Excited states from combined Green Function based methods and symmetry analysis: the emblematic case of 2D halide perovskite semiconductors

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The simulation of the excited state properties in molecules and solids is a hot topic in materials science, as it involves strategic application fields as solar energy conversion and light-emission. An emblematic case is represented by 2-dimensional (2D) lead-halide perovskites, currently at the center of a feverish research activity for their opto-electronic properties, [1] whose excited states are influenced by a series of exotic features. They feature both quantum and dielectric confinement, which require to consider electronic properties beyond single-particle picture and inhomogeneity in the screening of the carriers.[2] Furthermore, due to the presence of lead, they feature giant spin orbit coupling (SOC), which makes perturbative approaches unreliable.[2] To provide accurate excited state simulations of 2D lead-halide perovskites, we resorted to the solution of the Bethe-Salpeter equation, that is, the Green function-based equivalent to Time Dependent Density Functional Theory (TDDFT), from first-principles.[3] Furthermore, to gain a very detailed interpretation of our simulations, we compared our numerical results with predictions from symmetry analysis and from well-established models from the theory of conventional semiconductors. Interestingly, our results are readily interpreted on the basis of the Wannier exciton model in 2D semiconductors, with dielectric contrast inherently accounted, thanks to our first-principle approach. In addition, the predicted exciton fine structure well agrees with very recent magneto-absorption measurements, hence contributing to solve an ongoing debate in the literature.[4] Finally, we shed some light on the spin-properties of the excited states of 2D lead-halide perovskites. Due to the large SOC, excited states in this material have strongly mixed spin-singlet and spin-triplet character, which should be considered when discussing recent findings of perovskite-induced triplet-sensitization in organic molecules.[5] Apart solving some ongoing questions in the field of 2D halide perovskite, the approach proposed here, which encompasses electronic structure theories, symmetry analysis and simplified models for conventional semiconductor, showcases how it is possible to provide a very deep interpretation of the results from first-principle calculations.

References

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