Optimally-tuned range-separated hybrid functionals for accurately predicting valence-electron spectra of complex molecules

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To accurately predict the electronic structure of complex molecular systems on the basis of first-principles simulations is a key challenge of modern theoretical chemistry and physics. Density functional theory with optimally-tuned range-separated hybrid (OT-RSH) functionals has been recently suggested as a non-empirical approach to accurately predict the outer-valence electronic structure of organic molecules. The OT-RSH scheme relies on separating the inter-electron interaction into short- and long-range, and tuning the remaining parameters in the density functional from first-principles conditions, without recourse to fitting to experimental data. Here, we provide a quantitative evaluation of the OT-RSH approach and examine its performance in predicting the outer-valence electron spectra of the prototypical gas-phase aromatic rings benzene, pyridine and pyrimidine. For a range of up to several eV away from the frontier orbital energies, we find that the outer-valence electronic structure obtained from the OT-RSH method agrees very well (typically within 0.1-0.2 eV) with both experimental photoemission data from the literature and our many-body perturbation theory data in the GW approximation. The sole exception found is a high-symmetry orbital that is particular to small aromatic rings and occurs relatively deep inside the valence state manifold. We conclude that the OT-RSH approach is an efficient device for reliable electronic-structure calculations of finite systems, a feature we find to prevail also for more complex and practically relevant molecules such as terpyrimidinethiol and copper-phthalocyanine.