

# Ab-Initio Calculation of Electronic Structure of Lead Halide Perovskites with Formamidinium Cation as an Active Material for Perovskite Solar Cells

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**Abstract.** Organic lead halide perovskite material based solar cells show impressive power conversion efficiencies, which can reach above 19 percent for perovskite solar cell with methyl-ammonium cations. These efficiencies are originated from efficient photoexcitation and charge carrier transport and not observed in conventional perovskite crystals. In this preliminary research work, we therefore performed Density Functional Theory (DFT) calculation of formamidinium lead iodide (FAPI), an alternative to methyl-ammonium lead iodide (MAPI), to predict their electronic structure and density of state (DOS). The calculation result at the most stable lattice parameters show a good agreement with the experiment results. The obtained band gap energy is 1.307 eV. The valence band is dominantly formed by the 5p orbitals of I<sup>-</sup> anions, while the conduction band is dominantly formed by the 6p orbitals of Pb<sup>2+</sup> cations. The DOS of valence band of this perovskite seems smaller compared to the case of methyl-ammonium lead iodide perovskite, which then may explain the observation of smaller power conversion efficiencies in perovskite solar cells with this formamidinium cations.

## 1. Introduction

After its first synthesis in 1978, perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (methyl-ammonium lead iodide or shortly MAPI) has been widely utilized for solar cells application [1]. In addition of ease and low cost fabrication, the achieved efficiencies have already reached more than 19 % [2]. A number of reports explain that these high performances are originated by long exciton diffusion lengths, very high light absorption coefficients which increase with temperature, and high open circuit voltages [3] [4] [5].

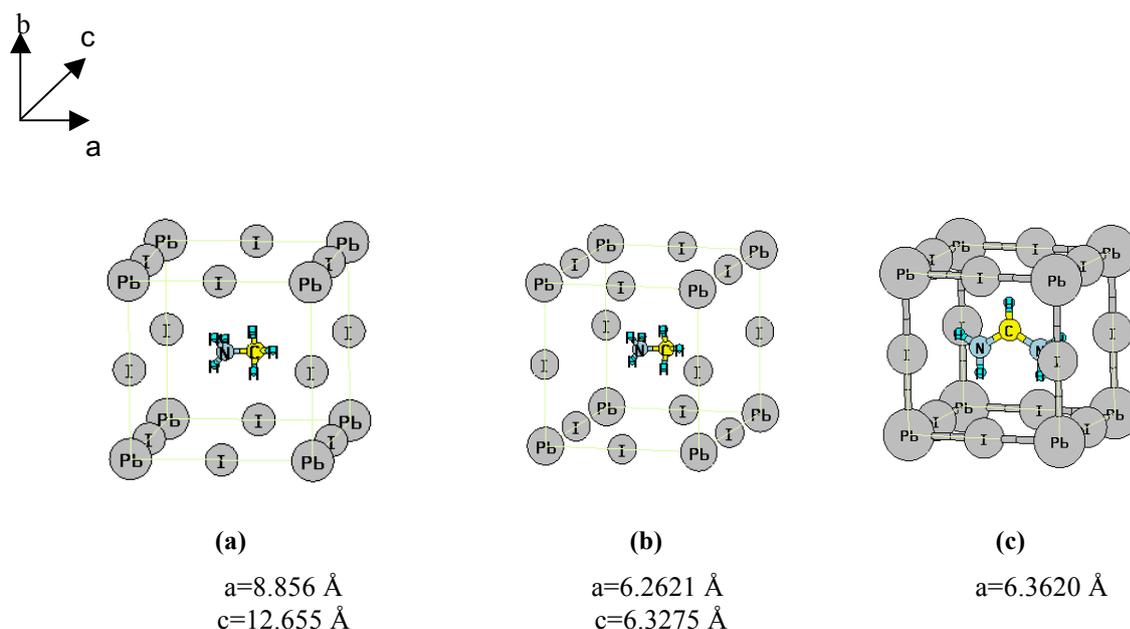
Owing to the success of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, scientists also explore the possibility to utilize other elements and/or molecules. One of the recently developed ones is taking an advantage of CH(NH<sub>2</sub>)<sub>2</sub> (formamidinium lead iodide or shortly FAPI) which has been investigated by several groups to have different performance to MAPI [3] [6] [7]. In this particular study, as the band gap value plays an important role to the solar cells performance, we aim to investigate the difference between the FAPI and MAPI systems with a focus in the electronic structure computationally by state of the art Density Functional Theory (DFT) method.



## 2. Computational Details

All computations were performed with Quantum Espresso software package based on DFT, plane waves, and pseudopotentials. Generalized Gradients Approximations (GGA) and Ultrasoft Pseudopotentials (US PPs) were utilized. Scalar relativistic exchange correlation functionals constructed by Perdew-Burke-Ernzerhof (PBE) were applied to all of the constituent atoms. Stand on the choices, the valence orbitals comprised of 2s and 2p of C, 1s of H, 2s and 2p of N, 5d, 6s, and 6p of Pb, as well as 5s and 5p of I. In order to limit computations reach infinity, the kinetic energy cut-off for wavefunctions were limited to 40 Ry.

The Brillouin zones were divided by Monckhorst Pack k-mesh with 4x4x3 grid 3x3x3 in the case of MAPI (both tetragonal and pseudocubic structure) and FAPI respectively for both structure optimizations and electronic structure calculations. Due to the presence of Pb atom, a smearing type of Methfessel-Paxton were employed [8]. The declared lattice constants were selected from experimental results reported by other groups [3] [9] [10]. The stable positions of organic molecules were declared by performing a pre-optimization and applying DFT technique with B3LYP (Becke, three parameter, Lee-Yang-Parr) exchange correlation functional [11]. The structures of each system are depicted in Figure 1.



**Figure 1.** Crystal structure of tetragonal **(a)** and pseudocubic **(b)** MAPI and **(c)** FAPI obtained from experimental results [3] [9] [10].

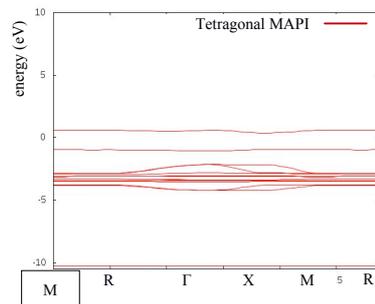
## 3. Results and Discussion

The electronic structure of each system was calculated after performing optimization calculation by which most stable lattice constants were obtained. To validate as well as to compare the calculation, we first computed the MAPI system. Jishi et al reported that MAPI exhibits tetragonal structure at room temperature [9]. However, the predicted electronic structure does not provide enough information to be interpreted as shown in band structure (see Figure 2). We think that the profile is caused by not close enough distance between neighbouring atoms and accordingly there is no enough interaction observed. Hereby, as also proposed by Baikie et al, we computed the MAPI system with

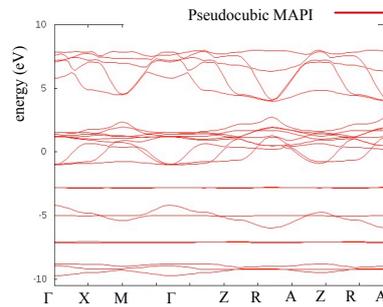
pseudocubic structure with  $a^*$  and  $c^*$  as the lattice constant ( $a^*=a^{1/2}$  while  $c^*=c/2$ ) [10]. The result of both tetragonal and pseudocubic structure of both systems are shown in Figure 2 and 3 respectively.

From Figure 3, it is then known that the band gap energy of pseudocubic MAPI is 1.232 eV at A high symmetry point which is lower than experiment result (1.51 eV) with an error of 18.42 %. Besides, the band gap energy of FAPI is 1.307 eV at R high symmetry point which is also lower than the reported experimental reports [3]. These lower values are due to the use of GGA exchange correlation functional and smaller lattice constants as depicted in Figure 1b for the case of pseudocubic MAPI [10].

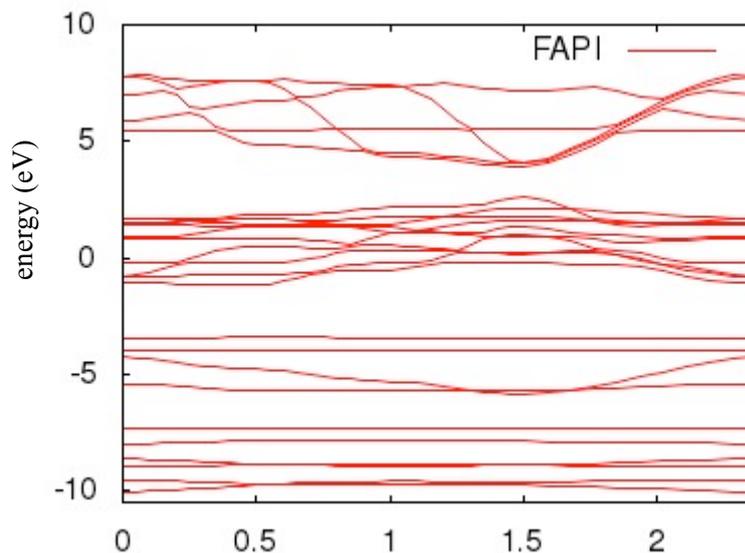
In addition, PDOS (Projected Density of State) computation which exhibits both the DOS (Density of State) values and the projection along each atomic orbital which are also performed to both pseudocubic MAPI and FAPI.



**Figure 2.** Band gap of tetragonal MAPI.



**Figure 3.** Band gap of pseudocubic MAPI.

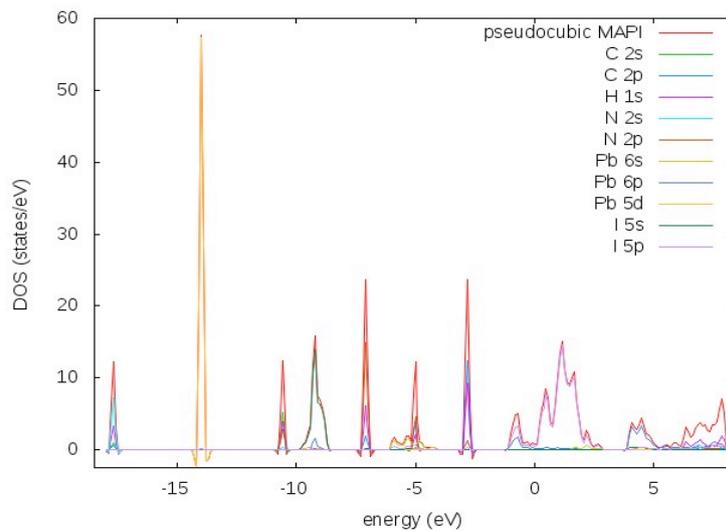


**Figure 4.** Band gap of FAPI.

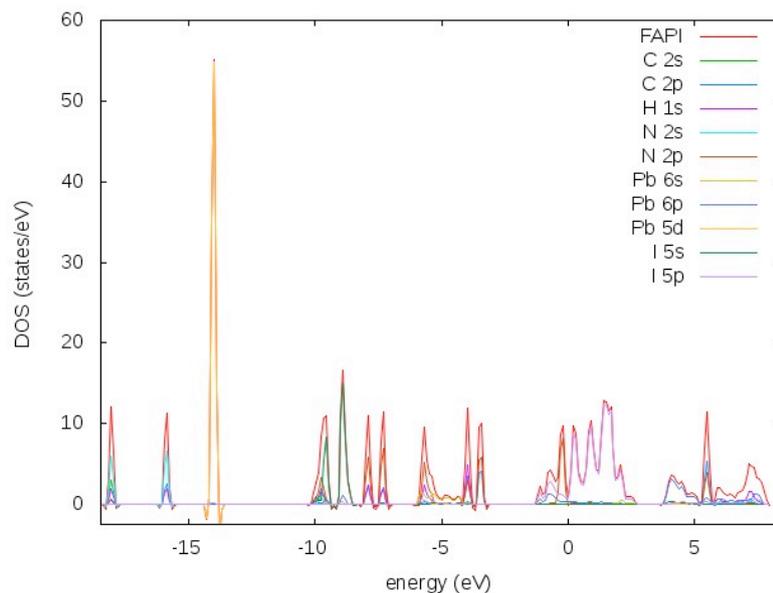
Figure 5 shows that the valence bands of pseudocubic MAPI are dominated by 5p orbitals of I while conduction bands are dominated by 6p orbitals of  $Pb^{2+}$ . In addition, it is also known that the organic molecule cation gives small contributions into both conduction and valence orbitals. Based on the value of DOS of pseudocubic MAPI and FAPI (Figure 5 and 6), it is clear that FAPI exhibits lower

DOS, which can be associated to lower amount of charge carriers at the valence band to be extracted into electricity. Hereby, this finding may explain smaller power conversion of FAPI based solar cells compared to the MAPI ones.

The charge distribution of valence and conduction bands over different atoms are further analyzed by looking at Lowdin charge profiles as shown in table 1 and 2. From both tables, it is known that there are partial charger transfers from the organic molecules to the inorganic domains. Carbon atoms in MAPI system accept charge carriers from their surrounding which is the contrast mechanism to the FAPI system. Owing to the symmetry of the organic molecules, the charge transfers experienced by symmetrical N and H atoms are the same (see Figure 1c).



**Figure 5.** PDOS of pseudocubic MAPI.



**Figure 6.** PDOS of pseudocubic FAPI.

**Table 1.** Lowdin charge orbitals of MAPI with spilling parameter of 0.0074.

MAPI atom	Valence electron number	Total charges	s	p	d
C	4	4.3365	1.0484	3.2881	0.0000
N	5	5.3442	1.2816	4.0627	0.0000
H	1	0.7757	0.7757	0.0000	0.0000
H	1	0.7751	0.7751	0.0000	0.0000
H	1	0.7756	0.7756	0.0000	0.0000
H	1	0.6437	0.6437	0.0000	0.0000
H	1	0.6351	0.6351	0.0000	0.0000
H	1	0.6343	0.6343	0.0000	0.0000
CH <sub>3</sub> NH <sub>3</sub>	15	13.9202	6.5695	7.3508	0.0000
Pb	14	13.4807	1.9681	1.5140	9.9985
I	7	7.4500	1.8755	5.5745	0.0000
I	7	7.1705	1.9414	5.2290	0.0000
I	7	7.6078	1.8510	5.7568	0.0000

**Table 2.** Lowdin charge orbitals of FAPI with spilling parameter of 0.0075.

FAPI atom	Valence electron number	Total charges	s	p	d
C	4	3.7564	0.9171	2.8393	0.0000
N	5	5.3681	1.2274	4.1406	0.0000
N	5	5.3681	1.2274	4.1406	0.0000
H	1	0.6599	0.6599	0.0000	0.0000
H	1	0.7551	0.7551	0.0000	0.0000
H	1	0.6599	0.6599	0.0000	0.0000
H	1	0.6656	0.6656	0.0000	0.0000
H	1	0.6656	0.6656	0.0000	0.0000

CH(NH <sub>2</sub> ) <sub>2</sub>	15	17.8987	6.7780	11.1205	0.0000
Pb	14	13.4787	1.9656	1.5147	9.9984
I	7	7.2321	1.9372	5.2949	0.0000
I	7	7.5691	1.8726	5.6965	0.0000
I	7	7.4141	1.8869	5.5271	0.0000

#### 4. Conclusion

In summary, we found out that the smaller power conversion performed by FAPI as the active material of hybrid perovskite solar cells may be explained by smaller value of the DOS. Both valence and conduction bands of MAPI and FAPI systems are dominated with 5p orbitals of I<sup>-</sup> ions and 6p orbitals of Pb<sup>2+</sup>. Partial charge transfers occurs in both system, from the organic molecules and inorganic domains. In case of organic molecules, symmetrical partial charge transfer occurs in FAPI which is not the case of MAPI. In contrast to MAPI system, atom C losses charge carriers instead of accepting them.

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