ab Initio Study of Electronic Structure Properties of Lead Halide Perovskites for Optical Performance of Solar Cell

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Abstract

The ever increasing demand of energy has necessitated the need of coming up with measures of seeking alternative energy sources. Solar energy is one of the most important alternative sources of energy. However,the use of the first and second generations solar cells made of silicon in making solar panels has notable shortcomings such as unaffordability and lack of longevity of the electric power generated. In this regard, therefore, We report the initial electronic structure results of lead halide perovskite (APbX3) where (X = I/Br/Cl and A=CH_3NH_3/$CH(NH_2)_2^+$/Cs^+) for application in solar cells. Calculations were done using density functional theory within generalized gradient (GGA) approximations, Projector augmented wave (PAW) pseudopotentials of the functional type Perdew-Burke-Ernzerhof (PBE).The calculated lattice parameter for $CH_3NH_3PbI_3$ is foundto be 6.27Å which compares relatively well with experimental value. Our band gap is 1.74 eV and is underestimated as expected. Understanding these electronic structure properties are critical in application of this material in optoelectronics.

Key words: Perovskites, halides, electronic structure, optoelectronics.

1.0 Introduction

The general formula of lead halide perovskites is $APbX_3$ where A represents an organic positively charged ion ($CH_3NH_3^+$; $CH(NH_2)_2^+$) or an inorganic cation (Cs^+) and X represents a halide such as Iodide (I^+), Bromide (Br^-), or Chloride (Cl^-). The electronic structure is as shown in Fig 1.
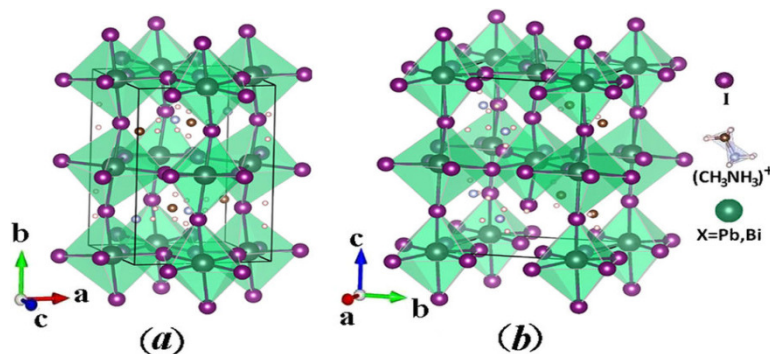
Figure 1: Electronic Structure of Lead Halide Perovskite (Zhu & Liu, 2016)

(Saliba *et al.,* 2016) stated that lead halide perovskites have become popular as photovoltaic materials due to their high power conversion efficiency (PCE). The PCE of the aforesaid perovskites is over 22%. According to (Miyata *et a.l,* 2017), lead halide perovskites shows great deal of defect tolerance due to their excellent optoelectronic properties.The lead halide perovskites are likely not to have mechanistic limitations in relation to charge carrier protection and mobility.

The growing need of electrical energy has made it imperative to devise measures of seeking alternative energy sources. One of the crucial alternative sources of electrical energy is solar energy. However, the upto this time, the use of the first and second generations solar cells made of silicon in making solar panels has various shortcomings. These include unaffordability and lack of longevity of the electric power generated by the solar energy (Manser *et al.,* 2016). The mentioned attributes imply that the solar energy so produced is relatively expensive and its sustainability cannot be guaranteed with precision. In this regard, therefore, it becomes imperative to conduct further analysis particularly in respect to third generation solar cells with the view of improving both durability and longevity. There is limited literature regarding lead halide perovskites. This necessitates an empirical study to analyze the electronic properties of lead halide perovskites in relation to optical performance of lead halide perovskite. The study seeks to examine the electronic properties with the view of finding ways of improving them in respect to optical performance. Moreover, the study intends to find ways in which the identified properties can enhance durability and efficiency of lead halide perovskite.

2.0Theory

(Phillppe *et al.,* (2015) conducted a photoelectron spectroscopy investigation on the chemical and electronic structure characterization of lead halide perovskites and also their stability behaviour under varied exposures. The study noted that there are hitherto two perovskite materials which have drawn a lot of interest in relation to solar cells. These materials are $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$. The study noted that photoelectron spectroscopy (PES) has the capacity to provide a generalized picture of the electronic structure of the perovskite and the relation of the same to mesoporous TiO_2 when studied with hard X-rays. It was further found that both $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$ exhibit very close electronic structure in spite of having very different morphologies and kinetics of formation.

A study conducted by (Pazoki *et al.,* 2017) analyzed the electronic structure of organic-inorganic lanthanide iodide perovskite solar cell materials. The electronic structure of various lanthanide-based materials investigated in the study had not been explored previously in the context of metalorganic halide perovskites. The study revealed that the localized f-electrons within the DFT+U approach make the dominant electronic contribution to the states are found atop the valence band. This results in a strong influence on the photo-physical properties of the lanthanide perovskites. This meant that the primary valence to conduction band electronic transition for $MAEuI_3$ is premised on inner shell f-electron localized states in a periodic framework of perovskite crystals. In different circumstances, the onset of optical absorption would be inert in respect to quantum confinement effects.

Similarly, Takaba, Kimura and Alam (2017) conducted a study on crystal and electronic structure of substituted halide perovskites with closer focus on density functional calculations and molecular dynamics. The study was premised on the acknowledgement that durability of organo-lead halide perovskite is paramount due to its practical application in solar cells. The study was guided by density functional theory (DFT) and molecular dynamics to investigate among others, electronic structure of partially substituted cubic $MA_{0.5}X_{0.5}PbI_3$ (MA = $CH_3NH_3^+$, X = NH_4^+ or $(NH_2)_2CH^+$ or Cs^+). The results of pertinent calculation indicated that a partial substitution on MA led to a lattice distortion. Consequently MA or X are prevented from the diffusion between A sites in the perovskite. More so, the calculations of DFT indicated that the electronic structures of the studied partially substituted perovskites were similar with that of $MAPbI_3$.

The size of the electronic band gap of a material is very critical for it to be used as solar cell absorbers since an appropriate band gap is required in the absorption of the photons located in the infrared region of the solar spectrum. The nature of the band gap assists in the estimation of the amount of light absorbed in the maximizing the efficiency of the solar cell with minimum optical losses(Mayengbam *et al.,*2018). Its therefore clear that the efficiency of a solar cell depends on the band gap of the material. It is for this reason that the electronic properties of $CH_3NH_3PbI_3$ are investigated with an aim of improving itsefficiencyfor use in solar cell.

3.0 Methodology

All calculations of relaxation, optimization and elastic constants were done within the Density Functional Theory implemented in the Quantum ESPRESSO (Giannozzi *et al*., 2009). This is done by employing for the exchange-correlation functional, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) and (PBE-sol) functional type (Perdew *et al.,* 1996) and Projector augmented wave (PAW) pseudo-potentials. Pseudopotentials were obtained from the Quantum-Espresso website(Giannozzi *et al*., 2009).The convergence test for plane-wave energy cut off and the k-point grid(7 x7 x7) was determined and the atomic position at fixed lattice constants relaxed at a temperature of 0K. (Beltracchi, 2015). The outermost s, p, and d electrons in (lead)Pb are taken to be the valence electrons whose interactions with the remaining ions is modeled by pseudopotentials generated within the projector-augmented wave (PAW) (Tao *et al.,*2017)The total energy convergence in the iterative solution of the Kohn-Sham equations was fixed at $2x10^8$Rydberge (Ry) (Nyawere *et al.,*2014).

4.0 Results and discussions

This is a very significant principle in any DFT calculation. The convergence of the cut-off energy with respect to the total energy was found at 30 Ry and is shown in Fig 1.
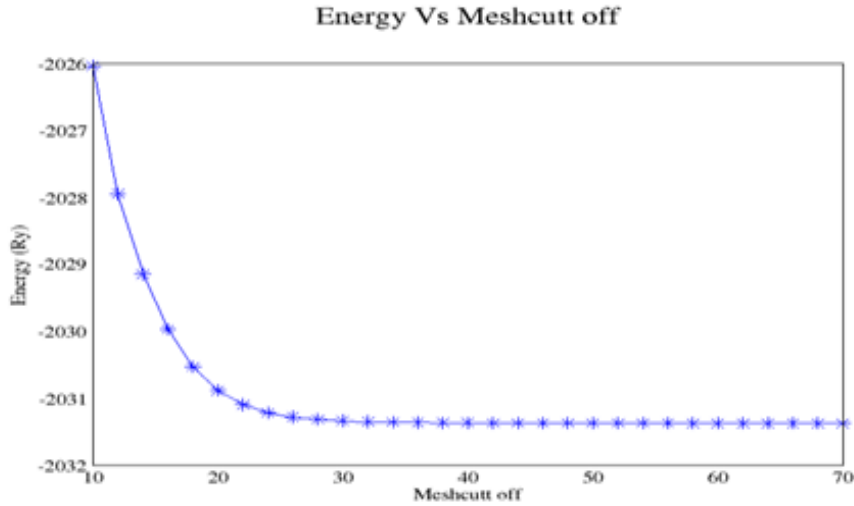
Fig 1: **convergence of Energy with the plane wave cut-off**

This shows that cut-off energy below 30Ry is inadequate. Therefore, one must select values greater than 30 Ry so as to obtain more precise results.

Convergence test for k-points was done and the results are as shown in Fig 2 below. The appropriate k-point mesh was taken at 7x7x7. Increase in the mesh consumes more computational time with no much difference.
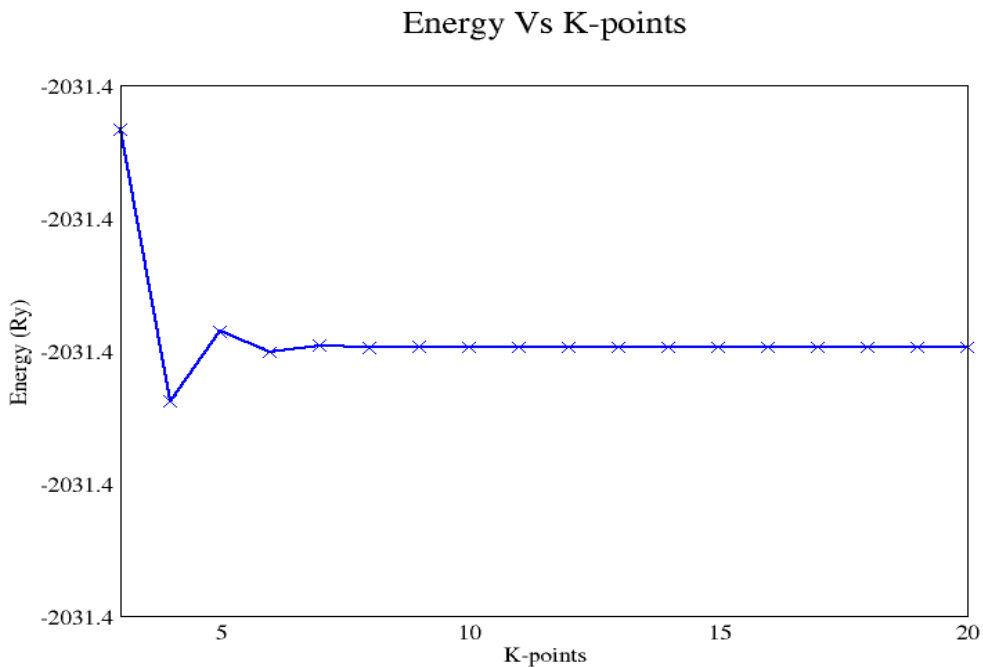
Fig 2: Convergence of total energy with k-point

The resulting total energies of the system and the volumes of the unit cell were applied to the Murnaghan equation of state (EOS) (Murnaghan, 1944), to get the equilibrium volume and bulk modulus.
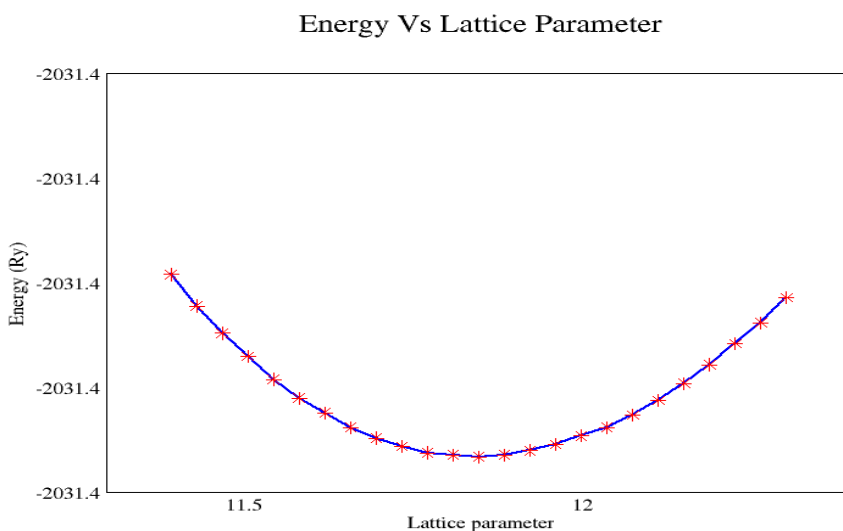

Fig 3:

Total energy Vs Lattice parameter

The lattice parameter was obtained to be 6.27Åwhich is equal to 11.85 Bohr as illustrated in Fig 3above.

Table 1: Calculated lattice parameter a (Å) of $CH_3NH_3PbI_3$ and volume $(Å)^3$ from this study compared with other work.

	a(Å)	Volume $(Å)^3$
This work	6.27	246.451
(Stoump *et al.,*2013)	6.31	251.240

	6.46	269.586
(Brivio *et al.,* 2013)		
	6.31	251.240
(Feng& Ciao, 2014)		
Ref.4 (Brivio *et al.,*2014)	6.28	247.673

Density of states calculations are shown in Fig 5. This shows that band gap of the optimized structures of $CH_3NH_3PbI_3$ is 1.74 eV without considering the spin orbit coupling (SOC). This band gap is in agreement with other theoretical values of other studies. The comparative results are shown Table 2. It is a well know fact that PBE pseudopotentials under estimates band gaps.Understanding band gap will enable us study the optical gap and other optical properties of $CH_3NH_3PbI_3$ and their photovoltaic applications.
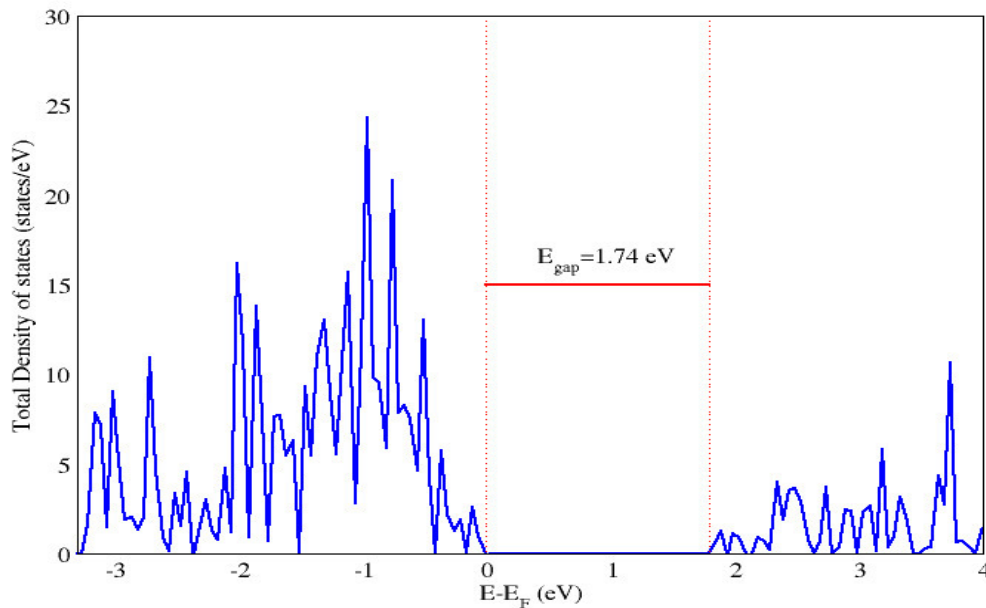

Fig 5: Total Density of States Vs Energy

Calculation of the bands was done and results presented in figure 6.It was observed that the gap was direct at the gamma point R.$CH_3NH_3PbI_3$ has a gap of 1.74eV.The top of the valence band and the bottom was dominated by Iodine orbitals.The direct gap is suitable for photo absorption since its signature for most optical materials.
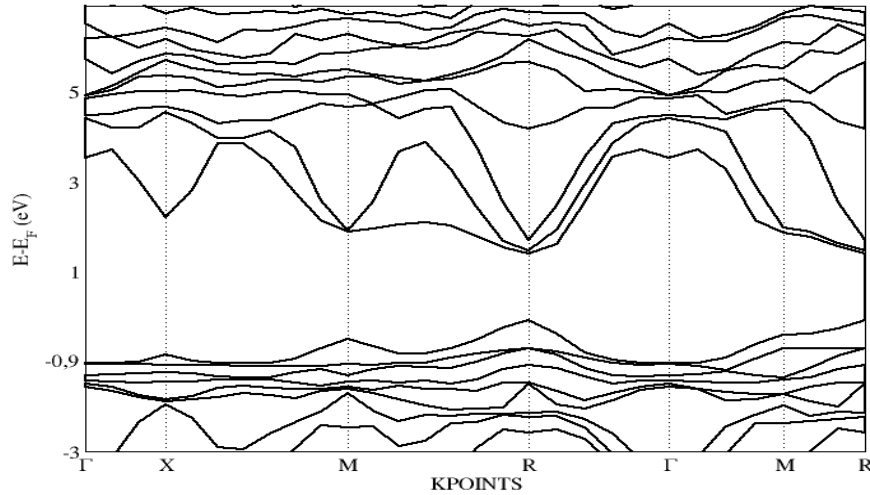
Fig 6: Band structure of **CH₃NH₃PbI₃**

Table 2: Value of Calculated without SOC Band gap of $CH_3 NH_3PbI_3$ in comparison with other studies

This work	(Brivio *et al.,*2014)	(Yamanda *et al.,*2014)	(Jishi *et al.,*2014)
QE	GW	Exp	WIEN2k code
1.74eV	2.73eV	1.61eV	1.54eV

5.0 Conclusions

The calculations on electronic structure of $CH_3NH_3PbI_3$ have been reported. The lattice parameter, density of states and band gap was determined. These parameters are in agreement with both experimental and other theoretical computations so far done on $CH_3NH_3PbI_3$.Its clear from the results obtained that $CH_3NH_3PbI_3$ has a small band gap which is requirement for any solar cell material.The the correct optimized lattice parameter was obtained which is dependent on the value of band gap energy.With these initial parameters in place, optical properties can be estimated.

Acknowledgement

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