Microscopic connection between absolute valence energy alignment and surface dipoles in halide perovskite heterostructures

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In recent years, hybrid organic-inorganic perovskites (HOP) have undergone extensive research due to their excellent photovoltaic and optoelectronic properties[1]. To further improve their device performance, there is a considerable ongoing research effort on their surface passivation and/or functionalization[2,3]. This stems from the fact that surface passivation and/or functionalization, including the combination of 2D and 3D perovskites, directly influences the surface dipoles between adjacent layers in a device stack, which in turn changes materials' work functions and absolute energy level alignments. However, the link between the two lacks a general framework bridging classical electromagnetism and modern atomistic approaches. Shedding more light on this link is of great technological importance to fully exploit the potentials of these semiconductors. Hence, this contribution[5] presents a theoretical methodology that clearly shows the relationship between surface dipoles and work functions. We rely on a semiclassical approach[4], that will allow scientists not specialized in DFT computation, to make use of their chemical or physical intuitions. We demonstrate the potentials of the methodology through a variety of cases to clearly show i) the effect of surface termination on the absolute energy level alignments, the ability to modulate the work function via ii) surface coating and iii) surface functionalization and/or passivation with molecules. Finally, we demonstrate the additivity of surface dipoles in heterostructures, which is analogous to the additivity of the dielectric susceptibility in these compounds[6]. Our methodology transcends the limits of halide perovskites and provides a computational strategy to fine-tune the absolute energy level alignments for optimizing the performance of broader families of optoelectronic devices

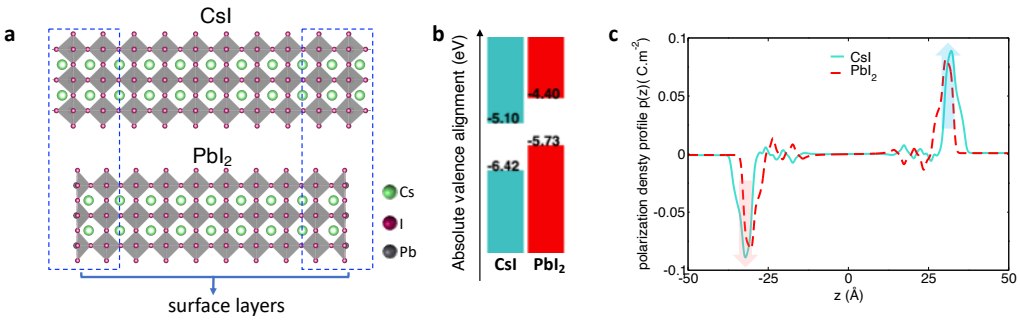

Figure 1 Effect of surface termination on absolute energy alignments and microscopic interpretation (a) $CsPbI_3$ structures with CsI and PbI_2 terminations with relaxed surface layers. The surface layers are shown by dashed rectangles on either side of the slab. (b) Computed absolute valence energy levels for CsI and PbI_2 terminated surfaces, respectively, for relaxed surface layers. (c) Polarization density profiles of the two slab systems showing different surface dipoles for relaxed surface layers. The arrows pointing the directions of the dipoles are guides to the eyes.

References:

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