1-1-14. Computational Chemistry

Overview

Since the early 2000s, the introduction of long-range correction functionals, which significantly improved the computational accuracy of TDDFT, has enabled excited-state calculations for relatively large molecular systems. This advantage has greatly expanded the use of computational chemistry in photochemical research. In addition, progress in exploring stable structures on excited states, conical intersections, and simulating excited-state dynamics has contributed to understanding photoreactions and photofunctional materials, as well as to materials design. Further developments are expected in computational approaches that can treat complex systems with high accuracy and low computational cost, as well as in the comprehensive exploration of photochemical reaction pathways.

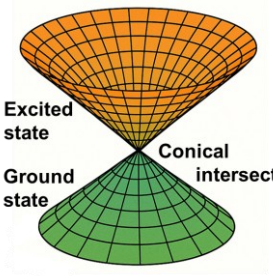

Figure 1. Conical intersection

Current Status and Frontiers

One of the greatest contributions of computational chemistry to photochemistry is the ability to compute excited states at a realistic computational cost. Traditionally, quantitative excited-state calculations required computationally demanding wavefunction methods such as MRCI or CASPT2, limiting their applicability to small molecules. Although time-dependent density functional theory (TDDFT) was available as a more affordable method, it was known to underestimate the energies of charge-transfer (CT) excited states. This often led to incorrect energetic ordering between π-π* and CT states, making even qualitative discussions difficult. Since the early 2000s, however, the development of long-range-corrected (LC) functionals, such as ωB97X-D and CAM-B3LYP, has significantly improved the reliability of excited state calculations using TDDFT. This enabled excited state calculations for relatively large molecules and metal complexes. In addition, the natural transition orbital (NTO) analysis, which represents excited states using only one or two pairs of orbitals, has enabled the visual and concise understanding of excitation properties.

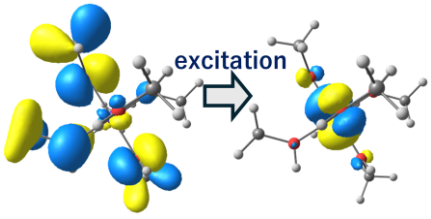

Figure 2. NTOs of a metal complex

The implementation of analytical energy gradients of excited states has enabled geometry optimization of local minimums and transition states on the potential energy surface (PES) of excited states. Additionally, geometry optimization of the minimum-

energy crossing points (MECPs) between the ground and excited states has also become feasible. However, when describing the singlet ground state (S_0) with DFT and the singlet excited state (S_1) with TDDFT, a problem arises: the PES cannot be smoothly described near the conical intersection (CI), making CI structural optimization impossible. Consequently, high-precision wavefunction methods remain necessary for calculating photo-processes involving CIs, thereby limiting system size. To address this issue, the spin-flip TDDFT method was developed (Krylov et al.), which describes both S_0 and S_1 via single-electron excitation from the triplet state (T_1). While locating CIs using this method is increasing, a drawback of significant spin contamination has also been reported. Another proposed approach is the energy shift method (Harabuchi, Hatanaka, Maeda), which slightly lowers the S1 energy and terminates the optimization before entering the region where the TDDFT PES becomes ill-defined. While this method is restricted to exploring a geometry near the CI, it is sufficiently accurate for qualitative analysis. This method was originally developed for lanthanide systems and enabled the theoretical design of strong luminescent materials and luminescent thermometers based on MECP calculations (Hatanaka, Morokuma et al.). Meanwhile, ab initio molecular dynamics simulations on excited states have become a valuable tool for elucidating excited-state dynamics, contributing particularly to deeper insights into time-resolved spectroscopic behavior (Taketsugu et al.).

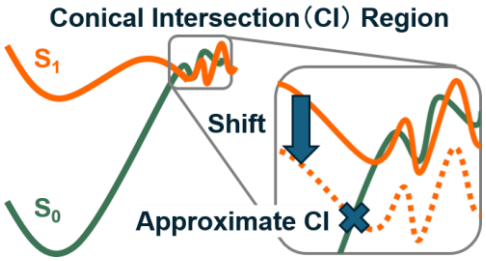

Figure 3. Exploration of an approximate CI using the energy shift method.

References

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Future Perspectives and Directions

Development of new approaches to calculate excited states in quasi-degenerate systems, core excited states, and multi-electron excited states with high accuracy and low computational cost. Comprehensive reaction path exploration methods for photoreactions and expansion of their application to large-scale systems.

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