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Atomistic Simulations of MAPbI Pm-3m Using First-Principles Calculations

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Abstract. The unprecedented fast increase in power conversion efficiency seen in photovoltaic devices based onhybrid halide perovskites have drawn significant research interests. Recent researches in this area have focused on finding different perovskites with better properties, especially stability.Atomistic simulations based on density functional theory were performed in order to investigate the electronic properties of MAPbIPm-3m using Projected Augmented Wave (PAW) pseudopotential withmodified Perdew-Burke-Ernzerhof (PBE) for solidsfunctional withingeneralized gradient approximation (GGA) as implemented in QUANTUM ESPRESSO simulation software. The results obtained gave 6.1248Åas the lattice parameter and 1.1019eVas the bandgapinMAPbIpm-3m perovskite, which shows the perovskite has a direct bandgap.

Keywords:MAPbI; Functional; Perovskite; Pseudopotential.

1. Introduction

Photo-electrochemical systems have been discovered to produce solar energy through sunlight,leading to an increased demand for photovoltaic cells [1]. Organic-inorganic halide perovskites (OIHP), exemplified by methylammonium lead iodide ($CH_3NH_3PbI_3$ or MAPbI), have emerged as an important class of materials used in photovoltaic cells. The current Power Conversion Efficiency (PCE) of MAPbI based solar cell is >21%, which is higher than the conventional solar cell technology output[2]-[3]. MAPbIas an organic metal halide perovskite solar cells have made significant strides [4]. Also, due to its excellent device-based performance as a light absorber, MAPbI based solar cell has created a

remarkable advance in the photovoltaic history of solar cell technology [5].For decades, optoelectronic properties of materials and cheaper methods of fabrication of optoelectronic devices have generated a great deal of interest [6]-[7].

Perdew-Burke-Ernzerhof revised for solids(PBEsol)functional withingeneralized gradient approximation (GGA) has shown an accurate tendency in results as used and reported by previous researchers in their works [8]–[11]. PBEsol functional has an overall highest performing density functional approximations in structure and elastic properties evaluation [8]. It also offers structural properties that are similar to the experimental values than the Perdew-Burke-Ernzerhof (PBE) findings[9]–[12].

Pseudopotentials are approximations of the physical potential of an atom that reproduce the correct wave function and single-particle eigenvalues outside a certain radius [13]. Functional is a function of a function [14]. Projected Augmented Wave (PAW) pseudopotential in theDensity Functional Theory (DFT) calculations decreases the number of plane waves that need to be expanded in the wave function. DFT has shown that using functional, multi-electron system properties can be determined [4].

Several efforts have been made to improve OIHP'sperformance by modifying the bandgap and other properties such as stability, toxicity, both chemically and structurally. However, there have been different variation in these results. Hence, this investigation is therefore geared towards finding out the electronic properties of MAPbI Pm-3m usingPAW pseudopotential with PBEsol functional. Computer simulation is ubiquitous in the study of properties of new materials [15], new and cheaper methods of fabrication [16], as well as in the solution of diverse problems [17].Hence, Quantum Espresso open-source simulation software was used throughout this research along with basic DFT like Exchange correlation functional, Local-density approximation of Kohn-Sham theory.

2. Computational Methods

Atomistic simulations based on DFT were performed using PAW pseudopotential and PBEsol functional within thegeneralized gradient approximation (GGA).The investigation of the electronic properties of MAPbIPm-3m were carried with QUANTUM ESPRESSO open-source simulation software.The organic

methylammonium ($CH^{3+}NH^{3+}$) cation was surrounded by PbI_6 octahedral. The crystal structure ofMAPbIPm-3m was relaxed fully with no obligation on the symmetry.The evaluation of band structure wasalso carried out on the perovskite. At absolute zero temperature, the fermi level described the top collection of electron energy levels.

For cut-off kinetic energy convergence test, a $4 \times 4 \times 4$ k-point for Brillouin zone integration was used for the calculations. The semi core states of Pb^{2+} atoms were treated as valence electrons, that is, 14 valence electrons for Pb^{2+} ($5d^{10}6s^26p^2$). The C-$2s^22p^2$, N-$2s^22p^3$, I-$5s^25p^5$, H-1s were also considered as valence electrons. Cell relaxation of MAPbI pm-3m was carried out in order to find equilibrium lattice parameter of the perovskite. The equation of state used to fit the energy-volume for lattice constant determined was Birch-Murnaghan. A denser $8 \times 8 \times 8$ k-grid was used to compute electron density of state (DOS), and 35 paths in the Brillion zone for MAPbI cubic unit cell were taken to plot electronic band structure. The density of state graph determines the range of electrons energies within MAPbI pm-3m structure. The results of the DOS obtained for the perovskite is shown in Fig. 2.

3. Results and Discussion

The result obtained in cut-off kinetic energy for the plane wave expansion of the wave function was 110Ry. It was observed that the required high energy cut-off in PAW pseudopotential makes it more accurate. The calculated lattice constant was 6.1248Å, 3.5455eVwas obtained as the fermi energy and 129.30GPa was obtained as the bulk modulus. 229.76Å³ was obtained as the volume.The lattice parameter obtained determined the physical dimension [18] of the MAPbI pm-3m lattices unit cell.

The optimized parameters were used to develop the band structure for MAPbI Pm-3m. Therefore, the band diagram obtained (Fig. 1) determines the basic understanding of fundamental photovoltaic properties of MAPbIpm-3m. Conduction Band Minimum (CBM) and Valance Band Maximum (VBM) occurred at the **R**high symmetry pointof the first Brillouin zone (BZ) as shown in Fig. 1. It was observed that MAPbIpm-3m has a direct bandgap. The bandgap obtained in PAW pseudopotential in MAPbI pm-3m is 1.1019eV, which is closer to results obtained by previous theoretical reports and experimental reports as shown below (Table 1).

Table 1: Calculated lattice constant (Å)and bandgap energy E_g(eV) ofMAPbI pm-3m compared with other theoretical and experimental results.

Lattice constant (Å)	6.1248
Reported Å	6.4380 [19], 6.4660 [20], 6.2760 [21], 6.3480 [22], 6.2057 [23].
Bandgap E_g (eV)	1.1019
Reported E_g (eV)	1.2000[19], 1.6800[20], 1.4600 [21], 1.5800 [22], 1.5100 [23].

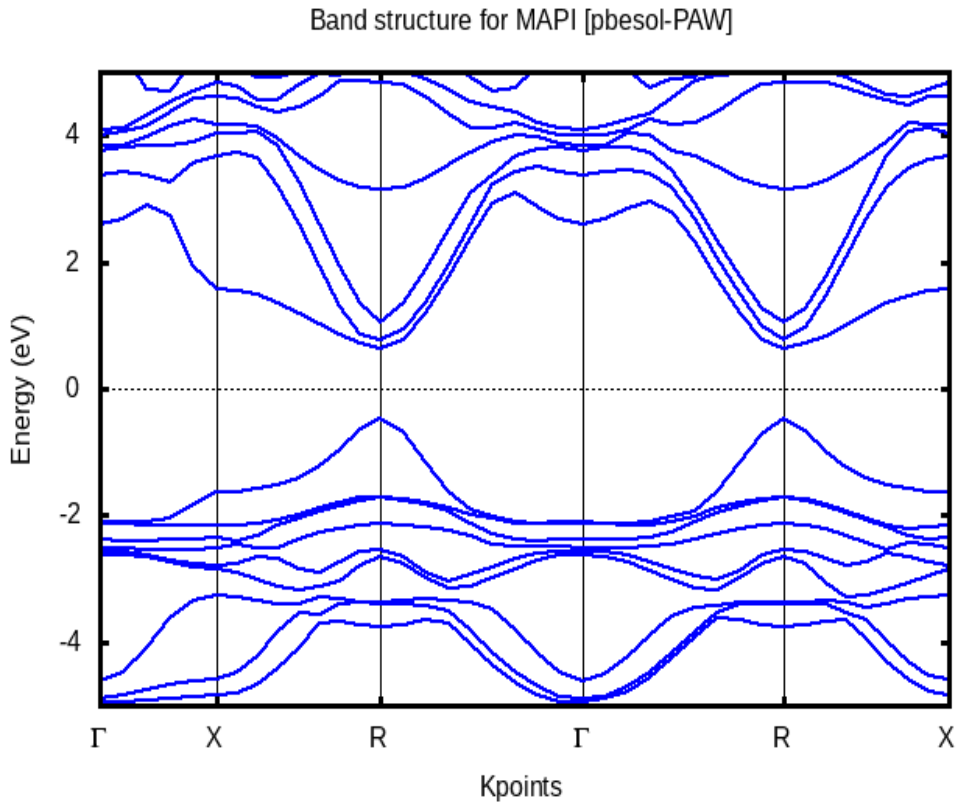

Figure 1: Band structure for MAPbIpm-3m.

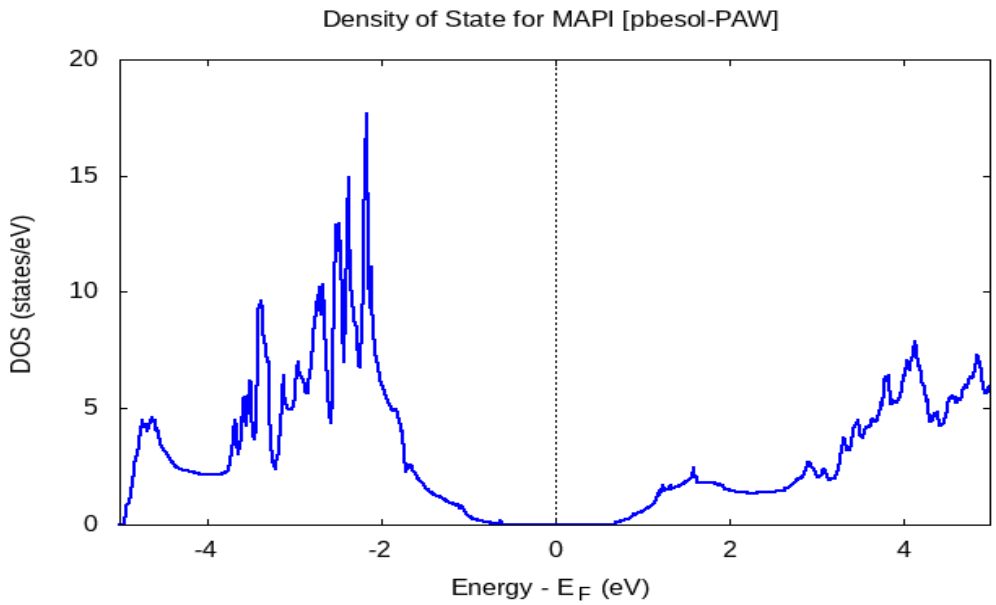

Figure 2: Density of state structure for MAPbIpm-3m.

With the DOS, the number of energy levels per unit volume was also measured for the PAW pseudopotential as shown in Fig. 3. The DOS further confirms the accuracy of the fermi-energy level which was calculated initially.

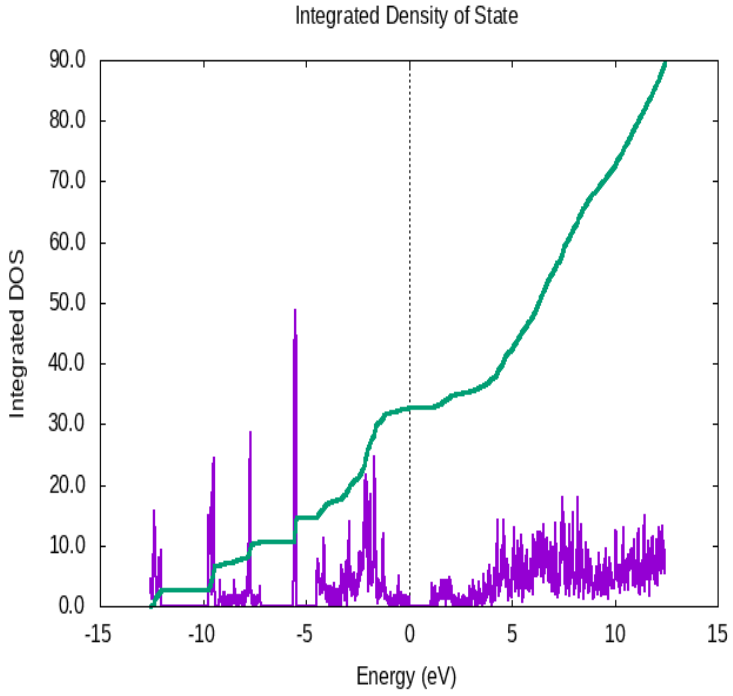

Figure 3: Integrated density of state structure for MAPbI pm-3m.

The effective massesare obtained from the curvature aroundthe Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). The obtained values for the mass of hole and electron are $0.01170m_o$ and $0.01861m_o$ respectively.

4. Conclusion and Future Work

This investigation focused onthe electronic properties of $CH_3NH_3PbI_3$Pm-3m perovskite.The calculations were done using PAW pseudopotential, PBEsol exchange-correlation (XC) functionalwith QUANTUM ESPRESSO software. The obtained results showed that MAPbI has a direct bandgap with the 1.1019eV, 6.12480Å lattice parameter and 229.76Å^3 volume which are in perfect agreement with experiment [22]-[23] and theoretical [19]–[21]reports. This study has revealed the direct gap, with the VBM and CBM at **R**-point of the Brillouin zone.Further ab-initio calculations based on DFT with Quantum Espresso will still be made to investigate the optoelectronic properties using different functionalsand compare the results accuracy with PAW pseudopotential and other experiments and theoretical reports.

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