Effect of formamidinium cation on electronic structure of formamidinium lead iodide

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Abstract. The emergence of hybrid organic-inorganic perovskites (HOIPs) have attracted considerable attention due to their electronic and optical properties leading to potential applications, especially photovoltaics technology. The effects of the Formamidinium cation (HC(CH2)2+) or FA cation on cubic/α-Formamidinium lead iodide (HC(CH2)2PbI3) or α-FAPI were thoroughly and systematically investigated. We calculated the electronic band structures and the density of states of FAPI and FAPI without the FA cation including spin-orbit coupling interactions based on the state-of-the-art density functional theory (DFT). The results suggest that, according to the band structures, the FA cation exhibits a couple of nearly non-dispersive bands, whereas it is revealed that the organic cation weakly interacts with the inorganic framework of PbI3 octahedral cage.

1. Introduction
Recently, attention from many researchers have been drawn to an emergence of the hybrid perovskite solar cells due to their novel applications, for instance, in optoelectronic, thermoelectric, and photovoltaic technology, which astoundingly result from their electronic, excitonic, and optical properties [1-4]. Formamidinium lead iodide (FAPI) possesses 1.41 eV [5] band-gap energy that is far better matched to solar spectrum than that of Methylammonium lead iodide (MAPI) –the sister compound [5]. FAPI has been confirmed to adopt a cubic structure, α-phase, at room temperature [6]. However, there has been a topic of discussion about what exactly is the role played by the inorganic molecule [7]. Some previously reported that FAPI exhibits indirect bandgaps due to the effect of strain induced by the interaction between the FA cation, the organic molecule, and the inorganic framework, PbI6 [8], as well as the calculation on the rotational effects of the methylammonium cation on MAPI and the formamidinium cation on FAPI [9-11]. Because of the reasons mentioned above, it is the objective of this work to thoroughly investigate the effect of the organic molecule on the inorganic framework by the DFT calculation including the spin-orbit interaction.

2. Calculation methods
In this work, ab-initio calculations were adopted using the state-of-the-art density functional theory (DFT) and applying the self-consistent method [12, 13], all implemented in the Quantum Espresso Package [14], to evaluate the optimised structure and the electronic band structure corresponding to
FAPI with and without the organic molecule dwelling at the centre of the unit cell. The Projected Augmented Wave (PAW) method with fully relativistic form was used to describe the core and valence electrons. The Generalised Gradient Approximation (GGA) method [15] has been selected including the spin-orbit coupling (SOC) [16] owing to a heavy atom, i.e. Pb atom in the system. However, the van de Waals corrections are beyond the scope of this work since we only focus on the spin-orbit effect.

The cubic FAPI with a lattice constant of 3.3613 Å, depicted in figure 1(a), is selected as an input structure in relaxation process wherein the internal atoms are optimised except the shape and volume, which are kept fixed. The relaxed structure is subsequently used to evaluate the electronic band structures corresponding to the ones with and without the FA cation, which are shown in figure 1(b) and 1(c), respectively.

*Figure 1.* (a) The structure of FAPI with labelled atoms with a lattice constant of 3.3613 Å. The relaxed structure with FA molecule lying in the central mirror plane of the unit cell is represented in (b). The framework of FAPI without organic molecule shown in (c).

### 3. Results and discussion

In light of the convergence tests, the cutoff energy of 80 Ry and *k*-point mesh of 8×8×8 were selected. The relaxed FAPI, with atomic positions presented in table 1, consists of slightly deviated internal atoms from their original positions. This structure is then used in the electronic properties calculation.

As for the electronic band structure, it was reported in the case of MAPI, a similar structure except for the organic molecule, that the CBM is attributed from the Pb(6p) – I(5p) anti-bonding states, while the VBM is predominantly governed by the I(5p) and Pb(6s) lone pair states [7]. These features are to some extent analogous to the case of FAPI as well. Performing SOC, the band structures corresponding to the relaxed FAPI with and without the FA cation are figure 2(a) and 2(b), respectively. It is found that the CBM bands are split due to the strong SOC effect on the Pb(6p) states—The CMB branches are dropped and the bandgaps are narrowed. Consequently, the bandgaps of both scheme are equal, i.e. 0.15 eV, which are tremendously lower than that of the experimentally reported value: 1.41 eV [5], yet it can be corrected by including the effects of the strongly correlated electrons that can be achieved by the \(GW\) method or the hybrid functionals [17-19].

However, this work rather focuses on the characteristics of the conduction and valence branches which are interestingly exhibit the nature of the interaction between the organic molecule and the inorganic framework. In figure 2(a), there lies a couple of nearly non-dispersive branches at 2.7 eV and -3.0 eV, which indicate that the FA cation hardly interacts with the other atoms, whereas, in figure 2(b), there are no such supposedly flat branches as observed in FAPI without the FA cation scheme. Moreover, the valence states of the latter are more likely to dwell in higher energy regions than that of the former, suggesting that FAPI with the FA cation is likely to be more comparatively energetically stable.
Table 1. Atomic fractional coordinates of relaxed FAPI.

| Atoms | Fractional coordinates |
|-------|------------------------|
|       | a          | b          | c          |
| C     | 0.572103  | 0.4997166 | 0.500000  |
| N1    | 0.478304  | 0.682889  | 0.500000  |
| N2    | 0.478309  | 0.316526  | 0.500000  |
| H1    | 0.743669  | 0.500131  | 0.500000  |
| H2    | 0.570939  | 0.813387  | 0.500000  |
| H3    | 0.319234  | 0.703188  | 0.500000  |
| H4    | 0.319128  | 0.296325  | 0.500000  |
| H5    | 0.571127  | 0.186119  | 0.500000  |
| Pb    | 0.001372  | 0.000009  | 0.000000  |
| I1    | 0.005391  | 0.499948  | 0.000000  |
| I2    | 0.493962  | -0.000113 | 0.000000  |
| I3    | -0.029541 | -0.000127 | 0.500000  |

Figure 2. The electronic band structures of the relaxed FAPI and of the relaxed structure without the inorganic molecule are displayed in (a) and (b), respectively.

4. Conclusion
Applying DFT within the GGA including SOC, the cubic FAPI was relaxed in order that it adopts the energy minimum structure. FAPI with and without the FA cation structures are then used in evaluation their band structures. The results reveal that, in this SOC calculation, the organic molecule weakly yet significantly interacts with the inorganic framework of FAPI: Moreover, the FAPI with the FA cation dwells in a relatively more stable states. The molecule-cage effect was thoroughly investigated in a recent work by applying Eulerian angles upon the organic molecule [11].

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