Coupling RISM with DMRG-CASPT2 for calculating photochemical properties of near infrared molecules

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[Abstract]

Recently, molecules with fluorescence in the so called "second near-infrared window" have been gaining attention for improving the performance of bio-imaging. Considering the difficulty of handling excited states through experiments, theoretical calculations hold a great advantage in studying these molecules. Still, the range of this region only spans for roughly 0.5 eV, hence highly accurate calculation results are required for discussion. To accurately calculate the photochemical properties of these molecules, proper treatment of the solvation effect and electronic structure of the excited state is essential; however, even with the conventional TD-DFT/PCM method, results were far from experimental results, making it difficult to analyze their photochemical properties. To overcome this problem, we have developed a new method based on a statistical approach (RISM) and a multi-reference perturbation theory (DMRG-CASPT2) in order to calculate the photochemical properties of these molecules with higher accuracy.

[Introduction]

In the field of bio-imaging, fluorescent molecules are very powerful tools for visualizing biological events. Fluorescence in the near-infrared (NIR) region is especially favored because of its efficiency in penetrating biological tissue. Recently, molecules with fluorescence in the so called "second NIR window," around 1000-1700 nm, have been especially gaining attention for their potential in improving the performance of bio-imaging [1]. Studying fluorescence of molecules experimentally is a pain from the difficulty of handling excited states. On the other hand, theoretical calculations have a great advantage in studying these molecules since handling excited states becomes relatively easier. Still, the range of interest, the "second NIR window," only spans for roughly 0.5 eV, thus highly accurate calculation results are required for discussion.

For accurately calculating the photochemical properties of fluorescent molecules, proper treatment of the solvation effect and the electronic structure of the excited state is essential. With the widely used TD-DFT/PCM method, results were far from experimental data, with the error being more than 0.5 eV. In order to overcome this problem, in this research, we have developed a new method by combining a multi-reference perturbation theory, DMRG-CASPT2 [2], with a solvation theory of a statistical mechanical approach, RISM-SCF-SEDD [3], for calculating the photochemical properties of fluorescent molecules with higher accuracy.

[Methods]

The free energy of the solute in solution was defined by the following equation:

$$\Delta G = \left\langle \Psi_{\mathrm{DMRG}} \left| \hat{H} \right| \Psi_{\mathrm{DMRG}} \right\rangle + E_2 + \Delta\mu$$

where Ψ_{DMRG} is the active-space DMRG wavefunction, $\hat{H}$ is the Hamiltonian constructed in the gas phase, and E_2 is the second-order energy, which are obtained from DMRG-CASPT2 [2], and $\Delta\mu$ is the solvation free energy, which is obtained from RISM-SCF-SEDD [3]. By taking the variation of this equation, the desired equation was obtained.

As an assessment of the newly developed method, RISM-DMRG-CASPT2, the absorption energies of the derivatives of BODIPY and cyanine 3 given in Scheme 1 were calculated in acetonitrile and DMSO respectively. Optimized geometries were computed using the CAM-B3LYP level of theory in acetonitrile and in DMSO at 300 K for BOIDPY and cyanine 3 respectively by TD-DFT/RISM. Basis sets employed were aug-cc-pVDZ for nitrogen and fluorine and cc-pVDZ for the other atoms. Geometry optimizations were conducted with the GAMESS program package in which our method has been implemented in the past. RISM-DMRG-CASPT2 was conducted with the orz program package in which we have newly implemented our method into.
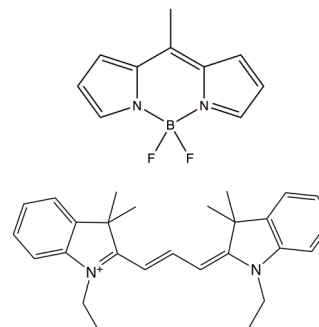
Scheme 1. Structure of BODIPY (top) and Cyanine 3 (bottom).

[Results and Discussion]

The error of the calculated absorption energies of BODIPY and cyanine 3 compared to the experimental data [4,5] are given in Figure 1. It can be observed that the newly developed method, RISM-DMRG-CASPT2, has greatly reduced the error compared to the TD-DFT/PCM method, being within a difference of 0.1 eV with the experimental data.

We have focused on the natural occupation numbers of the π and π^* orbitals to explain the high accuracy of the new method. In the case of TD-DFT, the character of the excitation was a dominant HOMO-LUMO single excitation. On the other hand, with DMRG, together with the HOMO-LUMO single excitation, other transitions also slightly existed. It is expected that the additional transitions worked to move HOMO and LUMO closer together and as a result improved the calculated absorption energy.

Fig. 1. Error in calculated absorption energies using TD-DFT/PCM (blue) and RISM-DMRG-CASPT2 (green) compared to experimental data [4,5].

Figure 1 shows that the high accuracy of the newly developed RISM-DMRG-CASPT2 method should enable the study of the fluorescent molecules of interest in the "second NIR window" through calculations.
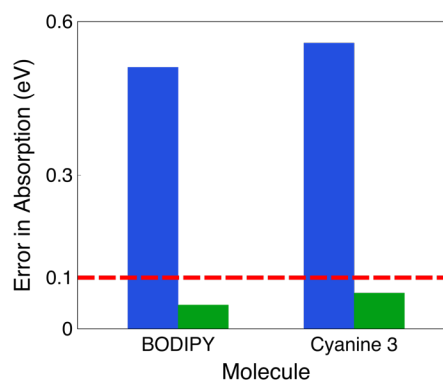
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