

Excited States and Spectroscopy of Organic Semiconductors from First Principles: Methods and Applications

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Organic semiconductors are a highly tunable, diverse class of cheap-to-process materials promising for next-generation optoelectronics, for example solar cells. Further development of new organic materials requires new intuition that links molecular-scale morphology to underlying excited-state properties and phenomena. Here, I will discuss strategies within first-principles density functional theory and many-body perturbation theory – within the GW approximation and the Bethe-Salpeter equation approach – for computing and understanding spectroscopic properties of selected organic molecules and semiconductor crystals, including acenes from benzene to hexacene; PTCD; perfluoropentacene; and TIPS-pentacene. For both gas-phase and crystals, our quantitative calculations agree with transport gaps extracted from photoemission data, and with measured polarization-dependent optical absorption spectra. Introducing a new analysis, we elucidate the nature of low-lying solid-state singlet and triplet excitons, which have significant binding energies and charge-transfer character in these systems. In addition, we rationalize trends in predicted singlet and triplet excitation energies in the context of singlet fission.