Role of an external electric field on hybrid halide perovskite CH$_3$NH$_3$PbI$_3$ band gaps

Denghui Ji$^1$,$^2$, Mula Na$^3$, Shuling Wang$^2$, Hong Zhang$^2$, Kun Zhu$^1$, CongMin Zhang$^1$ & Xiuling Li$^4$

The organic-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ has attracted much attention for its use as a photon absorber in thin-film solar cells. In addition, its synthesis is relatively straightforward and can be achieved by simple layer deposition$^{1-6}$. Although great success has been achieved in improving the photovoltaic energy conversion efficiency as a potential photovoltaic material, the role of an external electric field has not been well understood. Based on first-principles calculations, the effects of an external electric field (E) applied along the [111] direction of the orthorhombic perovskite, CH$_3$NH$_3$PbI$_3$, on its electronic structure and optical properties are investigated. Our results indicate that the electric field strength affects the band gap ($E_g$) of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$, MA = CH$_3$NH$_3$). The energy difference between the two peaks closest to the Fermi level in the density of states diagram decreases with increasing applied electric field strength along the [111] direction, indicating that the covalent character increases between A-sites cations and I-sites anions. Both the cell volume and the final energy show the same increasing trend. The absorption peaks move toward the visible-frequency range, with the optimal band gap of 1.1–1.45 eV and $E_g = 0.04$–0.06 eV/Å/e. In particular, the non-linear change of the second-order Stark effect causes a non-linear change in the band gap.

The organic-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ has attracted much attention for its use as a photon absorber in thin-film solar cells. In addition, its synthesis is relatively straightforward and can be achieved by simple layer deposition$^{1-6}$. Although great success has been achieved in improving the photovoltaic energy conversion efficiency of this perovskite$^{7-9}$, perovskites are ideal because they absorb most of the solar spectrum, from the ultraviolet region to the near-infrared region, generate more excitons as more photons absorbed, and bring the energy levels closer to that of the electron transport layer (ETL) or hole transport layer (HTL). The optimal band gap for a single junction solar cell is between 1.1 and 1.4 eV$^{8,9}$. However, CH$_3$NH$_3$PbI$_3$ has a narrow direct band gap energy ($E_g$) of 1.51 eV, which is not optimal and hinders its application.

Using first-principles calculations, Amat et al.$^{10}$ investigated tetragonal APbI$_3$ perovskites with A = Cs$^+$, (CH$_3$NH$_3$)$_+$, and (NH$_3$)$_2$CH$^+$ and found that CH$_3$NH$_3$PbI$_3$ and (NH$_3$)$_2$CHPbI$_3$ have the same band gap. Hao et al.$^{11}$ studied the performance of CH$_3$NH$_3$Sn$_{1-x}$Pb$_x$I$_3$ perovskite solar cells. Their results indicated that the band gaps of mixed Pb/Sn hybrid perovskites have two extremes, 1.55 and 1.35 eV, depending on the ratio of Pb to Sn, but the band gaps were narrow (<1.3 eV). Furthermore, a band gap of 1.60 eV for CH$_3$NH$_3$PbI$_3$ and 2.39 eV for CH$_3$NH$_3$PbBr$_3$, and 3.17 eV for CH$_3$NH$_3$PbCl$_3$ was obtained. Moreover, it was shown that the optical band gap can be tuned from a direct band gap of 1.52 eV to an indirect band gap of 2.64 eV by varying the CH$_3$NH$_3$I concentration$^{12}$. In addition, the band gap of the tetragonal phase of CH$_3$NH$_3$PbI$_3$ decreased with decreasing temperature$^{13}$, following the relationship $E_g (T) = E_g (T_0) - b \cdot k_B (T_0 - T)^2$. Thus, finding the optimal band gap structure remains an important physical problem.

In many cases, the electric field effect can change the geometric, electronic, magnetic, and band structures of materials, and thus regulate their physical properties. Zhao et al.$^{14}$ reported the influence of external electric fields on the electronic structure and optical properties of TiO$_2$. They found that the band gap of TiO$_2$ becomes narrower with increasing electric field strength, decreasing to 0 eV when the electric field is 0.25 eV. Varignon et al.$^{15}$ used an electric field to control the Jahn–Teller distortions in bulk perovskites such as SrTiO$_3$, BaMnO$_3$, and SrPb$_2$I$_5$. 

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1School of Electrical engineering, Liupanshui Normal University, Liupanshui City, 553004, People’s Republic of China. 2School of Mathematics and Physics, Hebei University of Engineering, Handan City, 056038, People’s Republic of China. 3Department of General Education Courses, Hebei Agricultural University Bohai Campus, Huanghua City, 061100, People’s Republic of China. 4College of Physics and Information Engineering, Hebei Advanced Thin Films Laboratory, Hebei Normal University, Shijiazhuang City, 050024, People’s Republic of China. Correspondence and requests for materials should be addressed to D.J. (email: jidenghui2007@163.com)
YMnO₃ and BiFeO₃. Bellaiche et al. reported that an external electric field could induce polarization paths in PbZr₁₋ₓTiₓO₃ perovskites and lead to the expected sequence of tetragonal, A-type monoclinic, and rhombohedral structures. Xu et al. demonstrated that electric fields could induce a change from a ferroelectric phase to an antiferroelectric phase in a lead-free NaNbO₃-based polycrystalline ceramic. Therefore, it is very important and valuable to investigate the relationship between external electric fields and the physical properties of the organic-inorganic hybrid perovskite CH₃NH₃PbI₃. CH₃NH₃PbI₃ undergoes two phase transitions, one at 160 K (orthorhombic to tetragonal) and the other at 330 K (tetragonal to cubic). Using Density functional theory (DFT) calculations, Leppert et al. investigated the Rashba effect induced by the electric field and strained in the hybrid halide perovskite CH₃NH₃PbI₃ with a tetragonal and cubic structure. Although the orthorhombic phase is realized with rotations about the C–N axis that freeze out when T ≤ 162 K, temperature is not the only factor affecting these properties. An external electric field or magnetic field could also be an important factor, so we chose the orthorhombic CH₃NH₃PbI₃ as our subject to investigate these effects.

In this article, we investigate the effects of an external electric field applied along the [111] direction on the geometry structure, electronic energy band structure, total density of states, and optical properties of CH₃NH₃PbI₃. This study provides a method for obtaining the optimal band gap of CH₃NH₃PbI₃ and expands the scope of its applications.

Results and Discussion

The effects of the external electric field (E) direction, including the [001], [010], [100], [110], and [111] directions, on the band structure of CH₃NH₃PbI₃ were studied. The application of an electric field along the [111] direction in CH₃NH₃PbI₃ decreases the band gap, while fields aligned along the other directions increase the band gap. Therefore, we only investigated the physical properties of CH₃NH₃PbI₃ under an electric field aligned along the [111] direction to obtain the optimal band gap of 1.1–1.4 eV.

**Band structure of CH₃NH₃PbI₃ under the external electric field.** The band structure of CH₃NH₃PbI₃ in the absence of an external electric field is shown in Fig. 1 (a,b). When the external electric field is equal to zero, the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the same Γ-point, which indicates that CH₃NH₃PbI₃ possesses direct semiconductor characteristics. The calculated band is 1.726 eV and 1.675 eV, corresponding to the generalized gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof PBE and PBEsol, which are similar to the results reported by Menéndez-Proupin et al. The detailed calculation methods were shown in the Method section. It should be noted that the number...
of conduction bands calculated using GGA + PBEsol is greater than that calculated using GGA + PBE. In the presence of an applied external electric field with a strength ranging from 0.01 to 0.06 eV/Å/e, the band structures of the orthorhombic CH$_3$NH$_3$PbI$_3$ are similar. Figure 1 (c,d) show the band structure when $E = 0.06$ eV/Å/e. The conduction band shifts downward to the Fermi level (0 eV) and the energy band near the CBM is more dispersed, resulting in a change in the band gaps. All the configurations indicate an indirect band gap semiconductor, and the VBM and CBM are located at the centre of the Γ-point in k space. Because of the narrower indirect band gap of the CH$_3$NH$_3$PbI$_3$ semiconductor, only a small amount of energy is required for the formation of excitons. However, the GGA + PBE and GGA + PBEsol methods underestimate the band gap because of self-interaction errors, suggesting that the actual band gap of CH$_3$NH$_3$PbI$_3$ is slightly smaller than the calculated values.

The band gaps of CH$_3$NH$_3$PbI$_3$ are strongly affected by the applied electrical field strength. As the external electric field strength increases, the band gaps calculated by GGA + PBE first decrease linearly, then increase slightly, and finally, decrease linearly. The band gaps calculated by GGA + PBEsol indicated the optimal value between 1.1 and 1.4 eV for all the structures under an external electric field, as shown in Fig. 2. Therefore, both the results indicated that the external electric field contributes to a decrease in the band gap.

**Density of states of CH$_3$NH$_3$PbI$_3$ under an external electric field.** Figure 3 (a) calculated by GGA + PBE and (b) calculated by GGA + PBEsol show the total density of states (TDOS) of CH$_3$NH$_3$PbI$_3$ in the presence of an external electric field ($E = 0.00–0.06$ eV/Å/e). As the external electric field increases, (i) the two peaks corresponding to orbital energies from −22.5 to −15 eV gradually broaden and then become narrow, reaching their maximum widths when $E = 0.03$ eV/Å/e. (ii) The five peaks corresponding to orbital energies between −15 and −5.5 eV gradually broaden. (iii) Parts of the TDOS of the orbitals crossing the Fermi level increase with increasing external electric field, suggesting that the band gap of CH$_3$NH$_3$PbI$_3$ decreases. (iv) The CBM gradually narrows and shifts to the Fermi level, which also decreases the band gap, suggesting a pseudo-energy gap decrease, while the strength of the covalent character increases between the MA-cations and I anions.

The electron densities of CH$_3$NH$_3$PbI$_3$ when $E = 0.00$ and 0.06 eV/Å/e were shown in Fig. 4 (a,b), calculated by GGA + PBEsol. It can be seen that: (i) the lost electronic ions are H and Pb cations, and the gain electronic ions are C, N and I anions. (ii) With increasing external electric field, the electron density of C-N increases, thus increasing the strength of the associated covalent bond. (iii) The exact value of gain or lost electrons can be obtained based on Milliken Charge Analysis Method of Wave Function. For the $E = 0.00$, the lost average H cations have three kinds including 0.34, 0.22, and 0.21 electrons, the lost average Pb cations have one kind with 0.88 electrons, the gain anions with C and N have 0.61 and 0.70 electrons, and the gain I anion have two kinds including 0.36 and 0.52 electrons. For the $E = 0.06$ eV/Å/e, the lost average H cations have seven kinds including 0.15, 0.16, 0.29, 0.30, 0.34, 0.35 and 0.44 electrons, the lost average Pb cations have one kind with 0.54 electrons, the gain C anions have 0.65 electrons, the gain N anions have two kinds including 0.77 and 0.76 electrons, and the gain I anion have six kinds including 0.29, 0.37, 0.38, 0.39, 0.40, and 0.41 electrons.

Figure 5 shows the partial density of states (PDOS) of CH$_3$NH$_3$PbI$_3$ (GGA + PBEsol) under applied external electric field strengths of $E = 0.00$ and 0.06 eV/Å/e. The electronic orbitals 5d6s6p, 5s5p, 2s2p, 2s2p, and 1s are modeled as the valence orbitals for Pb, I, C, N, and H, respectively. The s-p hybrid level increases with external electric field increasing, and the effect on the conduction band is much more pronounced than that on the valance band. The peak near the orbital energy level at −5.0 eV splits into two peaks, which is attributed to the Stark effect of the s and p electrons, and one peak position shifts to the Fermi level. The external electric field causes the d electrons of Pb to shift to higher energies, but the d electrons do not affect the s and p electrons.

The Stark effect can induce the splitting of degenerate energy levels. The degree of the band splitting increases with the electric field, and a smaller band gap can be obtained. All peaks of the orbital energy level in the DOS curves broaden and shift to lower energies as $E$ increases. The physical mechanisms underlying the change in the band structure of CH$_3$NH$_3$PbI$_3$ is ascribed to the C-N and Pb-I bond lengths, changes in the lattice structure, and charge transfer between the Pb and I atoms. The lattice distortion caused by the mutation of lattice parameters may lead to changes in the microscopic electric structure, band structure, and density of states, similar to the results reported in ref.17.
Optimized structure of CH$_3$NH$_3$PbI$_3$ under an external electric field. The crystal structure determines the physical properties of the material; the lattice parameters ($a$, $b$, and $c$), cell volume ($V$), bond length ($d$), and final energies ($E_{\text{final}}$) are listed in Table 1. The external electric field applied along the [111] direction stretches...
Optical properties of CH$_3$NH$_3$PbI$_3$ under an external electric field. CH$_3$NH$_3$PbI$_3$ may show different preferential growth directions with different substrates, so obtaining the optical performance in this growth direction is an important physical problem. Let us take the [100] direction as the preferred growth direction as an example to illustrate this problem. Figure 8 (a) calculated by GGA + PBE and (b) calculated by GGA + PBEsol show the optical absorption spectrum with polarized light, where the polarization is along the [100] direction of CH$_3$NH$_3$PbI$_3$. It is seen that the electric field significantly influences the optical absorption characteristics of CH$_3$NH$_3$PbI$_3$. We assume the highest intensity absorption peak as the main absorption peak. The values 5.5 eV and 3.68 eV in the range of 0~5 eV for CH$_3$NH$_3$PbI$_3$ calculated by the GGA + PBE and GGA + PBEsol methods are the positions of the main absorption peak without the external electric field. As the electric field increases, the peak positions shift to lower frequencies, approaching the visible light region, and full width at half maximum (FWHM) of the absorption peaks decreases, which makes light absorption more effective and thus improves the photovoltaic conversion. In addition, there are some absorption peaks at higher energies beyond the visible range, which do not play a major role in photovoltaic conversion, but can become a candidate for optical detection devices such as ultraviolet band.

As the first-order approximation, the band gap $E_g$ and wavelength should satisfy the following relation:

$$\lambda (\text{nm}) = \frac{1239.8}{E_g (\text{eV})}. \quad (1)$$

We can obtain the related data based on eq. 1, as shown in Table 2. The following can be deduced:

(i) The band gap decreases non-linearly with increasing external electric field. When $E \leq 0.03 \text{ eV/Å/e}$, $\nu$ and $\nu_{100}$ decrease with an increase in the external electric field; when $E \geq 0.04 \text{ eV/Å/e}$, $\nu$ and $\nu_{100}$ increase with external electric field increasing, except $\nu$ with 0.04 eV/Å/e based on the GGA + PBE. Here, $\nu$ is the frequency calculated by the band gap, $\nu_{100}$ is the frequency along the [100] direction based on the Fig. 8.

(ii) The band gap ($E_g$) based on the band structure is similar to $E_g'$ based on the optical properties. Based on adiabatic approximation and single electron approximation, the relationship between absorption coefficient and photon energy can be expressed as,

$$\alpha = B(\nu - E'_g), \quad \text{ (2)}$$
where \( a \) is the absorption coefficient, \( B \) is a fitting parameter, \( h \) is Planck's constant, \( v \) is frequency, and \( E_{g}' \) is the band gap. According to the data in Fig. 8, \( E_{g}' \) values based on the optic properties are shown in Table 2.

Moreover, although the preferred growth direction may be not [100] in practice, we provided a method to obtain the optical properties of CH\(_3\)NH\(_3\)PbI\(_3\) under an external electric field.

Why does the band gap decrease non-linearly? For CH\(_3\)NH\(_3\)PbI\(_3\) under an external electric field, the Hamiltonian can be written as,

\[
\hat{H} = \hat{H}_0 + \hat{H}'.
\]
\[
\vec{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(r); \vec{H}' = e\vec{E} \cdot \vec{r}' = e\vec{E} \cos \theta; e = 1.6 \times 10^{-19} \text{C}; E \text{ is the external electric field; and } \\
\theta \text{ is the angle between the direction of the electric field and the radius vector direction } \vec{r}'. \vec{H}' \text{ is the perturbation. Based on the perturbation theory, the energy levels } (E_i) \text{ will change to the initial values } (E^{(0)}_i) \text{ by an amount } \Delta E_i. \\
E_i = E^{(0)}_i + \Delta E_i, \quad (4)
\]

\(\Delta E_i\) can be expanded with the additional energy of the electric field, which are Stark effect orders denoted as first order \(\Delta E^{(1)}\), or second order \(\Delta E^{(2)}\).

Figure 7. Parameters \(n_1\) and \(n_2\) versus the external electric field \(E\). Here \(n_1 = \frac{b\sqrt{\mathcal{E}} - a}{a}\), and \(n_2 = \frac{b\sqrt{\mathcal{E}} - c}{c}\).

Figure 8. The optical absorption spectrum within the polarized with polarization \((1, 0, 0)\) for CH\(_3\)NH\(_3\)PbI\(_3\) with the external electric field \(E = 0.00 - 0.06 \text{ eV/Å/e}\).
The energy changes owing to the electric field, where $\langle \psi_i |$ is the initial state of the system, then we have,

$$\Delta E = \langle \psi_i | - e \vec{E} \cdot \vec{r} | \psi_i \rangle = \langle \psi_i | - e \vec{E} \cos \theta | \psi_i \rangle.$$

For second-order energy changes, the summation is over all possible states of the system, so,

$$\Delta E^{(2)} = \sum_{\text{all states}} \langle \psi_i | - e \vec{E} \cdot \vec{r} | \psi_k \rangle \langle \psi_k | - e \vec{E} \cdot \vec{r} | \psi_i \rangle, \quad (7)$$

If $E$ can be considered a constant over the perturbation volume,

$$\Delta E^{(1)} = - e \vec{E} \langle \psi_i | \vec{r} | \psi_i \rangle, \quad (8)$$

$$\Delta E^{(2)} = E \cdot \sum_{\text{all states}} \langle \psi_i | - e \vec{r} | \psi_k \rangle \langle \psi_k | - e \vec{r} | \psi_i \rangle \frac{E}{E_i - E_k}. \quad (9)$$

From Table 1, it can be seen that the movements of the I\textsuperscript{-} anions are coupled to the movements of the monovalent MA\textsuperscript{+} cations and the rotation of the MA dipoles. This change in polarizability in the domains can influence the second-order Stark effect through the change in the dielectric constant owing to the change in the optical absorption spectrum\textsuperscript{28}. Then, $\Delta E^{(2)}$ may reflect in two possible first-order Stark effects, as shown in Fig. 9. If the value of $\Delta E^{(2)}$ is positive, the band gap will widen; if the value of $\Delta E^{(2)}$ is negative, the band gap will shrink. However, the second-order Stark effect cannot be larger than the first-order Stark effect, so CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} without an external electric field has the maximum band gap. The non-linear extent of the second-order Stark effect cause a non-linear change in the band gap.

The device required that: (i) The Highest Occupied Molecular Orbital (HOMO) of TiO\textsubscript{2} as ETL layer must be lower than CBM of perovskite active layer. (ii) The Lowest Unoccupied Molecular Orbital (LUMO) of spiro-omeTAD as HTL layer must be higher than VBM of perovskite active layer. The external electric field induced the Stark effect, splitting energy levels for TiO\textsubscript{2} and spiro-omeTAD (shown in Fig. 10), which decreases the HOMO of TiO\textsubscript{2} and increases the LUMO of spiro-omeTAD.

### Functions

| Functions | $E$ (eV/Å/e) | $E_g$ (eV) | $\lambda$ (nm) | $\nu$ (10\textsuperscript{12} MHz) | $\nu_{100}$ (eV) | $E_g'$ (eV) |
|-----------|--------------|-------------|----------------|------------------|---------------|-----------|
| GGA + PBE | 0.00         | 1.700       | 729.29412      | 4.11357          | 5.41          | 1.72      |
|           | 0.01         | 1.658       | 747.7684       | 4.01194          | 3.73          | 1.63      |
|           | 0.02         | 1.567       | 791.19336      | 3.79174          | 3.55          | 1.55      |
|           | 0.03         | 1.587       | 781.22243      | 3.84014          | 3.44          | 1.57      |
|           | 0.04         | 1.437       | 862.76966      | 3.47717          | 2.30          | 1.43      |
|           | 0.05         | 1.213       | 1022.09398     | 2.93515          | 2.94          | 1.20      |
|           | 0.06         | 1.073       | 1155.452       | 2.59639          | 3.11          | 1.06      |
| GGA + PBEsol | 0.00      | 1.675       | 740.1791       | 4.05307          | 3.68          | 1.68      |
|           | 0.01        | 1.254       | 988.67624      | 3.03436          | 3.04          | 1.25      |
|           | 0.02        | 1.266       | 979.3049       | 3.0634           | 3.20          | 1.24      |
|           | 0.03        | 1.200       | 1033.1667      | 2.90369          | 3.08          | 1.19      |
|           | 0.04        | 1.405       | 882.41993      | 3.39974          | 2.96          | 1.40      |
|           | 0.05        | 1.330       | 932.18045      | 3.21826          | 3.19          | 1.34      |
|           | 0.06        | 1.254       | 988.67624      | 3.03436          | 4.07          | 1.25      |

Table 2. Related data obtained using eq (1). Here, $E$ is the external electric field, $E_g$ is the band gap based on the band structure, $\lambda$ is the wavelength, $\nu$ is the frequency calculated by the band gap, $\nu_{100}$ is the frequency along the [100] direction based on the Fig. 8, and $E_g'$ is the band gap based on the optical properties.
The device for realizing the external electric field is shown in Fig. 11, which is similar to the ref. reported by Li et al.\textsuperscript{30}. It noted that the device in this study only provide the external electric field, do not provide electrons. The large DC voltage near 100 V can be obtained by DC boost circuit, which can resolve the electric field strength. The positive electrode is connected with the transparent ITO for visible light, and the negative electrode is connected with Au; the directions of the two electrodes can control the direction of the electric field, including the [111] direction. Moreover, the distance between the positive and negative electrodes, as well as the insulation thickness and dielectric constant, influenced the electric field strength.

It noted that the external electric field of about 0.06 eV/Å is large, which is equal to 0.6 V/nm, but this external electric field can be carried out in practice. For example, Hsu et al. used an external magnetic field to adjust the relative energy levels between a skyrmion and a ferromagnet globally, and obtained an electric field of 1 V/nm, which corresponds to a magnetic field of about 40 mT for their system\textsuperscript{31}. Qin et al. applied an external electric field to drive the ultra-low thermal conductivity of silicene. Using an electric field ($E_z = 5$ V/nm), the lattice thermal conductivity of silicene can be reduce a record low value of 0.091 W m$^{-1}$ K$^{-1}$, which is comparable to that of the best thermal insulation materials\textsuperscript{32}. The main problem caused by the huge electric field may be the device breakdown, which is attributed to the self-sustainable discharge for uniform electric field. The more uniform the electric field is, the higher the self-sustainable discharge voltage is. So the transparent ITO as the positive electrode and the Au film as the negative electrode should possess the rule shapes and flat surfaces, which would decrease the degree of dielectric polarization, and reduce the possibility of the tip discharge.

**Conclusion**

In conclusion, we have used first-principles calculations to calculate the geometries, band structure, electronic properties, and optical absorption properties of perovskite CH$_3$NH$_3$PbI$_3$ under an external electric field aligned along the [111] direction. The external electric field increases the lattice parameters and the cell volume, stretching the c-axis and influencing the degree of lattice distortion. The external electric field controls the band gap
from 1.70 to 1.073 eV, corresponding to external electric field strengths of 0.00 to 0.06 eV/Å/e. The rotation of the MA dipoles induced a second-order Stark effect, and the non-linear change in the second-order Stark effect causes a non-linear change in the band gap. In addition, the absorption peaks and the peak locations are affected by the external electric field. Thus, this study provides a possible method to improve the photoelectric conversion of perovskite solar cells.

Methods

CH$_3$NH$_3$PbI$_3$ perovskite undergoes two phase transitions, one at 160 K (orthorhombic to tetragonal) and the other at 330 K (tetragonal to cubic). The orthorhombic CH$_3$NH$_3$PbI$_3$ structure could be closer to that at 0 K, so we chose this as the research object given the DFT calculations are performed at 0 K. Based on the structure reported by Menéndez-Proupin et al., CH$_3$NH$_3$PbI$_3$ perovskite has an orthorhombic crystal structure in the space group $Pnma$ (no. 62), with lattice parameters of $a = 8.8273$ Å, $b = 12.6793$ Å, and $c = 8.5099$ Å.

We calculated the physical properties including the energy band, the density of states (DOS), and optical absorption in the orthorhombic perovskite CH$_3$NH$_3$PbI$_3$ exposed to different external electric fields using the Cambridge Serial Total Energy Package (CASTEP) program. The generalized gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (1996, 2008, PBE, and PBEsol) was used. These exchange-correlation functionals employed were same as those in the study of the self-regulation mechanism for charged point defects in hybrid halide perovskites reported by Walsh et al. The spin-orbit coupling (SOC) effect is reported to have little influence on the geometric structures. Ultra-soft pseudopotentials with a cutoff energy of 310 eV (based on test results) were used to describe the interactions between the valence electrons and the ionic core, and including relativistic effects for Pb and I atoms. A $3 \times 2 \times 3$ Monkhorst-Pack $k$-point scheme was used to calculate the absorption spectra. We performed the convergence test, and found the results with 500 eV cutoff energy and $5 \times 5 \times 5$ Monkhorst-Pack $k$-point scheme to be similar to those with the above parameters. The convergence tolerances for geometry optimization calculations were set to a maximum displacement of $5.0 \times 10^{-4}$Å, maximum force of 0.01 eV/Å, maximum energy change of $5.0 \times 10^{-6}$ eV/atom, maximum stress of 0.02 GPa.

Table 3. The orthorhombic structure of CH$_3$NH$_3$PbI$_3$ reported by Menéndez-Proupin et al. Space group 62 ($Pnma$). Lattice parameters: $a = 8.8273$ Å, $b = 12.6793$ Å, $c = 8.5099$ Å.
According to the refs24,35, PBEsol as exchange–correlation functional is a revision of the PBE functional, which improves equilibrium properties of densely-packed solids and their surfaces, specifically tailored for solids. It has been shown to yield structural data in accordance with experiment reported by F. Brivio et al.37. This functional predicts the structure of common London-dispersion corrected functions without the addition of an empirical potential.

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Author Contributions
Denghui Ji designed and conducted all the calculations, and wrote the paper. Mula Na prepared the figures 1, 2 and 3, Shuling Wang, and Hong Zhang prepared the Figures 4, 5, 6, 7, 8, 9, 10, 11 and 12. Kun Zhu and Congmin Zhang analysed the data. Xiuling Li prepared the Tables. All the authors commented on the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

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