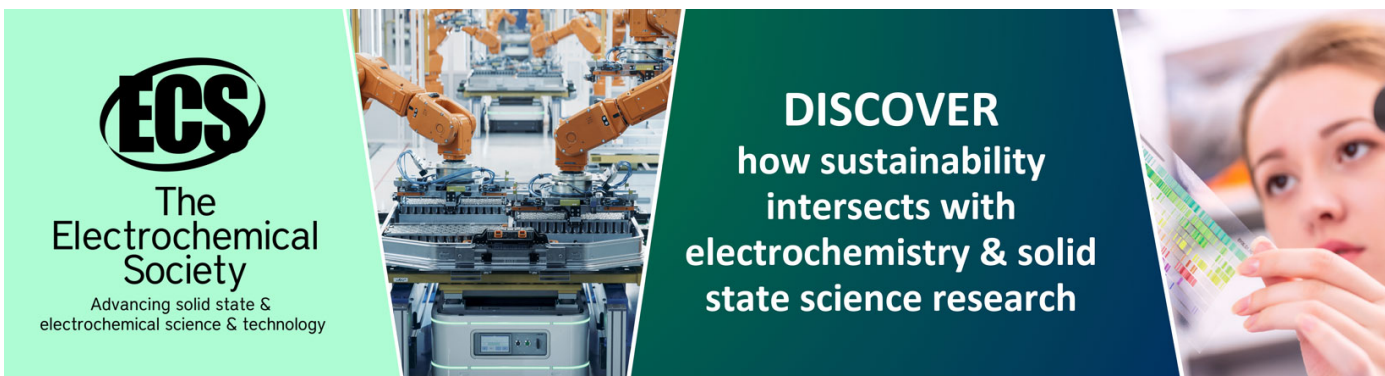**PAPER • OPEN ACCESS**

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To cite this article: Emeka Micheal *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **655** 012060

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First principles assessment of the performance of pseudopotentials on cubic phase MAPbI₃ perovskite using PBE functional

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ABSTRACT.   Perovskites have shown to be an excellent material for photovoltaics applications, due to its opto-electronic properties and low cost of fabrication. This paper is focused on assessing the performance of different pseudopotentialsinpredicting some opto-electronic properties of methyl ammonium lead iodide (MAPbI₃) cubic phase perovskite in comparison with experimental results using ab initio density functional theory (DFT) as implemented in Quantum-espresso software. The pseudopotentials used were; Projector Augmented Wave (PAW) and Ultra-soft (US). From the study, it was observed that Perdew Burke Enzerhof (PBE) functional with Ultra-softpseudo potential gave a lattice constant of 6.20 A^0 while the mixed pseudopotentials gave a band gap value of 1.64 eV, which were in closer agreement with experimental results of 6.27 A^0 and 1.60 eV respectively. These simulated results suggested that PBE-US pseudopotentials give a better lattice constant estimate, while the mixed pseudopotentials give a better estimate of the band gap of cubic phase MAPbI₃ perovskite.

1.   INTRODUCTION

Among several kinds of renewable energy sources available around the globe, solar energy is the most promising source due to its abundance and eternal nature. Therefore, it is necessary to develop efficient techniques and devices for harnessing solar energy, which can contribute to resolving the energy demand of the world [1]. Perovskite-based solar cells (PSCs) are championing this course as economic and environmentally viable options to conventional solar cells. Perovskite is the name given to a group of materials [2] with general formula ABX3, having the same structure as the mineral calcium titanate (CaTiO₃). 'A' is a monovalent cation (organic or inorganic), 'B' is a divalent cation and 'X' is an anion (halide or oxide).

One benefit of Photovoltaics based on perovskite over their counterparts is their low-cost production due to the possibility of fabricating them in a number of ways, which include vacuum techniques among others [3]. A vacuum processing and fabrication technique involving ion-beam sputtering of materials is an area of current intensive research as a cost-effective method of surface analysis, processing and fabrication of self-organized nano-structures for opto-electronic applications [4-9]. They are employed as light-harvesting layers and charge carrier mediators in solar cells [10].

Lead halide perovskites have tremendous potential for use in solution-based photovoltaics (e.g. solar cells), with higher power conversion efficiencies (PCEs) compared to silicon-based photovoltaics [11]. For such applications, however, they experience a significant setback due to the toxicity of lead and its solubility in water. Consequently, in recent years there has been an intense research interest with promising findings on less toxic metal substitutions [12-16]. The most popularly studied perovskites [17] are methyl ammonium lead halide (MAPbX₃) and formamidinium lead halide (FPbX₃). Only ten years after the initial report of a working solar cell

[18] based on methyl ammonium lead iodide $CH_3NH_3PbI_3$, these devices are routinely reaching efficiencies above 20% with the record currently at 25.2%.

Pseudopotentials are approximations of the physical potential of an atom that reproduce the correct wave function and single particle eigenvalues outside a certain radius. Normally the nucleus and inner electrons are treated as a single entity and only the valence (and semi-core) electrons are modelled [19]. They are used to reduce the numerical effort to determine the energies and wave functions, by neglecting cleverly the bound states, necessary to account for the singularity caused by the nuclei. Within the framework of density functional theory (DFT), the computational accuracy of materials properties are dependent on a number of factors, in which the choice of pseudopotential is. In that vein, it is pertinent to assess the performance of pseudopotentials in term of accuracy and exactness of computed results in comparison with experimental findings.

In the course of this research, the performance of pseudopotentials on the optoelectronic properties of methyl ammonium lead iodide perovskite was assessed. The pseudopotential type used were the projector augmented wave (PAW) and ultra-soft (US) pseudopotentials with the Perdew-Burke-Ernzerhof (PBE) as our exchange correlation functional. In the first two simulations, PAW and US pseudopotentials were separately employed for the computations. While for the third simulation, the two pseudopotentials (US-PAW) were mixed and then used for subsequent calculations.

2.   COMPUTATIONAL METHODS

Three separate simulations were performed. One each for projector augmented wave (PAW)[20], ultrasoft (US)[21] and a combined US-PAWpseudopotentialswith the Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA)[22] exchange correlation potentials as implementedin Quantum-espresso software package[23-24]. For the ground state calculations, a 12-atom primitive unit cell ofa simple cubic crystal structure (Pm-3m) for the MAPbI$_3$perovskite was considered. A rigorous convergence study of total energy for geometry optimisation was also carried out. Such convergence tests include the kinetic energy cut-off, the k-point sampling and the lattice constant. The cut-off energies for the expansion of the wave functions of the plane waves were 45 Ry, 40 Ry, and 85Ry for PAW, US, and US-PAWpseudopotentials respectively as shown in Figure 1(a-c) below. All atoms in the unit cell were completely relaxed until the forces of Hellman-Feynman are less than 0.002 eV/A^0. The 4 x 4 x 4 Monkhorst-Pack grid of k-points for Brillouin zone integration was used in all the calculations for Pm-3m structures. To calculate the energy band structure of MAPbI$_3$, seven points of high symmetry with gamma as the origin were selected. Finally, the density of state (DOS) of the optimized structure was also computed.

3.   RESULTS AND DISCUSSION
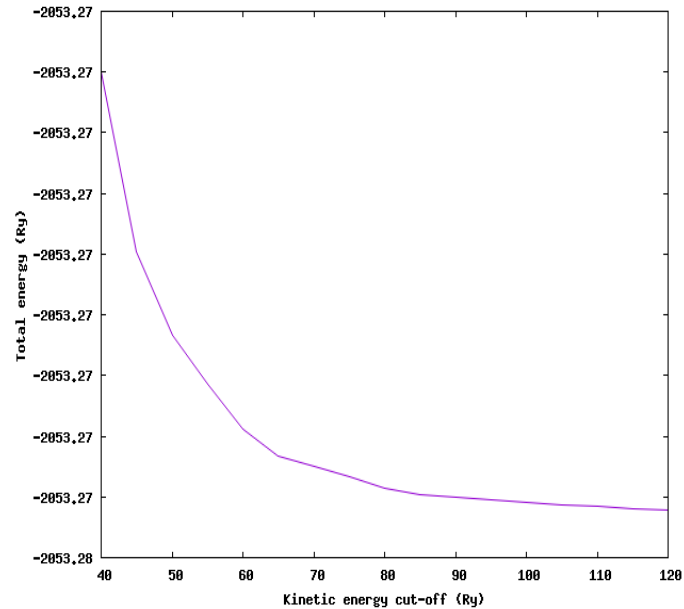
The simulated results are presented and discussed in this section.
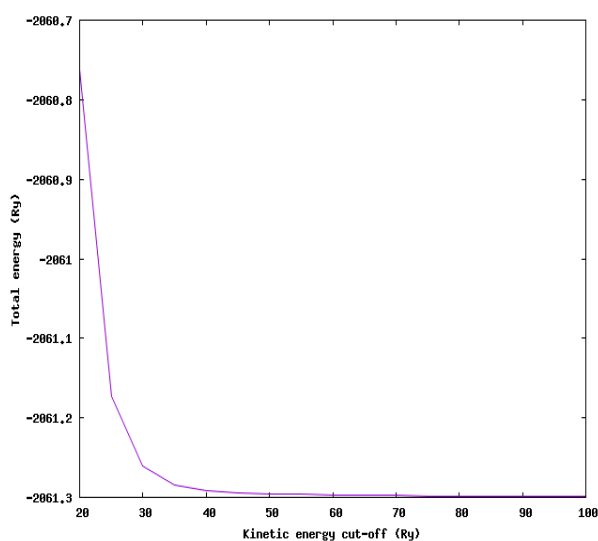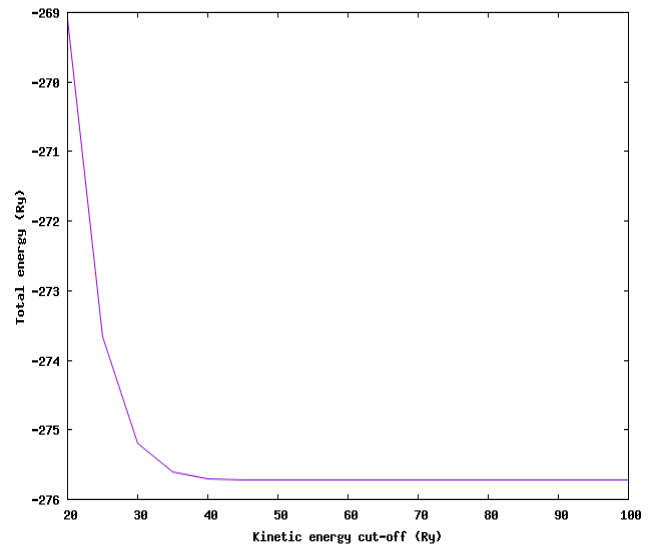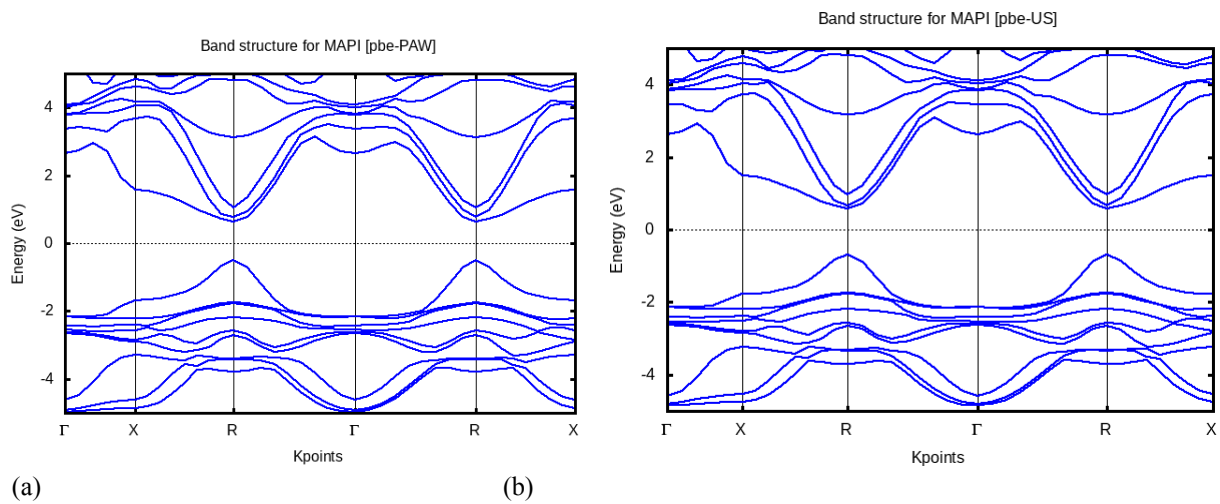

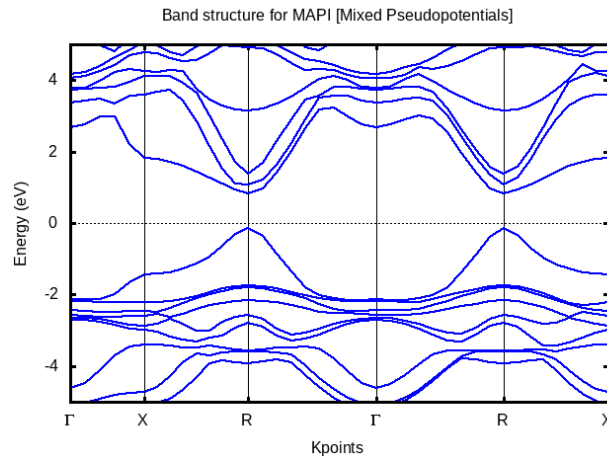(a)   (b)

(c)

Figure1: Optimized kinetic energy cut-off of MAPbI$_3$ using (a) PAW Pseudopotentials (b) US Pseudopotentials(c) US-PAWPseudopotentials.

Ultrasoftpseudopotentials are known to have large cut-off radii which allows them to converge very fast. This accounts for the kinetic energy cut-off of 40 Ry obtained for US as against the 45 Ry obtained for PAW pseudopotentials and 85 Ry obtained for the mixed pseudopotentials as shown in Figure 1(a-c) above.

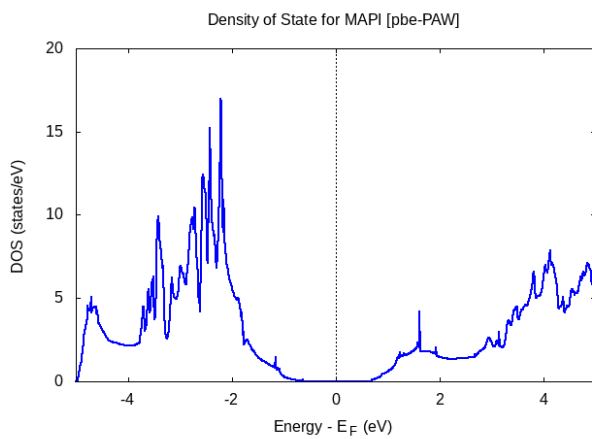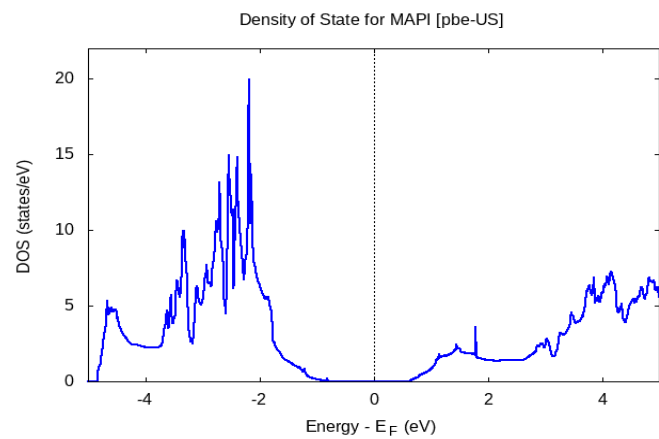(a)   (b)

(c)

Figure 2: Band structure diagram of MAPbI$_3$ using(a) PAW pseudopotentials (b) US pseudopotentials(c) US-PAW pseudopotentials.

The band structure diagrams in Figure 2 (a-c) describe the allowed and forbidden bands. The direct band gaps and Fermi levels can be viewed from the band structure diagrams of Figure 2 (a-c) above. It is important to note that for all diagrams, the Fermi level has been set at 0 eV.
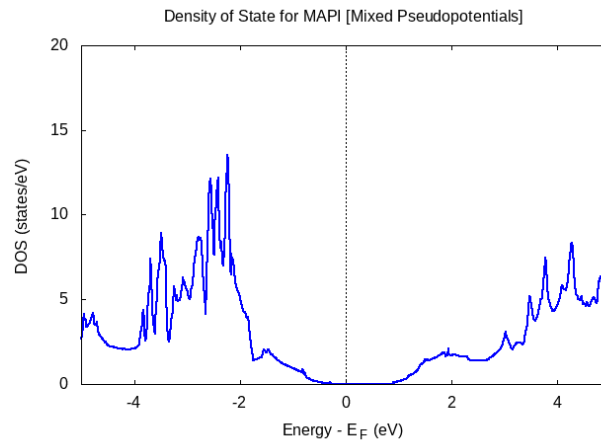
The band structure diagrams in Figure 2 (a-c) show that the conduction band minimum (CBM) and the valence band maximum (VBM) occurred at the high symmetry R point, which accounts for the direct band gaps of 1.13 eV, 1.26 eV and 1.64 eV using PAW, US and US-PAW pseudopotentials respectively. The band gap of 1.64 eV obtained in this work was also reported in [25].

(a)

(b)

(c)

Figure 3: DOS of MAPbI$_3$ using(a) PAW pseudopotentials (b) US pseudopotentials (c)US-PAWpseudopotentials.

From Figure 3 (a-c) above, the density of states describe the number of states that are to be occupied by the atoms at each energy level. It is important to note that for all diagrams the Fermi level has been set at 0 eV.In terms of orbital contribution to the conduction band and valence band, the DOS diagrams show clearly that there are more contributions of orbitals below the Fermi level (that is at the valence band).

Table 1: Summary of Simulated Results Obtained for MAPbI$_3$Perovskites

Properties	PAW	US	US-PAW	PREV. WORK
Kinetic energy cut-off (Ry)	45	40	85	-
Lattice constant (A^0)	6.12	6.20	6.12	6.27[26]
Equilibrium Volume (A^0)^3	230.15	118.56	230.15	247.10[26]
Bulk modulus (GPa)	150.10	211.90	216.60	-
Band gap (eV)	1.13	1.26	1.64	1.63[25], 1.30[26] &1.62[27]

Table 1 presents the results of the Kinetic energy cut-offs, lattice constants, equilibrium volumes, bulk moduli and band gaps computed with PBE functional and the various pseudopotentials used.
From the results, it was observed that PBE functional with US pseudopotential gave a better lattice constant that is approximately 6.20 A^0 which is closer to experimental result of 6.27 A^0 [26]. In addition, the mixed pseudopotentials (US-PAW) gave a better band gap of 1.64 eV which is closer to experimental result of (1.5-1.6 eV) [27].

4.   CONCLUSION
In this study, assessment of two pseudopotentials with PBE functional has been carried on simple cubic phase MAPbI$_3$perovskite to ascertain their performance in the investigation of some structural and opto-electronic properties.It wasobserved that PBE functional using US pseudopotential gave a better lattice constant that is approximately 6.2 A^0 which is closer to experimental result. In addition, the mixed pseudopotentials(US-PAW) gave a better band gap of 1.6 eV which is closer to experimental result. Hence, this study has revealed that US pseudopotential performed better in predicting the lattice constant of cubic phase MAPbI$_3$perovskite when compared to experimental results. On the other hand, the mixed pseudopotentials (US-PAW) performed better in predicting the band gap of cubic phase MAPbI$_3$perovskite when compared to experimental results.

5.   ACKNOWLEDEMENTS

REFERENCES

[1] Yu, C-J. (2019): Advances in modelling and simulation of halide perovskites for solar cell applications. {Journal of Physical Energy}. 1 022001.

[2] Jaffe, B., Cook Jr., W.R., and Jaffe, H. (1971): Piezoelectric Ceramics. Academic Press, London and New York.

[3] S. Hoefler, G. Trimmel, T. Rath, Progress on lead-free metal halide perovskites for photovoltaic applications: a review, Monatsh Chem. 148 (2017) 795.

[4] Emmanuel O. Yewande, Alexander K. Hartmann, and Reiner Kree (2005): Propagation of Ripples in Monte Carlo models of Sputter-induced Surface Morphology. Physical Review B 71, 195405.

[5] Emmanuel O. Yewande, Reiner Kree, and Alexander K. Hartmann (2006): Morphological Regions and Oblique-incidence Dot Formation in a Model of Surface Sputtering. Physical Review B 73, 115434.

[6] Emmanuel O. Yewande,Reiner Kree,and Alexander K. Hartmann (2007): Numerical analysis of quantum dots on off-normal incidence ion sputtered surfaces. Physical Review B 75, 155325.

[7] Oluwole E. Oyewande and AkinwumiAkinpelu (2018): An ion-beam surface sputtering approach to the quest for lead-free metal halide perovskite for solar cells. Nuclear Inst. and Methods in Physics Research B.

[8] Oluwole E. Oyewande, Israel B. Babalola and MojisolaUsikalu (2019): Effect of surface diffusion algorithm on nanostructure formation in a semi-empirical Monte Carlo model of sputter erosion of materials. Journal of Physics: Conf. Series 1299(2019) 01212.

[9]AkinwumiAkinpelu, Oluwole E. Oyewande, Onumejor C. Adaeze, Arijaje T. Emuobor, Olawole C. Ogunrionola I and Ogundile O. Paul (2019): Analytical Form of Sputtering in Relation to Surface Binding Energy for Different Types of Perovskites. Journal of Physics: Conf. Series 1299 (2019) 012022.

[10] Zhou, D., Zhou, T., Tian, Y., Zhu, X. and Tu, Y. (2018): Perovskite-Based Solar Cells: Materials, Methods, and Future Perspectives. {Journal of Nanomaterials}. 2018:15; doi:10.1155/2018/8148072.

[11] Photovoltaics, National Renewable Energy Laboratory, 2018.

[12] N. Noel, S. Stranks, A. Abate, C. Wehrenfennig, S. Guamera, A. Haghighirad, A. Sadhanala, G. Eperon, S. Pathak, M. Johnston, A. Pertozza, L. Herz, H. Snaith, Energy Environ. Sci. 7 (2014) 3061.

[13] T. Krishnamoorthy, H. Ding, C. Yan, W. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M.N. Asta, S. Mhaisalkar, J. Mater. Chem. A3 (2015) 23829.

[14] X. Cui, K. Jiang, J. Huang, Q. Zhang, M. Su, L. Yang, Y.-L. Song, X.-Q. Zhou, Synth 209 (2015) 247.

[15] B. Park, B. Philippe, X. Zhang, H. Rensmo, G. Boschloo, E. Johansson, Adv. Mater 27 (2015) 6806.

[16] P. Harikesh, H. Mulmudi, B. Ghosh, T. Goh, Y. Teng, K. Thirumal, M. Lockrey, K. Weber, T. Koh, S. Li, S. Mhaisalkar, N. Mathews, Chem. Mater 28 (2016) 7496.

[17] Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009): {Journal of American Chemical Society}. 131: 6050-6051.

[18] A Decade of PerovskitePhotovoltaics (2019). {Journal of Nature Energy}. 4(1).

[19] Philip Beltracchi. (2015).A First-Principles Study of Hybrid Organic-Inorganic Perovskites for Photovoltaic Applications. Theses and Dissertations.

[20] P. E. Blöchl, "Projector augmented-wave method," *Phys. Rev. B*, vol. 50, no. 24, pp. 17953–17979, Dec. 1994, doi: 10.1103/PhysRevB.50.17953.

[21] D. Vanderbilt, "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism," *Phys. Rev. B*, vol. 41, no. 11, pp. 7892–7895, Apr. 1990, doi: 10.1103/PhysRevB.41.7892.

[22] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, 1996, doi: 10.1103/PhysRevLett.77.3865.

[23] P. Giannozzi *et al.*, "QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials," *J. Phys. Condens. Matter*, vol. 21, no. 39, 2009, doi: 10.1088/0953-8984/21/39/395502.

[24] P. Giannozzi *et al.*, "Advanced capabilities for materials modelling with Quantum ESPRESSO," *J. Phys. Condens. Matter*, vol. 29, no. 46, p. 465901, Nov. 2017, doi: 10.1088/1361-648X/aa8f79.

[25] O. O. Johnson, P. E. Olutuase and O. E. Oyewande (2019): First principles calculations of the optoelectronic properties of magnesium substitutes in Lead based ABX_3 compounds. Journal of Physics: Conf. Series 1299 (2019) 012129.

[26] Baikie, T., Yanan F., Jeannette M.K., Martin S., Fengxia W., Subodh G.M., Michael G., and Tim J.W. (2013): Synthesis and Crystal Chemistry of the Hybrid Perovskite $CH_3NH_3PbI_3$ For Solid-State Sensitised Solar Cell Applications. {Journal of Material Chemistry}. 1: 5628-5641.

[27] Leguy, A.M.A., Azarhoosh, P., Alonso, M.I., Campoy-Quiles, M., Weber, O.J., Jizhong Y., Bryant, D., Weller, M.T., Nelson, J., Walsh, A., Schilfgaarde, M.V., and Barnes, P.R.F. (2016): Experimental and Theoretical Optical Properties of Methyl ammonium Lead Halide Perovskites. {Journal of Royal Society of Chemistry}. 8: 6317-6327.