bifurcations of periodic orbits that occur away from the central sphere. The saddle node bifurcation of the PODS is the reason for this because it creates a new PODS. Therefore, we have several PODSs and hence TST fails.

The research presented in this thesis has raised a number of interesting questions that could be taken up in future work. One can be extended by studying other reactive systems with asymmetric molecules. The $H_2 + H$ reaction example can be used as a basic theory of TST failure due to the nature of molecule. Generally, to determine the TST breakdown for any dynamical system firstly we suggest to examine the simple case (say system with two degrees of freedom) and check at which energy level the first bifurcation occurs. Then we use this energy level as a limit to study the TST in a higher dimensional system. The TST will fail either at this level or below. In our example $(H_2 + H \text{ reaction})$, we have found that both in collinear subsystem and in full system TST breaks down at the same energy level. This equivalence may be due to the symmetry property in our example. TST may break down in higher dimensional systems at lower energy than in the simple case. The geometric properties of molecules play an important role for determining the TST failure. Of course the symmetry property is one of the most effective features. Moreover, we have studied our example from the threshold until the conical intersection energy level and focused lower energies at where TST fails. The dynamical behaviour at high energies, including cylindrical manifolds structure, chaos and bifurcations would be noteworthy outcomes.

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