2-5-4. Design of Luminescent Molecules by Theoretical Calculations

Overview

If we unravel the history of the development of theoretical computation for molecules, one of the major components of the development of computational methods is how to obtain the electronic state, energy, and molecular structure in the excited state with high accuracy and efficiency. In quantum chemical calculations, it is generally difficult to achieve both high accuracy and computational efficiency by introducing higher-order electron correlations, so it is necessary to determine whether the computational method adopted is suitable for the target system when using it in molecular design.

Current Status and Frontiers

The outline of the calculation method for the excited state is classified into the following three categories.[1]

1. Time-dependent density functional theory (TDDFT)

Since the 1990s, the Density Functional Theory (DFT) has been implemented in various quantum chemical calculation software to determine the electronic state and molecular structure of the ground state. It is well known that DFT calculations have become indispensable for the theoretical analysis of most molecular systems. The same thing happens with excited state calculation. The TDDFT method derived from the linear response theory based on DFT has been used most frequently in recent years due to the light computational cost that it is only required by the one-electron excitation function. As with the calculation of ground state, many results corresponding to actual measurement data have been obtained by appropriately combining functional and basis set.

On the other hand, some problems unique to TDDFT have been pointed out, and more recently, negative views on the theorem itself on which TDDFT is based have been published.[2]

2. Single-reference multi-electron excitation calculations.

Even before the TDDFT became widespread, a computational method that incorporates double and higher-order excitations with a single Slater determinant as reference has been widely used in small molecules, and it has been found to be effective for excited states that cannot be described by a single-electron excitation method. One of the examples of where TDDFT is not suitable is the S_1 excited state of anthracene, and we have shown that the S_1 excited state structure optimized by the SAC-CI method,[3] one of the coupled cluster methods, accurately reproduces the rotational constant obtained from the high-resolution spectra.[4]

Although incorporating multi-electron excitation can yield high-precision results, it

is difficult to apply this method to large-scale systems because the computational cost increases exponentially with the size of the system.

3. Multi-reference theory[5]

In systems that cannot be described by a single Slater determinant, such as a potential energy surface involving bond-breaking, the wave function obtained by the multiconfiguration self-consistent field (MCSCF) method is used as a reference function. The complete active space SCF (CASSCF) method, which considers all possible configuration interactions (full configuration interaction, FCI) within the selected orbitals as the active space, is frequently used within the MCSCF method and is implemented in many applications. However, it is difficult to calculate the wider active space because the size of FCI has increased significantly. It is advisable to consult an expert on the calculations because setting the active space that matches the purpose of the calculation is necessary.

References

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Future Perspectives and Directions

In considering the future development of excited state calculations, it is essential to apply artificial intelligence (AI) technology, which has been adopted in various fields of science and technology in recent years and has achieved great success. It has already begun to be used for prediction of potential energy surfaces of excited states [J. Westermayr, P. Marquetand, *Chem. Rev.*, **121**, 9873–9926 (2021)].

Challenges expected to be resolved or achieved within the next five years: High-precision prediction of physical properties and molecular design in the excited state using AI technology. To improve the accuracy of excited state calculations, it is common to consider as much electron excitation as possible, but this is difficult due to the increase in computational cost.

Challenges expected to be resolved or achieved within the next ten years: Development of a general-purpose and highly efficient multi-reference and multi-electron excitation calculation method.

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