

HYBRID-PEROVSKITE STRUCTURES FROM FIRST PRINCIPLES

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Hybrid-perovskite research has become a very active field in the photovoltaic community in recent years. Only four years after their discovery, the light-to-energy conversion efficiency of hybrid perovskite photovoltaics (HPPVs) broke the 20% mark, approaching the best performing inorganic-based single-junction cells such as CdTe (see the left panel of Fig. 1). Unlike the conventional inorganic materials, hybrid perovskites are cheap and environmentally friendly, therefore they are promising for emergent solar-cell technologies.

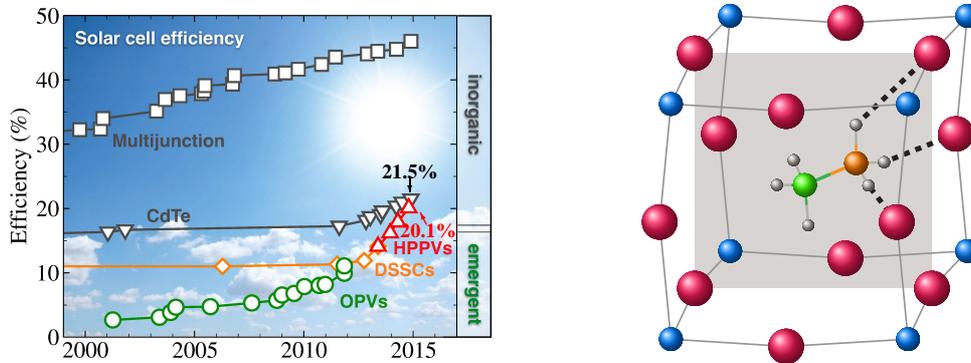


Figure 1: Left: efficiency evolution of HPPVs (and other emergent solar cells) compared to the inorganic single-junction CdTe and multijunction cells. Right: an optimized lattice structure of CH₃NH₃PbI₃.

To understand the properties of the most effective hybrid perovskite methylammonium lead triiodide (CH₃NH₃PbI₃), we present a quantum-mechanical study of its atomic structure, with a particular focus on the orientation of CH₃NH₃⁺ cations and their interplay with the inorganic PbI₃²⁻ matrix. Relativistic density functional theory (DFT) calculations were performed using the all-electron local-atomic-orbital code *FHI-aims* [1]. Our results [2] indicate that (i) the lattice constants obtained by incorporating van der Waals interactions (using the Tkatchenko-Scheffler method [3]) in the PBE functional agree well with experiments; (ii) hydrogen bonding plays a decisive role in the position of the CH₃NH₃⁺ cation and the deformation of the PbI₃²⁻ framework (see the right panel of Fig. 1); (iii) the reorientation of CH₃NH₃⁺ is limited due to relatively high barriers (~ 80 meV). Based on these findings we establish a self-consistent multiscale model, in which the alignment of CH₃NH₃⁺ dipoles in the material is determined by combining classical electrostatics and statistics with structure relaxation in DFT. Our procedure produces representative “pseudo-random” methylammonium lead triiodide supercells that will form the basis of further quantum mechanical work.

[1] V. Blum et al., *Comput. Phys. Comm.* **180**, 2175 (2009).

[2] J. Li and P. Rinke, *Phys. Rev. B* *submitted*.

[3] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).