

First-principles study of the electronic structure of organic semiconductors

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Organic semiconductors are promising materials for next generation electronics, with the characterization of their spectroscopic properties vital to improving the potential of the technology. Here, we characterize such properties for two prototypical organic semiconductor crystals, pentacene and PTCDA, with a combination of density functional theory and many-body perturbation theory. Quasiparticle spectra, computed within the GW approximation, and neutral excitation energies, computed via the solution of the Bethe-Salpeter equations, are directly compared with valence band photoemission and optical absorption data, and accuracy of the methods is studied. Additionally, comparison of computed gas-phase ionization energies and electron affinities with calculated crystal-phase quasiparticle band structures shows a strong red-shift of the gap in the bulk relative to gas phase, a reduction that can be described almost entirely as an electrostatic polarization effect. Lastly, we compute large exciton binding energies within these organic crystals (~ 1 eV), a prediction that has significant implications for the interpretation of photoemission spectra and the performance of organic photovoltaic devices. We acknowledge DOE, NSF, and BASF for financial support, and NERSC for computational resources.