

# Normally Hyperbolic Invariant Manifolds (NHIMs): Saddle Points, Periodic Orbits, Spheres, and Their Role in Phase Space Reaction Dynamics

Stephen Wiggins  
School of Mathematics  
University of Bristol

## 1 Introduction

Concepts arising in nonlinear dynamical systems theory, such as periodic orbits, normally hyperbolic invariant manifolds (NHIMs), invariant spheres, and stable and unstable manifolds have been introduced into the study of chemical reaction dynamics from the phase space perspective. A fairly substantial literature has developed on this topic in recent years (see, for example [Wiggins(2016)Wiggins, Waalkens and Wiggins(2010)Waalkens and Wiggins, Waalkens *et al.*(2007)Waalkens, Schubert, and Wiggins, Wiggins(2013)Wiggins], and references therein), but it is fair to say that it has a more mathematical flavour, which is not surprising since these dynamical concepts originated in the mathematical dynamics literature. The purpose of this short note is to describe how these dynamical notions arise in the simplest possible physically motivated settings with the hope of providing a more gentle entry into the field for both applied mathematicians and chemists.

Molecules are made up of a collection of atoms that are subject to chemical bonds. Reaction is concerned with the breaking, and creation, of bonds between atoms. Hence, the following concepts are fundamental to the description of this phenomena.

**Coordinates.** The locations of the atoms in a molecule are described by a set of coordinates. The space (i.e. all possible values) described by these coordinates is referred to as *configuration space*.

**Degrees-of-Freedom (DoF).** The number of DoF is the number of independent coordinates required to describe the configuration of the molecule, i.e. it is the dimension of the configuration space.

**Reaction.** The breaking of a bond can be described by a coordinate (s) characterizing the bond becoming unbounded as the bond(s) evolve(s) in time.

**Reaction coordinate(s).** The particular coordinate(s) that describe the breaking of the bond are referred to as the *reaction coordinates*.

**Energy.** The ability of a bond to break can be characterised by its energy. A bond can be "energized" by transferring energy from other bonds in the molecule to a particular bond of interest, or from some external energy source, such as electromagnetic radiation, for example.

**Total Energy, Hamiltonian.** The total energy (i.e. the sum of kinetic energy and potential energy) can be described by a scalar valued function called the Hamiltonian. The Hamiltonian is a function of the configuration space variables *and* the canonically conjugate variables corresponding to each configuration space variable, which are referred to as the momentum variables.

**Phase Space.** The collection of all the configuration and momentum variables is referred to as the phase space of the molecule. The dynamics of a molecule (i.e. how it changes in time) is described by Hamilton's differential equations defined on phase space.

**Dimension count.** If the number of configuration space variables is  $n$ . then the phase space has dimension  $2n$ , The Hamiltonian is a scalar valued function of these  $2n$  variables. The level set of the Hamiltonian, i.e. the energy surface, is  $2n-1$  dimensional. The energy surface is invariant for a time-independent Hamiltonian system, i.e. *energy is conserved*.

**Dividing Surface (DS).** A DS is a surface in the energy surface that is of dimension  $2n-2$ , i.e. codimension 1 in the  $2n-1$  dimensional energy surface. A DS has the "no-recrossing" property. This means that the Hamiltonian vector field is everywhere transverse to a DS, i.e. at no point is it tangent to the DS. While a codimension one surface has the dimensionality necessary to divide the energy surface into two distinct regions (it is the boundary between these regions), the obvious question is what is the nature of these two distinct regions? The two regions are referred to as *reactants* and *products*, and reaction occurs when trajectories evolve from reactants to products through the DS.

**The DS and the Reaction Coordinate.** Following our definitions of reaction, reaction coordinate, and DS it follows that the reaction coordinate should play a role in the definition of the DS. This will be an important point in our discussions that follow.

**Flux across the DS.** The flux of trajectories crossing the DS is related to the rate of reaction ("reaction rate"). Computation of the flux is greatly facilitated if the DS has the "no-recrossing" property.

Hence, in order to understand the dynamics of a particular molecule we need to choose coordinates that describe the locations of the atoms that make up the molecule. This step should not be taken for granted because a "clever" choice of coordinates can greatly facilitate the subsequent analysis. Next, the Hamiltonian is constructed, which we will take to be the sum of the kinetic and potential energies ("natural Hamiltonians"). The kinetic energy term involves the the momentum coordinates, i.e. the variables canonically conjugate to the configuration space coordinates. It is typically a quadratic function of the momenta and its form, in various settings, is well understood. The potential energy is a function of the configuration space variable, but obtaining a specific form for this function for a given molecule is a more difficult matter. One approach to this problem is through the solution of the Schrodinger equation utilizing the Born-Oppenheimer approximation and specification of the configuration of the electrons. Through this approach one can obtain a potential energy function that describes the motion of the much heavier protons and neutrons. In this way we can, in principle, obtain a classical Hamiltonian for the motion of the protons and neutrons of the molecule. With a Hamiltonian in hand, one can compute trajectories, explore phase space structure, compute DSs, rates, etc.

The focus of this article is to start at the end of this process. That is, we will consider Hamiltonians, of the form of the sum of the kinetic and potential energies, for one, two, and three DoF systems. For each of these Hamiltonians we will be concerned with the issue of reaction, and reaction coordinates, and how understanding phase space structures, such as saddle Points, periodic orbits, and invariant spheres, naturally arise as a function of the number of DoF to govern this type of dynamics. It is insightful to carry out explicit analytical calculations when possible. Towards this end we will consider quadratic Hamiltonians;

We begin by considering a one DoF Hamiltonian system.

## 2 A One Degree-of-Freedom Saddle Equilibrium Point

This is a "trivial" cases, but it is always useful to start with the basics to fix ideas.

The Hamiltonian for a (linear) one DoF saddle point is given by:

$$H = \frac{\lambda}{2} (p^2 - q^2) = \underbrace{\frac{\lambda}{2} p^2}_{\text{kinetic energy}} - \underbrace{\frac{\lambda}{2} q^2}_{\text{potential energy}} \quad \lambda > 0, \quad (1)$$

and the associated Hamilton's equations are:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \lambda p, \\ \dot{p} &= -\frac{\partial H}{\partial q} = \lambda q. \end{aligned} \quad (2)$$

In Fig. 1 a) we show a graph of the potential energy,  $V(q) = -\frac{\lambda}{2}q^2$  and in Fig. 1 b) we show the phase portrait corresponding to (1).

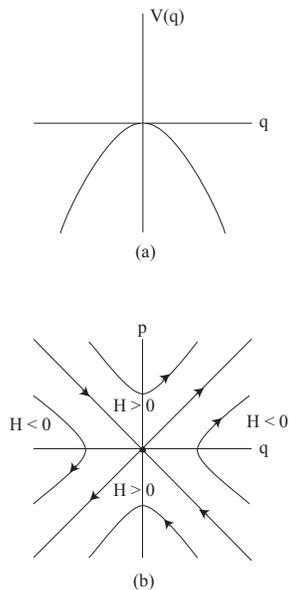


Figure 1: a) The potential energy,  $V(q) = -\frac{\lambda}{2}q^2$ , for a one DoF saddle. b) The phase space for the one DoF saddle.

This is the archetypical one DoF Hamiltonian system modelling reaction dynamics associated with a saddle point. The only configuration space coordinate,  $q$ , is the reaction coordinate. In this simple system ‘‘reaction’’ corresponds to trajectories that change sign in  $q$ , which requires  $H > 0$  (as shown in Fig. 1 b)). Non-reacting trajectories have  $H < 0$ .

Now we discuss the NHIM, its stable and unstable manifolds, and their role in constructing the DS. All of these notions are ‘‘trivial’’ in this simple setting, but they will serve to focus the ideas when we consider more DoF.

For this case the NHIM is the saddle point at the origin (a single ‘‘point’’ is a trivial example of a manifold). It only exists on the  $H = 0$  energy surface (this is very different when we go to two, and more, DoF) and its stable and unstable manifolds are the diagonal lines (also on the  $H = 0$  energy surface—the stable and unstable manifolds of a NHIM have the same energy as the NHIM).

The non-isoenergetic DS can be taken as the line  $q = 0$ . Clearly, it has the ‘‘no-recrossing’’ properties and all reacting trajectories must cross this line. The DS at a fixed (positive) energy is given by

$$\frac{\lambda}{2}p^2 = H = \text{constant}, \quad (3)$$

or

$$p = \pm \sqrt{\frac{2}{\lambda}H}.$$

So for a fixed energy  $H > 0$  the DS consists of two distinct *points*:  $p = +\sqrt{\frac{2}{\lambda}H}$  (the dividing surface for forward reactions) and  $p = -\sqrt{\frac{2}{\lambda}H}$  (the dividing surface for backward reactions). These points are just the intersections of the reacting trajectories with  $q = 0$ .

## 2.1 A Two Degree-of-Freedom Saddle-Center Equilibrium Point

We consider a quadratic 2 DoF Hamiltonian:

$$H = \underbrace{\frac{\lambda}{2} (p_1^2 - q_1^2)}_{H_1} + \underbrace{\frac{\omega}{2} (p_2^2 + q_2^2)}_{H_2}, \quad \lambda, \omega > 0, \quad (4)$$

with the corresponding Hamilton's equations given by:

$$\begin{aligned} \dot{q}_1 &= \frac{\partial H}{\partial p_1} = \lambda p_1, \\ \dot{p}_1 &= -\frac{\partial H}{\partial q_1} = \lambda q_1, \\ \dot{q}_2 &= \frac{\partial H}{\partial p_2} = \omega p_2, \\ \dot{p}_2 &= -\frac{\partial H}{\partial q_2} = -\omega q_2, \end{aligned} \quad (5)$$

These equations have an equilibrium point of saddle-center equilibrium type (index one saddle) at the origin. In Fig. 2 a) we show contours of the potential energy and in Fig. 1 b) we show the phase portrait corresponding to (4). Since the Hamiltonians  $H_1$  and  $H_2$  are uncoupled we can sketch the phase portraits for each separately. and discuss the distribution of total energy between each DoF in a simple manner.

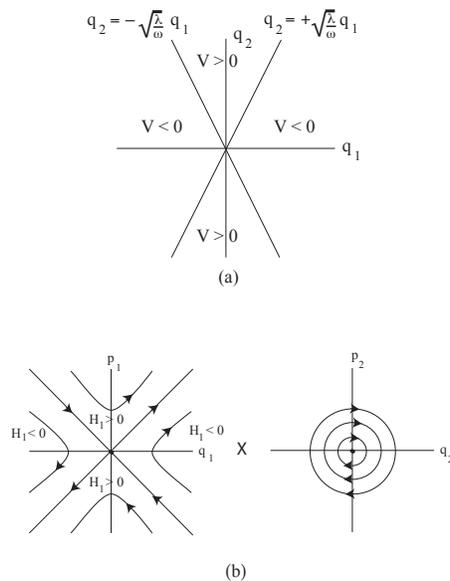


Figure 2: a) Contours of the potential energy,  $V(q_1, q_2) = -\frac{\lambda}{2}q_1^2 + \frac{\omega}{2}q_2^2$ , denoting the sign of  $V(q_1, q_2) = \text{constant}$ . b) The phase space for the two DoF saddle defined by (5).

Note that trajectories corresponding to  $H_1$  can become unbounded and trajectories corresponding to  $H_2$  are bounded. Hence in this system reaction occurs when the  $q_1$  coordinate of a trajectory changes sign. Therefore, a ‘natural’ dividing surface would be  $q_1 = 0$ . This is a three dimensional surface in the four dimensional phase space. We want to examine it’s structure more closely and, in particular, its’ intersection with a fixed energy surface. We will also utilize terminology from chemistry by referring to  $H_1$  as the ‘reactive mode’ and  $H_2$  is the ‘bath mode’

First, note that for reaction to occur we must have  $H_1 > 0$ , since the  $q_1$  component of reacting trajectories changes sign. Also, it is clear from the form of  $H_2$  that  $H_2 \geq 0$ . Therefore, for reaction we must have  $H = H_1 + H_2 > 0$ . The energy surface is given by:

$$\frac{\lambda}{2} (p_1^2 - q_1^2) + \frac{\omega}{2} (p_2^2 + q_2^2) = H_1 + H_2 = H > 0, \quad H_1 > 0, H_2 \geq 0. \quad (6)$$

The intersection of  $q_1 = 0$  with this energy surface is given by:

$$\frac{\lambda}{2} p_1^2 + \frac{\omega}{2} (p_2^2 + q_2^2) = H_1 + H_2 = H > 0, \quad H_1 > 0, H_2 \geq 0. \quad (7)$$

This is the isoenergetic DS. It has the form of a 2-sphere in the four dimensional  $(q_1, p_1, q_2, p_2)$  space. It has two ‘halves’ corresponding to the forward and backward reactions, respectively:

$$p_1 = +\sqrt{\frac{2}{\lambda}} \sqrt{H_1 + H_2 - \frac{\omega}{2} (p_2^2 + q_2^2)}, \quad \text{forward DS}, \quad (8)$$

$$p_1 = -\sqrt{\frac{2}{\lambda}} \sqrt{H_1 + H_2 - \frac{\omega}{2} (p_2^2 + q_2^2)}, \quad \text{backward DS}. \quad (9)$$

Since  $\dot{q}_1 = \lambda p_1$  it is clear that the DS, being defined by  $q_1 = 0$  is a surface having the ‘no-recrossing’ property.

The forward and backward DS ‘meet’ at  $p_1 = 0$ :

$$\frac{\omega}{2} (p_2^2 + q_2^2) = H_1 + H_2 \geq 0, \text{NHIM}, \quad (10)$$

which is an unstable periodic orbit in the  $p_2 - q_2$  plane. This is the NHIM for this 2 DoF system. In this particular example, and in the case where the NHIM is one orbit, normal hyperbolicity is easy to understand. The orbit is normally hyperbolic if it is of saddle-type stability. From (5), we see that the coordinates ‘normal’ to the periodic orbit are  $q_1 = p_1$ , and the dynamics in these coordinates is linear and of saddle type.

## 2.2 The Three Degree-of-Freedom Saddle-Center-Center Equilibrium Point

We consider a quadratic 3 DoF Hamiltonian:

$$H = \underbrace{\frac{\lambda}{2} (p_1^2 - q_1^2)}_{H_1} + \underbrace{\frac{\omega_2}{2} (p_2^2 - q_2^2)}_{H_2} + \underbrace{\frac{\omega_3}{2} (p_3^2 - q_3^2)}_{H_3}, \quad \lambda, \omega_2, \omega_3 > 0 \quad (11)$$

with the corresponding Hamilton’s equations given by:

$$\begin{aligned} \dot{q}_1 &= \frac{\partial H}{\partial p_1} = \lambda p_1, \\ \dot{p}_1 &= -\frac{\partial H}{\partial q_1} = \lambda q_1, \\ \dot{q}_2 &= \frac{\partial H}{\partial p_2} = \omega_2 p_2, \\ \dot{p}_2 &= -\frac{\partial H}{\partial q_2} = -\omega_2 q_2, \\ \dot{q}_3 &= \frac{\partial H}{\partial p_3} = \omega_3 p_3, \\ \dot{p}_3 &= -\frac{\partial H}{\partial q_3} = -\omega_3 q_3, \end{aligned} \quad (12)$$

These equations have an equilibrium point of saddle-center-center equilibrium type (index one saddle) at the origin. Since the Hamiltonians  $H_1$ ,  $H_2$  and  $H_3$  are uncoupled we can analyze the phase portraits for each separately. As in the previous examples,  $H_1$  corresponds to the ‘reactive mode’ (trajectories can become unbounded) and  $H_2$  and  $H_3$  are ‘bath modes’ (trajectories are bounded).

In this system reaction occurs when the  $q_1$  coordinate of a trajectory changes sign. Hence, as in the 2 DoF example, a ‘natural’ dividing surface would be  $q_1 = 0$ . This is a five dimensional surface in the six dimensional phase space. We want to examine its’ structure more closely and, in particular, its intersection with a fixed 5 dimensional energy surface.

First, note that for reaction to occur we must have  $H_1 > 0$ . Also, it is clear from the form of  $H_2$  that  $H_2 \geq 0$ . Therefore, for reaction we must have  $H = H_1 + H_2 > 0$ . The energy surface is given by:

$$\frac{\lambda}{2} (p_1^2 - q_1^2) + \frac{\omega_2}{2} (p_2^2 + q_2^2) + \frac{\omega_3}{2} (p_3^2 + q_3^2) = H_1 + H_2 + H_3 = H > 0, \quad H_1 > 0, H_2 \geq 0. \quad (13)$$

The intersection of  $q_1 = 0$  with this energy surface is given by:

$$\frac{\lambda}{2} p_1^2 + \frac{\omega_2}{2} (p_2^2 + q_2^2) + \frac{\omega_3}{2} (p_3^2 + q_3^2) = H_1 + H_2 + H_3 = H > 0, \quad H_1 > 0, H_2, H_3 \geq 0. \quad (14)$$

This is the isoenergetic DS. It has the form of a 3-sphere in the four dimensional  $(q_1, p_1, q_2, p_2, q_3, p_3)$  space. It has two ‘halves’ corresponding to the forward and backward reactions, respectively:

$$\frac{\lambda}{2} p_1^2 + \frac{\omega_2}{2} (p_2^2 + q_2^2) + \frac{\omega_3}{2} (p_3^2 + q_3^2) = H_1 + H_2 + H_3 = H > 0, \quad p_1 > 0, \quad \text{forward DS}, \quad (15)$$

$$\frac{\lambda}{2} p_1^2 + \frac{\omega_2}{2} (p_2^2 + q_2^2) + \frac{\omega_3}{2} (p_3^2 + q_3^2) = H_1 + H_2 + H_3 = H > 0, \quad p_1 < 0, \quad \text{backward DS}. \quad (16)$$

The forward and backward DS ‘meet’ at  $p_1 = 0$ :

$$\frac{\omega_2}{2} (p_2^2 + q_2^2) + \frac{\omega_3}{2} (p_3^2 + q_3^2) = H_2 + H_3 \geq 0, \text{NHIM}, \quad (17)$$

which is a normally hyperbolic invariant 3 sphere. It is *invariant* because on this set  $q_1 = p_1 = 0$  and, from (12), if  $q_1 = p_1 = 0$  the  $\dot{q}_1 = \dot{p}_1 = 0$ . Hence,  $q_1$  and  $p_1$  always remain zero, and therefore trajectories with these initial conditions always remain on (17). In other words, it is invariant. It is normally hyperbolic for the same reasons as for our 2 DoF example. The directions normal to (17), i.e.  $q_1 - p_1$ , are linearized saddle like dynamics.

## 2.3 Summary: NHIMs and DSs in Phase Space

Here we summarize the main ideas from above.

How did the NHIMs arise in these different systems? The key was that we were able to isolate different types of behaviour in each Hamiltonian. The common behaviour in each was reaction dynamics, which was embodied in  $H_1$ , and  $H_2, H_3$ , etc. ??just went along for the ride???they were exhibited oscillatory motion (i.e. ??bath modes??). In the reaction component of the Hamiltonian ( $H_1$ ) a change of sign of  $q$  denoted reaction. Hence setting  $q = 0$  and the conjugate momentum  $p = 0$  gave the saddle point. On a fixed (positive) energy surface including the bath modes gave rise to the NHIMs? a periodic orbit for 2 DoF, a 3 sphere for 3 DoF, and, in general, a 2n-3 sphere for n DoF. The DS? were obtained by setting  $q = 0$ .

**1 DoF:** This is a ‘degenerate case’ in the sense that the only candidate for a NHIM, the saddle equilibrium at the origin, only exists on the  $H = 0$  energy surface. On a given, one dimensional energy surface, the forward DS consists of a single point, which is the intersection of the energy surface with the positive  $p$  axis and the backward DS consists of the single point, which is the intersection of the energy surface with the negative  $p$  axis. This case has no ‘bath modes’, only a ‘reactive mode’.

**2 DoF:** On a fixed three dimensional energy surface the NHIM is an unstable periodic orbit. In this 3D energy surface the DS is a 2 dimensional sphere ( $S^2$ ). The 1 D NHIM serves as the equator of this sphere, dividing the DS into the forward DS and the backward DS. The periodic orbit ‘NHIM’ occurs as a result of ‘1 DoFs worth of bath modes’.

**3 DoF:** On a fixed five dimensional energy surface the NHIM is a normally hyperbolic invariant three dimensional sphere,  $S^3$ . In this 5D energy surface the DS is a 4 dimensional sphere ( $S^4$ ). The 3 D NHIM serves as the equator of this 4 dimensional sphere, dividing the DS into the forward DS and the backward DS. The 3 sphere ‘NHIM’ occurs as a result of ‘2 DoFs worth of bath modes’.

**n DoF, n i 3:** In general, on a fixed  $2n-1$  dimensional energy surface the NHIM is a normally hyperbolic invariant  $2n-3$  dimensional sphere,  $S^{2n-3}$ . In this  $2n-1$  dimensional energy surface the DS is a  $2n-2$  dimensional sphere ( $S^{2n-2}$ ). The  $2n-3$  dimensional NHIM serves as the equator of this  $2n-2$  dimensional sphere, dividing the DS into the forward DS and the backward DS. The (periodic orbit ( $2n-3$ ) sphere "NHIM" occurs as a result of "n-1 DoFs worth of bath modes".

**Finding NHIM:** Finding NHIMs in 2 DoF systems is equivalent to finding unstable periodic orbits. A simple algorithm for this is given in [Pollak *et al.*(1980)Pollak, Child, and Pechukas]. For systems with more than 2 DoF the problem is much more difficult. The Poincaré-Birkhoff normal form theorem can be used to find NHIMs near index one saddle points for general n DoF systems, see [Waalkens *et al.*(2007)Waalkens, Schubert, and Wiggins]. A more recent approach for finding NHIM using Lagrangian descriptors is described in [Naik and Wiggins(2019)Naik and Wiggins].

**Acknowledgements.** I acknowledge the support of EPSRC Grant no. EP/P021123/1 and Office of Naval Research (Grant No. N000141712220).

## References

- [Naik and Wiggins(2019)Naik and Wiggins] Naik, S. and Wiggins, S. (2019). Finding normally hyperbolic invariant manifolds in two and three degrees of freedom with h enon-heiles-type potential. *Physical Review E*, **100**(2), 022204.
- [Pollak *et al.*(1980)Pollak, Child, and Pechukas] Pollak, E., Child, M. S., and Pechukas, P. (1980). Classical transition state theory: A lower bound to the reaction probability. *The Journal of Chemical Physics*, **72**(3), 1669–1678.
- [Waalkens and Wiggins(2010)Waalkens and Wiggins] Waalkens, H. and Wiggins, S. (2010). Geometrical models of the phase space structures governing reaction dynamics. *Regular and Chaotic dynamics*, **15**(1), 1–39.
- [Waalkens *et al.*(2007)Waalkens, Schubert, and Wiggins] Waalkens, H., Schubert, R., and Wiggins, S. (2007). Wigner’s dynamical transition state theory in phase space: classical and quantum. *Nonlinearity*, **21**(1), R1.
- [Wiggins(2013)Wiggins] Wiggins, S. (2013). *Normally hyperbolic invariant manifolds in dynamical systems*, volume 105. Springer Science & Business Media.
- [Wiggins(2016)Wiggins] Wiggins, S. (2016). The role of normally hyperbolic invariant manifolds (nhims) in the context of the phase space setting for chemical reaction dynamics. *Regular and Chaotic Dynamics*, **21**(6), 621–638.