First-Principles Photoemission Spectroscopy in Molecules and Electronic Structure of Extended Systems from Koopmans-Compliant Functionals

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While density functional theory (DFT) provides an efficient and reliable method for computing the ground state energetics for a wide variety of materials, the eigenstates obtained by solving the Kohn-Sham equation do not formally correspond to charged excitation energies. This is particularly evident when comparing photoemission spectra, computed with the local or semi local exchange correlation functionals, with experiments. In this work, we show that Koopmans-compliant functionals [1], constructed to enforce piecewise linearity in energy functionals with respect to fractional occupations - i.e., with respect to charged excitations - can predict not only frontier ionization potentials and electron affinities of molecules with an accuracy comparable with that of higher-level quantum chemistry and many-body perturbation methods but also molecular photoemission spectra, that are shown to be in excellent agreement with experimental ultraviolet photoemission spectroscopy data [2]. These results highlight the role of Koopmans-compliant functionals as accurate and inexpensive quasiparticle approximations to the spectral potential. Furthermore, we discuss how to apply these functionals to extended systems, with results for semiconductor band gaps and band structures.