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Tight binding modeling of halid perovskites

Soline Boyer-Richard¹, Reinhard Scholz², Jean-Marc Jancu¹, Claudine Katan³, Jacky Even¹

¹Université Européenne de Bretagne, INSA, FOTON UMR 6082, 35708 Rennes, France

²Institut für Angewandte Photophysik, TU Dresden, Deutschland

³Institut des Sciences Chimiques de Rennes, UMR 6226, CNRS – Université de Rennes 1, France

The free-electron model is built upon the assumption that electrons propagate almost freely and that their wave functions can be approximated by plane waves. As an “opposite” starting point, one can use localized atomic orbitals as a basis set to perform band-structure calculations; this is the tight binding (TB) or linear combination of atomic orbitals (LCAO) approach. This method has been introduced for periodic crystals by Slater and Koster¹ and was extensively used in the past to rationalize the physical properties of a wide range of compounds, from transition metals to semiconductor crystals².

In this paper we use this approach to investigate the properties of HOP, considering the reference cubic structures of the 3D ABX₃ family. Our tight-binding model is based on a 16 functions basis without SOC or a 32 functions basis with SOC. For cubic ABX₃ halide perovskites, we consider one “s” and three “p” orbitals for the B atom, and the same for each of the three X atoms in the simple cubic unit cell, as already presented for a qualitative analysis of the band structure³. No basis function is taken into account for the A organic molecule, which’s position is not fixed because it has rotational degrees of freedom/disorder in the cubic phase. We only consider first neighbor interactions, only between B and X atoms. We have chosen the minimal *sp*³ basis as developed by Slater and Koster and we have tried to reproduce the already known experimental data like energy band-gap and effective masses around the bandgap with our semi-empirical TB model. Nine parameters are considered without SOC: four different diagonal matrix elements related to the atomic energies of the chemical constituents B and X: E_{sB} , E_{pB} , E_{sX} and E_{pX} . Five transfer matrix elements refer to the overlap integral of atomic functions: V_{ss} , V_{sBpX} , V_{sXpB} , $V_{pp\sigma}$, $V_{pp\pi}$. SOC only appears for *p* orbitals with two SOC values Δ_{soB} and Δ_{soX} .

MAPbI₃ dispersion relation has been calculated using the *sp*³ tight binding method including SOC. Figure 1 presents the band diagram obtained, fitting existing experimental results recalled in ref. 2. The bandgap is obtained at R point with $E_G = 1.620$ eV. Effective masses around the bandgap are the following: $m_h^* = 0.235 m_0$ and $m_e^* = 0.229 m_0$. The dispersion relation shape is in very good agreement with the one presented by Brivio using DFT calculation⁴ and with previous symmetry analyses^{5,6}.

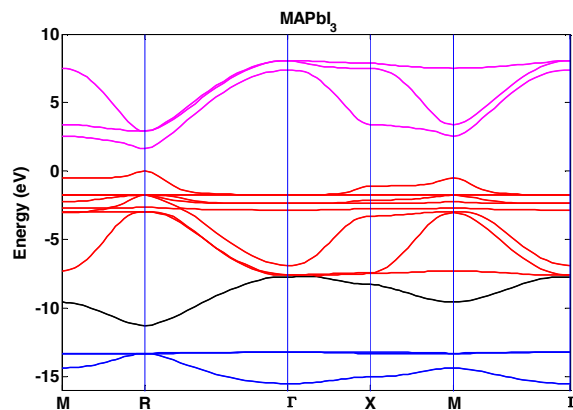


Figure 1. MAPbI₃ band diagram obtained within the TB scheme with SOC. The energy of valence band maximum is set to zero. Bands are colored according to their main orbital character: red depicts I 5*p*, pink depicts Pb 6*p*, black depicts Pb 6*s* and blue depicts I 5*s*. Points denoted M, X and R are zone-boundary points close to (1/2,1/2,0), (1/2,0,0) and (1/2,1/2,1/2) respectively. The Γ point is the BZ center.

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