

Structural and Electronic Features of Hybrid Organic–Inorganic Halide Perovskite Clusters and Surfaces: Insights from First Principles

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We discuss the properties of zero- (cluster) and two- (surface) dimensional hybrid organic–inorganic halide perovskites in view of their possible applicability in photovoltaics, light emitting and lasing devices. $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), by “cutting” its bulk. Interesting properties of such clusters include their charge distribution, bandgap, wave function localization, and reduced effective mass. When increasing the size of the models, we found an unequivocally evident relationship between the total dielectric dipole moment of the investigated cluster and the wavefunction spatial distribution of the frontier molecular orbitals. This result rationalizes the structural and electronic properties of such zero-dimensional systems and supports the localization at the nanoscale of the wavefunction of the frontier orbitals as a function of the local fluctuations of the potential, which are mainly associated with the organic cation orientation. Charge carrier trapping at defects on surfaces or grain boundaries is detrimental for the performance of perovskite solar cells. In practice, it is one of the main limiting factors for carrier lifetime. Also, it causes hysteresis in the current-voltage curves, which has been considered as a serious issue for operation of perovskite solar cells. Surface defects responsible for carrier trapping are clarified by comprehensive first-principles investigations and it is proposed that PbI₂-rich condition is preferred to MAI-rich one, while intermediate condition has possibility to be the best choice.