Generalized Energy-Based Fragmentation Approach for Electronic Absorption and Emission Spectra of Large Systems

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The excited-state (ES) calculation of a large system is a great challenge in quantum chemistry. Previously, a generalized energy-based fragmentation (GEBF) approach[1] has been implemented for the localized excited states of large states and applied to the electronic absorption spectra of macromolecules and large clusters.[2] In this approach, the ES energy for a localized ES of a large system can be obtained by combining the ES energy of the subsystems including local excitation center (defined as active subsystems) and the ground-state ones of the remaining subsystems. However, the ES geometry optimization is still a challenge for fragmentation approach due to the difficulties of state-classification and state-tracking. Very recently, in order to overcome the two difficulties, we have developed a transition orbital projection (TOP) algorithm[3] for state-tracking and adopted an improved density-based spatial clustering applied with noise (DBSCAN) algorithm. With the two approaches, the GEBF approach could be employed to compute the localized ES geometries and vibrational frequencies of large systems.[4] Our results show that the GEBF approach can accurately compute the electronic absorption and emission (fluorescence or phosphorescence) spectra of large systems with local chromophores at the time-dependent density functional theory (TDDFT) level.

References

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