

Transition States, Stability, and Correlated Dynamics

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Abstract

The notion of a transition state is one of the grand unifying concepts in chemistry. Many theories of chemical reactions explicitly assume that once reactants pass through the transition state then they cannot return. This no-recrossing rule serves to define the transition state and is central to transition state theory. Despite its ubiquity in chemistry it is only recently that the existence of the transition state in more than two degrees-of-freedom has been proven. No general theory has existed for actually finding the transition state. Here, combining methods of celestial mechanics with recent advances in dynamical systems theory, we provide a theory that is rigorously valid for an arbitrary number of degrees-of-freedom. Equally important, advances in computational power make the method applicable in practice for large systems. Knowledge of the transition state, a phase space object, allows us to differentiate, with exquisite precision, between reactive and nonreactive molecular configurations wherever they lie in phase space.

Transition States

The idea of a transition state can be traced back to the scientific memoirs of A. Marcelin (A. Marcelin, *Ann. Chim. Phys* **3**, 158 (1915)). However, it was Eyring and Polanyi who first introduced a quantitative definition of the transition state (H. Eyring and M. Polanyi, *Z. Physik. Chem. B* **12**, 279 (1931)).

The transition state was initially defined in coordinate space as a surface that divided coordinate space into two regions. On one side of the transition state we find reactants and on the other side we find the products. Thus, we can speak of the reaction occurring when the system crosses the transition state.

In the 1930's two distinct views of the transition state emerged. The first due to Eyring and Polanyi was statistical in nature. Here, the central assumption is that the energy is redistributed rapidly among the internal degrees of freedom and that the rate of reaction is determined by the flux across the transition state.

The second view, due to Wigner, is dynamical in nature. Here it is recognized that the dynamics partitions the state space into reactive and nonreactive regions and that once these regions are determined the probability and rate of reactions can be determined.

It was recognized early that defining the transition state in terms of the geometry of the potential energy surface is not satisfactory (E. P. Wigner, J. Chem. Phys. **5**, 720 (1937)). This is due to the fact such a definition will not in general yield a surface of no return.

Yet much effort has been expended in an effort to define transition states in coordinate space. The basic goal has been to define transition states in such a way as to minimize the number of recrossings.

Working in phase space eliminates this difficulty.

The first modern steps toward a “correct” definition of the transition state had to wait the formulation of variational transition state theory. Pechukas solved this variational problem (See E. Pollak, in *Theory of Chemical Reactions*, M. Baer, Ed. (CRC Press, Boca Raton, FL, 1985), Chap. 2.) for systems having two degrees of freedom.

He showed that a periodic orbit whose projection in coordinate space connects the two branches of the equipotentials of the potential energy surface is a solution of the variation problem.

Extending Pechukas’ ideas to systems with more than two degrees of freedom has been problematical until recently.

Chemistry
Atomic Physics
Celestial Mechanics
Cosmology
Trapping of the solar wind by Earth's magnetic field
Blackholes
Economics???

Stability

Consider a system with N degrees of freedom. Phase space will have $2N$ dimensions. The points of stationary flow in phase space are given by

$$\begin{aligned}\dot{p} &= - \left(\frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial q} \right) = 0 \\ \dot{q} &= \left(\frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial p} \right) = 0\end{aligned}\tag{1}$$

The stability of these equilibrium points are very important. We are principally interested points characterized as Center $\times \dots \times$ Center \times Saddle.

The Hamiltonian has a very special form in the vicinity of a equilibrium point of this form: It can be transformed into the following normal form

$$\begin{aligned}
 H(\mathbf{p}, \mathbf{q}) &= \sum_{\ell=1}^{N-1} \frac{\omega_{\ell}}{2} (p_{\ell}^2 + q_{\ell}^2) + \lambda p_N q_N \\
 &+ f_1(p_1, \dots, p_{N-1}, q_1, \dots, q_{N-1}, I_N) \\
 &+ f_2(p_1, \dots, p_{N-1}, q_1, \dots, q_{N-1})
 \end{aligned}$$

where $I_N = p_N q_N$, f_1 and f_2 are at least third order and $f_1(p_1, \dots, p_{N-1}, q_1, \dots, q_{N-1}, 0) = 0$.

This is the fundamental result from which everything else follows.

The equations of motion have the form

$$\dot{q}_\ell = \omega_\ell p_\ell + \left(\frac{\partial f_1}{\partial p_\ell} \right) + \left(\frac{\partial f_2}{\partial p_\ell} \right)$$

$$\dot{p}_\ell = -\omega_\ell q_\ell - \left(\frac{\partial f_1}{\partial q_\ell} \right) - \left(\frac{\partial f_2}{\partial q_\ell} \right)$$

(2)

$$\dot{q}_N = \lambda q_N + \left(\frac{\partial f_1}{\partial I_N} \right) q_N$$

$$\dot{p}_N = -\lambda p_N - \left(\frac{\partial f_1}{\partial I_N} \right) p_N$$

The Center Manifold

The center manifold is given by $p_N = q_N = 0$.

$$M = \sum_{\ell=1}^{N-1} \frac{\omega_\ell}{2} (p_\ell^2 + q_\ell^2) + f_2(p_1, \dots, p_{N-1}, q_1, \dots, q_{N-1})$$

The equations of motion become

$$\begin{aligned} \dot{q}_\ell &= \omega_\ell p_\ell + \left(\frac{\partial f_1}{\partial p_\ell} \right) + \left(\frac{\partial f_2}{\partial p_\ell} \right) & \dot{q}_N &= 0 \\ \dot{p}_\ell &= -\omega_\ell q_\ell - \left(\frac{\partial f_1}{\partial q_\ell} \right) - \left(\frac{\partial f_2}{\partial q_\ell} \right) & \dot{p}_N &= 0 \end{aligned}, \quad (3)$$

thus we see that this manifold, which is $2N - 2$ dimensional, is invariant.

The Normally Hyperbolic Invariant Manifold

We are interested in systems for which the energy is conserved. The center manifold spans many energy shells. If we consider the intersection of the center manifold with a particular energy shell we obtain the desired manifold. Thus, in addition to requiring

$$p_N = 0 \quad q_N = 0 , \tag{4}$$

we require

$$H(\mathbf{p}, \mathbf{q}) = E. \tag{5}$$

The resulting surface is $2N - 3$ dimensional. It is invariant and it is *normally hyperbolic*.

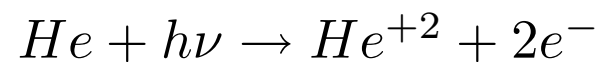
Normally hyperbolic means that any perturbation normal to the surface results in hyperbolic (unstable) motion. The only direction normal to the surface (and confined to the energy shell) is in the saddle direction.

This surface, which we call the NHIM, is the fundamental geometrical object in which we are interested. It is the multidimensional generalization of Pechukas' PODS.

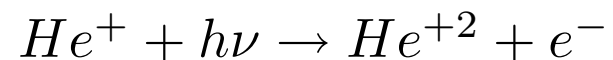
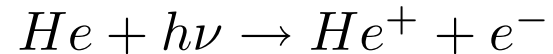
The transition state is defined by $H = E$, $q_N = 0$ and $p_N \geq 0$.

Correlated Dynamics

Sequential and Non-sequential double ionization of helium



versus



Correlated and Non-correlated double amine inversion in Urea

Celestial examples also exist!!!

Rank-One Saddle Points

The stability of these equilibrium points are very important:

Center $\times \dots \times$ Center \times Saddle.

For a system having N degrees of freedom:

phase space will be $2N$ dimensional,

the center manifold will be $2N - 2$ dimensional,

the NHIM will be $2N - 3$ dimensional,

the stable and unstable manifolds of the NHIM will be $2N - 2$ dimensional,

the *transition state* will be $2N - 2$ dimensional.

As a consequence the *transition state* is codimension-one in the energy shell and partition the energy shell into reactant and product volumes.

Rank-Two Saddle Points

The stability of these equilibrium points are very important:

Center $\times \dots \times$ Center \times Saddle \times Saddle.

For a system having N degrees of freedom:

phase space will be $2N$ dimensional,

the center manifold will be $2N - 4$ dimensional,

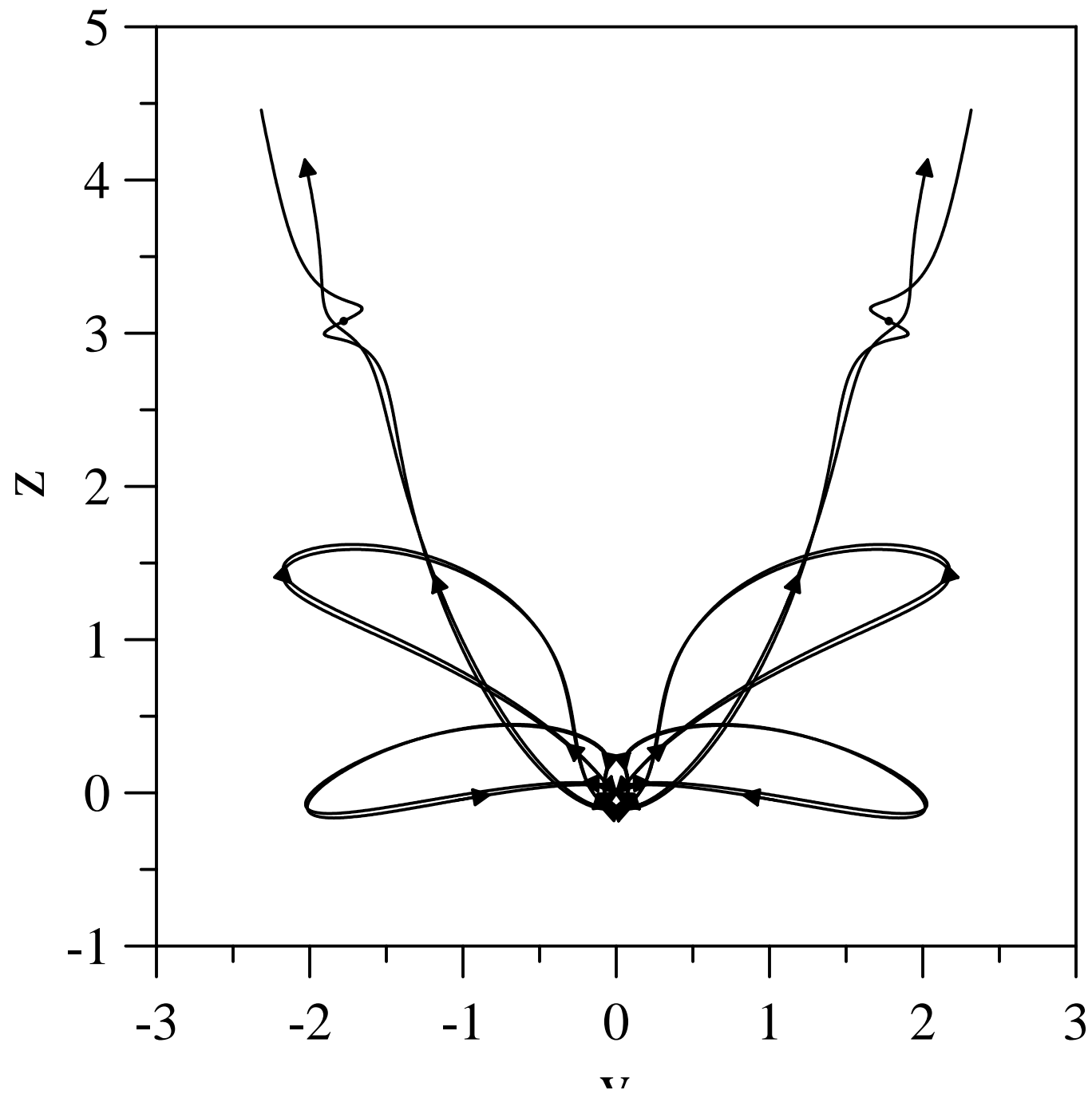
the NHIM will be $2N - 5$ dimensional,

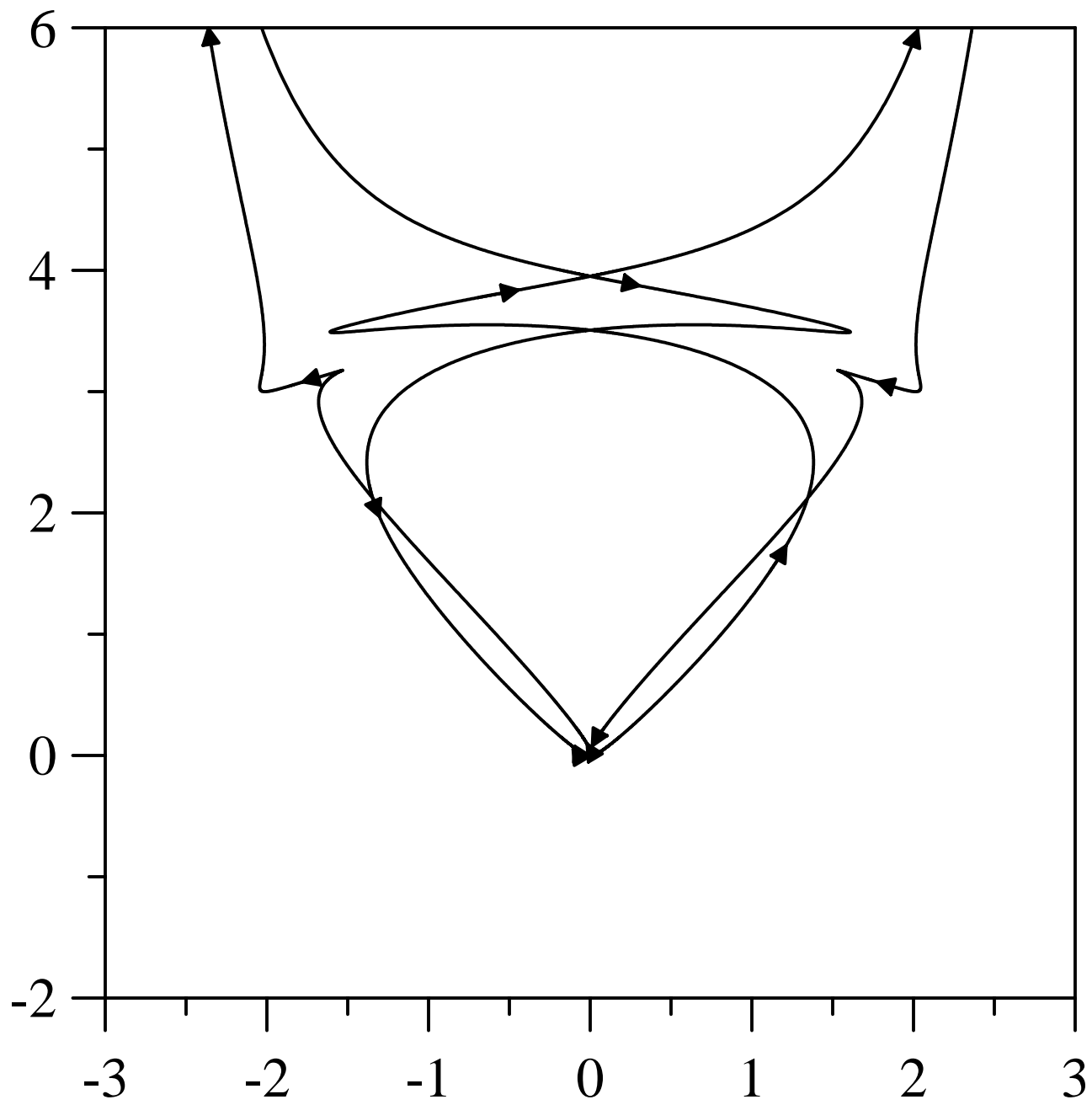
the stable and unstable manifolds of the NHIM will be $2N - 3$ dimensional,

the “transition state” will be $2N - 3$ dimensional.

As a consequence the “transition state” is codimension-two in the energy shell and does not partition the energy shell into reactant and product volumes.

For the non-sequential double ionization of Helium, the model can be reduced to 5 degrees of freedom. The normal mode analysis of the rank-two saddle of He enables one to partition the system into three decoupled problems. Two have 2 degrees of freedom and the third has one degree of freedom. The point group symmetry of the saddle point is C_{2v} and the three decoupled systems transform as A_1 , B_2 and B_1 .





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