Analysis of Reaction Mechanisms in the New Millenium: Derivatives of the Potential Energy

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Abstract

The first and second derivatives of the potential energy along an intrinsic reaction coordinate ξ correspond physically to the negative of the (reaction) force, $\mathbf{F}(\xi)$, and the (reaction) force constant, $\kappa(\xi)$, respectively. The minima and maxima of $\mathbf{F}(\xi)$ divide the process into regions which are either structurally or electronically intensive. $\mathbf{F}(\xi)$ also divides the activation barrier into structural and electronic components, which helps to elucidate the effects of catalysts and solvents. $\kappa(\xi)$ characterizes the transition regions of reactions, and serves as an indicator of degrees of nonsynchronicity, as well as other specific features. Practical examples will be presented, e.g. in Diels-Alder reactions.