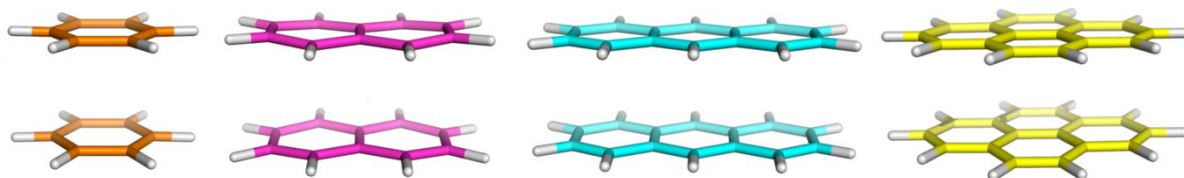


Exploring noncovalent excited-state interactions in aromatic dimers with TD-DFT approaches

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Excimers—excited dimers—are supramolecular systems whose unique excited-state binding comprises many components that are ongoing challenges for the computational treatment of excited states, such as charge transfer, exciton coupling, and London dispersion interactions. In two recent studies, we focused on the binding of four excimer systems as a challenging test case for current time-dependent density functional theory (TD-DFT) methods, both with and without the application of additive dispersion corrections.^{1,2} More recently, we extended this study to higher-lying excited states of the same stacked dimers.³ This extension allowed us to investigate the performance of ground-state-based dispersion corrections across multiple excited states. We found that without dispersion correction, double hybrids, especially those with range-separation (recently published in our group),⁴ best recover the excited-state interaction energy curves of these dimers. This corroborates their success in single chromophore studies. With dispersion correction, the performance of TD-DFT was improved across multiple excited states, but the degree of improvement varied depending on the system and electronic state. Our work highlights the need for development of excited-state-specific dispersion correction approaches for more accurate and practical application of TD-DFT methods.



References

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