

Module 7 : Theories of Reaction Rates

Lecture 35 : Potential Energy Surfaces (PES) II

Objectives

After studying this Lecture you will learn to do the following

- Relate a trajectory on a PES to a collision process.
- Distinguish between reactive, non-reactive, associative and dissociative trajectories.
- Plot the interatomic distances as a function of time and characterize the reactants and products through the plot.
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- Distinguish between classical trajectories and quantum mechanical state to state rate processes.
- Relate microscopic state - to - state rates to bulk or macroscopic rate constants.

Introduction

In the previous lecture (lecture 34), we have studied the details of the shapes of the potential energy surfaces (PESs) for $\text{H}_2 + \text{H}$, $\text{HC} + \text{N}$ and a few other systems. In the present lecture, we relate these surfaces to the dynamics involved in the process of a chemical reaction. Imagine a ball rolling on this surface. Normally a ball rolls from a high value of potential energy to a low value. However, the usual starting point of a reaction is a reaction valley, wherein one of the reactant is at a minimum potential energy configuration and the other reactants are far away. Such a situation corresponds to a point on the PES. With reference to the $\text{H}_\text{A}\text{H}_\text{B}$ and H_C collision (See Fig 35.1), as H_C approaches $\text{H}_\text{A}\text{H}_\text{B}$ with $\text{H}_\text{A}\text{H}_\text{B}$ distance nearly constant, we move towards the transition state in the valley. Each point on the surface along the trajectory corresponds to one collinear configuration of $\text{H}_\text{A}\text{H}_\text{B} \dots \text{H}_\text{C}$. The collision process is thus a path along the potential energy surface. If the collision is reactive, we will get H_A and $\text{H}_\text{B}\text{H}_\text{C}$ and the point moves over the barrier to the product valley. Such a trajectory is called a reactive trajectory. What causes the collision to be reactive? There are several driving forces. The first is the high translational energy of the reactants (high relative velocity) which can be used to bind the products $\text{H}_\text{B}\text{H}_\text{C}$ and the rest of the energy can be transferred to H_C as its kinetic energy. Another possibility is the high vibrational energy of $\text{H}_\text{A}\text{H}_\text{B}$. This can be transferred to the vibrational energy of $\text{H}_\text{B}\text{H}_\text{C}$ (which will now possibly have a lower vibrational energy than of $\text{H}_\text{A}\text{H}_\text{B}$) and the translational energy of the product H_A . A similar argument can be made for the high rotational energy of $\text{H}_\text{A}\text{H}_\text{B}$. All the above factors lead to product formation.

If the relative kinetic energy of the reactants is small, and the vibrational energy of the polyatomic reactants is also small (we have considered only diatomic reactants), then the the system does not have sufficient energy to go over the transition region into the product valley and returns to the reactant state fairly early in the reactant valley. In Fig 35.1, reactive, non reactive and dissociative trajectories are indicated. The probabilities of dissociative collisions are rather small. In a dissociative collision, $\text{H}_\text{A}\text{H}_\text{B}$ is hit by H_C from the right, H_B stays where it was, H_C moves to the right opposite to its direction of approach in the early part of collision and H_A moves to the left.

Figure 35.1 Reactive (R), dissociative (D) and nonreactive (NR) trajectories on the $\text{H}_2 + \text{H}$ potential energy surface.

Time Dependence of interatomic distances.

A good way to show the formation of products is to plot interatomic distances as a function of time. In Fig 35.2, R_{AB} and R_{BC} for the $\text{H}_2 + \text{H}$ reaction are shown. In the reactive collision shown in the figure, the switch over to the products begins after about 25 fs (femtoseconds) and the separation into the products is complete by 40 fs.

Figure 35.2 Interatomic $\text{H}_\text{A}\text{H}_\text{B}$ (R_{AB}) and $\text{H}_\text{B}\text{H}_\text{C}$ (R_{BC}) distances as a function of time.

In Fig 35.3, the time dependence of several pairs of distances in the reaction $\text{NaBr} + \text{KCl} \rightarrow \text{NaCl} + \text{KBr}$ is shown. The transition state is fairly long lived (for 4 ps from 1.5 ps (pico seconds) to 5.5 ps). In this transition region, the distances between all the pairs NaBr, BrCl and KBr are around 500 pm during this period. We can thus conclude that the activated complex is tetraatomic. The complex undergoes nearly 15 oscillations before decomposing into the products. The collision is not a direct one wherein the products are formed "instantly" as in the $\text{H}_2 + \text{H}$ (Fig. 35.2) case.

Figure 35.3 A trajectory for the $\text{NaBr} + \text{KCl} \rightarrow \text{NaCl} + \text{KBr}$ reaction showing the long lived ($\text{NaBr}\dots\text{KCl}$) tetraatomic activated complex.

Example 35.1

Indicate reactive trajectories on an attractive and repulsive PES.

Solution : The trajectories are sketched in Fig. 35.4

Figure 35.4 Reactive (R) and nonreactive (NR) trajectories on an attractive and a repulsive PES.

35.3 Classical Trajectories

The movement of a point on a PES is associated with the changes in the potential energy and the kinetic energy of the system. The PES gives the changes in the potential energy alone and the changes in kinetic energies can be assessed from the velocities of the particles at each point. The position (x) and velocity (v) at any time ($t + \Delta t$) can be calculated from the position and velocity at a nearby time (t) by solving the equations of motion.

$$x(t + \Delta t) = x(t) + (dx/dt) \Delta t + 1/2(d^2x/dt^2) \Delta t^2 + \dots \quad (35.1)$$

$$v(t + \Delta t) = v(t) + (dv/dt) \Delta t + 1/2(d^2v/dt^2) \Delta t^2 + \dots \quad (35.2)$$

In (35.1) and (35.2), $dv/dt = d^2x/dt^2$ = acceleration in the x direction which is nothing but force per unit mass, F_x/m .

The force is given in terms of the PE (V) at the point (corresponding to time t) by

$$F_x = - \partial V / \partial x; \quad V = PE \quad (35.3)$$

Since the form of the PES is known, $\partial V / \partial x$ can be calculated at each point. For small Δt , if we know $x(t)$ and $v(t)$, $x(t + \Delta t)$ and $v(t + \Delta t)$ can be calculated from eq. (35.1) and (35.2) very easily if we neglect the Δt^2 term in eq (35.2). This approach constitutes the simplest algorithm for the time evolution of the point on a PES. Other more sophisticated algorithms are available. A large number of trajectories can be generated starting from different initial conditions. From these, an energy or velocity dependent reactive cross sections can be calculated. One actually computes the probability of a reaction (i.e., a reactive cross section) for a given initial velocity and then averages the product $[\sigma(R) \cdot v]$ to get a rate constant, as was done in the collision theory. This is a direct application of (35.1) and (35.2). These equations are not "symmetrical" in x and v . E.g., $x(t + \Delta t)$ needs $v(t)$, but $v(t + \Delta t)$ does not need $x(t)$. More symmetrical form of the equations of motion are the Hamiltons equations, which are

$$\partial x / \partial t = \dot{x} = \partial H / \partial p_x \quad (35.4)$$

$$\partial p_x / \partial t = \dot{p}_x = - \partial H / \partial x \quad (35.5)$$

Where H = hamiltonian = KE + PE. Usually these are solved for obtaining classical trajectories. These equations are completely equivalent to the Newtons Laws of motion.

35.4 State to state rate constants.

The above approach to obtain the average of the product $\sigma(R) \cdot v$ considers the ground state potential (electronic) energy surface with no vibrational and rotational structure. To get the true microscopic rate, we need the state to state reaction cross section $\sigma_R(n_R \rightarrow n_P)$ where n_R and n_P are the complete set of reactant and product quantum numbers. The state to state rate constant can then be obtained from:

$$k\{(n_R \rightarrow n_P); T\} = \langle v \sigma_R(n_R \rightarrow n_P) \rangle \quad (35.6)$$

The averaging (which is commonly denoted by $\langle \rangle$) is usually done by using the Maxwell-Boltzmann velocity distribution $f(v)$ at temperature T

$$k(n_R \rightarrow n_P; T) = \int dv f(v) v \sigma_R(n_R \rightarrow n_P) \quad (35.7)$$

To obtain $\sigma_R(n_R \rightarrow n_P)$ we need to study the evolution of the reactant wavefunction by solving the time dependent Schrodinger equation. This gives us the probabilities of obtaining the products in various states (i.e., through the "extent" of the reactant wave function going over to those various product wave functions). From the state to state rate constants, the macroscopic rate constant k can be obtained by the procedure outlined in Fig (35.5). There is an averaging over all the reactant and product quantum states. We have also introduced here the concept of the differential cross section, $\sigma_R(n_R \rightarrow n_P, \theta, v)$ where θ is the relative orientation of the products. The integral cross section $\sigma_R(n_R \rightarrow n_P, v)$ is obtained by integrating the differential cross sections over all possible orientations (θ) in three dimensions.

Figure 35.5 Different stages in going from the differential cross section $[\sigma_R (n_R \rightarrow n_P, \theta, v)]$ and the microscopic rate constant $[k_{ij}^{lm}(T)]$ to the macroscopic rate constant k .

35.5 Problems

- 35.1) On the $H_2 + H$ PES, sketch a trajectory wherein
 - a) high vibrational energy of reactants is converted to translational energy of products.
 - b) high translational energy of reactants is converted into high product vibrational energy.
- 35.2) Can rotational energies of reactants be indicated on the PES? Justify your answer.
- 35.3) Sketch an associative $HC + N$ trajectory on the HCN PES. Also indicate a reactive $HC + N \rightarrow H + CN$ trajectory and a dissociative trajectory $HC + N \rightarrow H + C + N$.
- 35.4) Sketch two PESs; one with a deep reactants valley and a shallow product valley and another with a shallow reactant valley, moderate product valley and a very low dissociative plateau. How is the dynamics in these surfaces expected to differ from the $H_2 + H$ dynamics?
- 35.5) What are the qualitative differences between classical trajectories and "quantal trajectories" which are studied through the time evolution of wave functions?
- 35.6) For the simple harmonic oscillator, $H = (1/2) k x^2 + 1/2 p_x^2 / m$ show that the Hamilton's equations are fully equivalent to Newton's laws. Here x is the position of the particle which is harmonically bound by a force constant k .

Recap

In this Lecture you have learnt the following

Summary

In this lecture, we have related a trajectory or a path on a PES to a collision process. Collisions can be classified into various categories. In a reactive collision, the trajectory moves from the reactant valley to the product valley by going through the region associated with the activated complex. In a non-reactive trajectory, the path returns to the starting reactant valley from an unfavourable configuration near the activated complex barrier.

The path along a classical trajectory can be investigated in time by solving the Newtons equations (or equivalently the Hamiltons equations) of motion. Although classical trajectories give an excellent picture of the passage of reactants to products, the correct picture is quantum mechanical wherein one obtains state to state rate constants, $k \{ n_R \rightarrow n_P \}$ wherein n_R and n_P represent the complete set of quantum numbers specifying the reactants and products. The macroscopic or the bulk rate constant can then be obtained by averaging over all the state to state rate constants by using an appropriate initial distribution over reactant states.