Understanding of chemical reaction mechanism and dynamics in terms of natural reaction orbital (NRO) and reaction space projector (ReSPer) approaches

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Frontier orbital theory and intrinsic reaction coordinates (IRC) developed by Fukui have been used in discussions of chemical reaction mechanisms based on quantum chemical calculations. Frontier orbital theory can predict reactivity in the initial stage of a reaction by focusing on the HOMO and LUMO of reactant molecules, but it is not necessarily a method to understand the entire reaction process. If there are multiple reaction pathways for a given reactant molecule, the molecular orbital that drives the reaction should be different for each reaction. In other words, to understand the reaction mechanism, we need to study the movement of electrons along the IRC. We have developed a method to extract pairs of occupied and virtual orbitals that characterize the movement of electrons along a reaction pathway and named it the Natural Reaction Orbital (NRO) method [1,2]. NRO analysis allows us to know where and how electrons move along the IRC. Using a group of structures on the IRC as reference structures, we developed a method to visualize the reaction path network in low-dimensional coordinate space by applying a classical multidimensional scaling method, which we named the Reaction Space Projector (ReSPer) method [3,4]. By projecting on-the-fly molecular dynamics trajectories onto this reaction space, reaction dynamics can be discussed based on the reaction path network. In this talk, I will introduce the new quantum chemical analysis methods, the NRO and ReSPer methods, with examples of their applications.

References

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