Electronic properties of hybrid metal halide perovskites: Contemporary understanding and future challenges

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Metal halide perovskites are semiconductors that exhibit the rich electronic phenomena known from their more established counterparts, such as interface- and dopant-induced band bending, surface states and surface band bending, and surface photovoltage. But they feature even more complexity due to moderate stability under optical excitation in vacuum that can induce surface states, and reversible p-doping by (ambient) oxygen. The simultaneous occurrence of all these phenomena has initially retarded progress towards a comprehensive understanding of their electronic properties, because the most direct experimental method to assess these properties – photoelectron spectroscopy – has been insufficiently adapted to the needs of the perovskites. Now that several important fundamental questions are resolved, such as those discussed here, we can look forward to obtaining deeper insight into even more complex properties and processes of this fascinating material class. In addition, novel interfacial phenomena have been identified, such as photo-induced energy level re-alignment at charge-selective contacts. This necessitates careful photoelectron spectroscopy studies under *operando* conditions, in order to reliably link interface energetics and solar cell performance.