

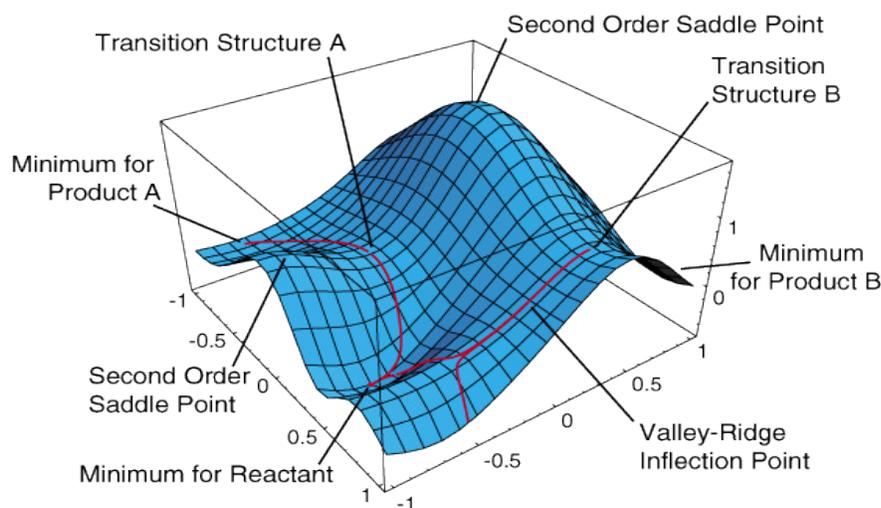
Exploring Potential Energy Surface

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Overview

Potential energy surface is the potential interaction energy of nuclei in a molecular system. It is a function of the nuclei internal coordinates (bonds, angles, and dihedral angles). If a molecular has N atoms, it has 3 degrees of freedom for translational motions of the whole molecule and 2 or 3 overall rotational motions if it has a linear or non-linear structure, respectively. Thus, the potential energy surface has a $(3N - 5)$ or $(3N - 6)$ dimensions. The simplest potential energy surface is the potential curve of a diatomic molecule that is a function of only the bond distance. Below is an illustration of a potential energy surface with identifications of its topological features.



A local minimum corresponds to a stable structure or conformer. A saddle point indicated by either the transition structure A or B has only one direction going downhill while other directions going uphill. Saddle point is important for elucidating reaction mechanism and chemical kinetics. Higher-order transition states have more than one direction going downhill and often is not important in chemistry. Reaction path is defined by the steepest descent path connecting a saddle point to its nearest local

minima on both sides as shown by the red curve connecting minimum for Reactant to transition structure A and minimum for Product A.

Potential energy surface is calculated by solving the Schrodinger equation using the Born-Oppenheimer approximation which assumes the electron motions can be separated from the nuclear motions for a large number of geometrical structures. Generate a complete PES quantum mechanically is computationally very expensive procedure since it has $(3N-6)$ or $(3N - 5)$ dimensions. To elucidate reaction mechanism often one only needs to identify minima that correspond to the reactant and product of interest and the saddle point connecting them. Reaction path is often calculated to confirm the saddle point actually connecting the reactant and product of interest but not to other local minima. Since the Schrodinger equation can only be solved approximately for multi-electron systems, depending on the level of approximation (method/basis set) used locations of these stationary points (minimum or transition state) may vary from their 'true' structures. Thus, comparisons between predicted structures with those from experimental observations provide an indication on the accuracy of the method used.

Stable or equilibrium structure

Experimentally observable molecular species corresponds to a local minimum on the potential energy surface. Its structure is referred to as an equilibrium or stable structure. To find it one must first guess its structure and then find a nearby local minimum using an optimization technique. Since typical optimization procedure locates a nearby stationary point which can be either a minimum or transition state, vibrational analysis should be done on the optimized structure to confirm that it is a local minimum by having all real frequencies. Furthermore, since this local minimum is not necessarily the global minimum guessing the correct conformer is essential for obtaining accurate energetic information such as relative stability, reaction energy, barrier height, etc.

Transition State structure

Transition state of a chemical reaction corresponds to a saddle point on the potential energy surface. Searching for a local maximum is more difficult than a local minimum. One needs to provide a rather good guess in order for the optimization procedure to converge. For this reason, finding the transition state for a chemical reaction is not always trivial particularly large molecular systems. Once the transition state is located or optimized, it must be confirmed by performing a vibrational analysis. A saddle point should have one imaginary frequency (often printed as negative value by many quantum chemistry programs) and its vibrational mode should correspond to the motion that connects the reactant and product. One can visualize this vibrational mode by using PsiViewer tool in Avisto. A better and more precise means to confirm that one gets the correct transition state is to perform the reaction path calculation.

Reaction Path

Reaction path has several names, Minimum Energy Path (MEP) or Intrinsic Reaction Coordinate (IRC), is the steepest descent path starting from the saddle point toward both sides of the downhill direction. A typical procedure is to first step from the saddle point in the direction (forward and backward) of the vibration corresponding to the imaginary frequency and then follow the downhill gradient direction in small steps. One can animate how the geometry of the system changes along the reaction coordinate to confirm that the saddle point is in fact connecting the reactant(s) and product(s).

References (To be added)