DIVIDING SURFACES AND REACTION RATES IN THE $H + H_2 \longrightarrow H_2 + H$ CHEMICAL REACTION

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keywords: Bifurcation theory and analysis; Chaos in Hamiltonian Systems.

1. DYNAMICAL TRANSITION STATE THEORY

The Transition State Theory (TST) is a theory developed to understand chemical reactions. The Transition State (TS) is a set of states that all reactive trajectories must cross. Usually, the TS is determined by searching for saddle points on the potential energy surface (PES), and the TS is a dividing surface in the configuration space. However, it was soon recognized that the TS as defined above was not a surface of no return [1] due to the existence of re-crossing trajectories which lead to a overestimation of the reaction rates. Wigner [2] was the first to suggest that the TS should be defined in phase space. At this point the key question of how to construct analytically the TS arises. However, progress in this direction had to wait for advances in nonlinear dynamics.

We consider a n-DOF Hamiltonian $\mathcal{H}$ with an equilibrium point of $center \times center \times ... \times saddle$ type (a rank one saddle). Around the saddle, the phase space geometry becomes transparent when normal form coordinates are used. The transformation from the primitive to these new coordinates is constructed using the Poincaré-Birkhoff normalization procedure [3]: This algorithm yields the back and forth canonical transformation between the original and the normal form coordinates and all the geometrical structures can be expressed by explicit equations. A sequence of canonical transformations expresses $\mathcal{H}$ into its normal form $\mathcal{K}$:

$$\mathcal{K} = \sum_{i=1}^{n-1} J_i + \mathcal{I}_n + \mathcal{F}(J_1, ..., J_n, \mathcal{I}_n), \qquad (1)$$

$$\mathcal{I}_n = \frac{p_n^2}{2} - \frac{\omega_n^2}{2}q_n^2, \quad J_i = \frac{p_i^2}{2} + \frac{\omega_i^2}{2}q_i^2.$$

The term $\mathcal{F}$ is responsible for the nonlinear terms. If the linear case is considered $\mathcal{F} = 0$. For $E < 0$, $\mathcal{K}$ is a (2n-1)-spherical cone and there are no reactive trajectories. When $E > 0$, $\mathcal{K}$ is a (2n-1)-spherical cylinder and there are reactive trajectories (see Fig. 1). Because all and only reactive trajectories cross the line $q_n = 0$, we define the TS by setting
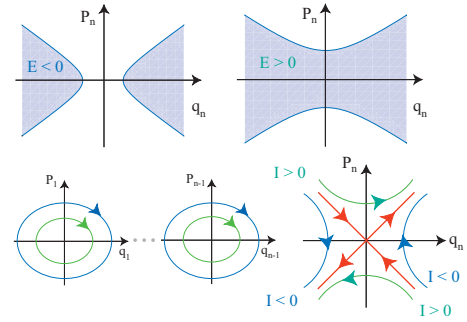

Figure 1 – Upper panel: Proyection of energy surfaces to the plane of normal form coordinates. Lower panel: Proyection of typical reactiv and non reactive trajectories.

$q_n = 0$ in (2):

$$\mathcal{K}_{TS} = \sum_{i=1}^{n-1} J_i + \frac{p_n^2}{2}. \qquad (2)$$

$\mathcal{K}_{TS}$ is a (2n-2)-dimensional sphere. From the Hamiltonian equations of motion, it can be seen that the manifold $q_n = p_n = 0$ is a Normally Hyperbolic Invariant Manifold (NHIM)[4]:

$$\mathcal{K}_{NHIM} = \sum_{i=1}^{n-1} J_i. \qquad (3)$$

For $E > 0$, $\mathcal{K}_{NHIM}$ is a (2n-3)-dimensional sphere acting like a multidimensional saddle point. $\mathcal{K}_{NHIM}$ has (2n-2)-dimensional stable W^s and unstable W^u manifolds (cylinders) which are separatrices in the (2n-1)-energy surface. The two "halves" of the TS are crossed by forward/backward reactive trajectories. The TS is divided in these halves by the NHIM. $W^{s,u}$ are attached to the NHIM.

When $\mathcal{F}$ is considered, ones arrives to the same qualitative conclusions. The TS is a deformed (2n-2)-sphere whose equator is the NHIM. The NHIM has attached the (2n-2)-dimensional $W^{s,u}$ which are deformed cylinders. $W^{s,u}$ divide the energy shell: they are impenetrable barriers in phase space that separate reactive from non-reactive trajectories.

For a deep revision of the state of the art, we refer the reader to [5] and references therein.

1.1. Phase flux and reaction probability

Usually, the calculation of reaction rates is carried by using expensive Monte Carlo methods. However, the DTST, provides a "cheaper" method to calculate the reaction rate $P(E)$ of a given chemical reaction. It was shown that $P(E)$ is proportional to the directional phase flux TS across the TS [6]. From the Stokes' theorem, TS is the action integral over the NHIM and can be easily computed from KN-HIM. Indeed, if $\mathcal{S}$ is the "area" enclosed by the contour $\mathcal{K}_{NHIM} = E$, the flux is given by:

$$\Phi = (2\pi)^{n-1}\mathcal{S}$$

2. APPLICATION TO THE $H + H_2 \longrightarrow H_2 + H$

For this reaction, we use the BKMP potential energy surface $V(r_1, r_2, \theta)$ [7]. The Hamiltonian of the system is:

$$\mathcal{H} = \frac{p_1^2 + p_2^2 - p_1 p_2}{m_H} + V(r_1, r_2, \theta). \qquad (4)$$

The above Hamiltonian presents a rank one saddle point at $r_1 = r_2 = 1.757\,a0$ and $r_3 = r_1 + r_2$ (Collinear directions). We use the DTST to determine the objects that control this reaction in the collinear case and to calculate P(E) as a function of the energy E. The application of the DTST is carried in three steps (see [8] for a different example):

- We apply a change of coordinates that carries the saddle point to the origin.

- We express $\mathcal{H}$ as a N order Taylor expansion around the origin.

- We transform $\mathcal{H}$ into its normal form $\mathcal{K}$ up to the desired accuracy: $\mathcal{K} = J_1 + I + \mathcal{F}(J_1, I)$.

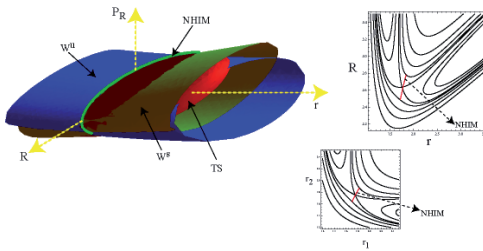Now, all the geometrical objects controlling the reaction are determined (see Fig. 2).

Figure 2 – Projection of the TS**,** $NHIM$ **and** $W^{s,u}$ **manifolds for the collinear** $H + H_2 \longrightarrow H_2 + H$ **reaction.**

For a given energy E, the reaction probability $P(E)$ is the fraction of the total phase flux that cross the TS: The flux TS is computed as the action of the NHIM and it is easily obtained from the Normal Form:

$$P(E) = \frac{\Phi_{TS}}{\Phi_{TOTAL}} \qquad (5)$$

To compute total flux Φ_{TOTAL} we assume that trajectories are launched from $r_2 \to \infty$ (the H atom is far away from the H_2 molecule and the PES do not depend on r_2. Thence, for a given energy E, Φ_{TOTAL} is the flux across the two-dimensional (forward) surface $\mathcal{S}_F$:

$$\mathcal{S}_F \equiv E = \frac{p_1^2 + p_2^2 - p_1 p_2}{m_H} + V(r_1, r_2 \to \infty, \theta = \phi) \quad (6)$$

The limit of $\mathcal{S}_F$ is a closed curve $\mathcal{C}$, and the Φ_{TOTAL} is the curl integral over that curve. In Fig. 3 is shown a comparison between the probability $P(E)$ calculated by Monte Carlo method and by the DTST method. The agreement between the results of both procedures is very good. It is worth noting that the method based on DTST is computationally much more efficient than the standard Monte Carlo procedure.
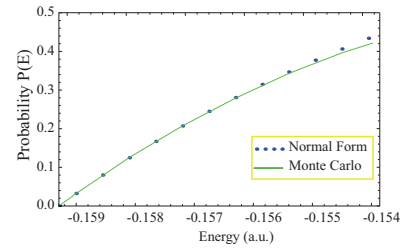

Figure 3 – Reaction probability as function of the energy.

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