The structural complexity of emerging materials for the next generation of optoelectronic devices requires a synergistic interplay between experiments and theory to unveil the fundamental mechanisms of light-matter interaction. First-principles all-electron methods based on density-functional theory and many-body perturbation theory are particularly suited for this purpose, as they are able to describe on the same footing excitations over the entire spectrum, from the optical to the x-ray region. I will demonstrate the predictive power of such ab initio approaches by considering three technologically promising examples: graphene/boron-nitride heterostructures, transparent conducting oxides, and hybrid inorganic-organic perovskites. An accurate description of correlation effects ruling the interaction with electromagnetic radiation is essential not only to correctly reproduce absorption spectra, but also to characterize the spatial distribution of the electron-hole pairs. This approach, complementary to experiments, enables unprecedented understanding of the physical processes ruling excitations in complex materials.