Novel quantum chemical approach to chemical reactions: reduced-dimensionality reaction space and natural reaction orbital

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ABSTRACT

ICReDD promotes fusion research to accelerate the development of useful chemical reactions through "*Chemical Reaction Design and Discovery (CReDD)*" by integrating computational science, information science, and experimental science. As a quantum chemical computation team, our group is working on elucidating the mechanism of complex chemical reactions in collaboration with experimental and information science groups by applying the artificial force induced reaction (AFIR) method, an automated reaction path search method, which is a fundamental technology of ICReDD. We are also developing new methodologies for chemical reaction analysis based on quantum chemistry. In this talk, I will introduce the reaction space projector (ReSPer) method [1] and natural reaction orbital (NRO) concept [2] as newly developed methods for chemical reaction analysis in our group.

In the quantum chemical approach, the mechanism of a chemical reaction is investigated based on the intrinsic reaction coordinate (IRC) defined on the potential energy surface (PES). The AFIR method allows us to construct a global reaction route map containing multiple IRCs, while the on-the-fly molecular dynamics method, which is based on electronic structure calculations to determine the forces acting on atoms, generate classical trajectories with unrestricted motion on the full-dimensional PES. We have developed a method to visualize the reaction route map in a low-dimensional space by introducing inter-structure distances for structure pairs, and named it ReSPer. It is also possible to project dynamical trajectories onto the reaction space defined based on the reaction route map, which is expected to serve as a general method for analyzing chemical reaction mechanisms and dynamics.

Electronic degrees of freedom dominate the potential energy surface that determines reaction paths and dynamical trajectories, and it is no exaggeration to say that the elucidation of chemical reaction mechanisms is only complete when we understand the movement of electrons associated with changes in molecular structure. The NRO method elucidates the electron motion associated with the movement of nuclear coordinates by pairs of occupied and virtual orbitals, and can extract regions along the reaction path where the electron motion is more pronounced. In this talk, I will demonstrate the usefulness of NRO analysis by applying it to several reactions.

References

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