Theoretical Description of the Excited States of Extended Pi-Conjugated Molecules

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Abstract

Description of the excited states of large molecules remains a challenge because of their large size and complex nature, and time-dependent density-functional theory (TDDFT) is widely used for the description of such excited states. However, extended, pi-conjugated systems are especially challenging for TDDFT because of problems of existing functionals using the local-density approximation. Quantum-correlated methods, such as configuration interaction or coupled-clusters, have a large computation demand, and may only be applied presently to the smallest molecules of interest. We will present descriptions of the electronic structure of these extended pi-systems using a variety of semi-empirical and first-principles methods, including the extend Hückel theories, time-dependent Hartree-Fock, TDDFT, and coupled-cluster theories. Emphasis will be placed on size-extensive methods. That is, methods that maintain a degree of precision with increases in the size of the material system. Phenomena studied include the low-lying singlet excitations and emissions for individual oligimers and pi-pi stacked systems.

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