The structural, electronic, and optical properties of $CH_3NH_3PbI_3$

Aya S A Sidahmed[1,2] and Daniel P Joubert[1]

[1] The National Institute for Theoretical Physics, School of Physics and Mandelstam Institute for Theoretical Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa.

[2] Department of Physics, Sudan University, Khartoum, Sudan.

E-mail: ayasedig@gmail.com

Abstract.

Organic-inorganic halide perovskites are promising candidates for low cost, high-efficiency solar cells. We examined the structural, electronic, and optical properties of the low temperature tetragonal phase of the halide perovskites $CH_3NH_3PbI_3$ using Density Functional Theory (DFT). Our numerically predicted structure is in agreement with existing experimental data. DFT electronic structure calculations show that relativistic effects are important for the heavy lead atom and spin-orbit coupling has to be included for accurate results. The experimental band gap of 1.63 to 1.66 eV is similar in magnitude to the DFT direct gap of 1.72 eV, which suggests that many-body and relativistic effects cancel in this compound. Our calculated fundamental gap, at the G_0W_0 level of approximation, is 2.48 eV. Optical anisotropy of tetragonal $CH_3NH_3PbI_3$ was investigated by including many-body effects at the time dependent Hartree Fock and the Bethe-Salpeter equation level of approximation, with input data from a range separated Heyd-Scuseria-Ernzerhof DFT functional calculation. The optical edge for radiation polarized parallel to the *a*- and *b*-axes differ by about 0.15 eV and for polarization parallel to the *b*- and *c*-axes the difference is about 0.05 eV.

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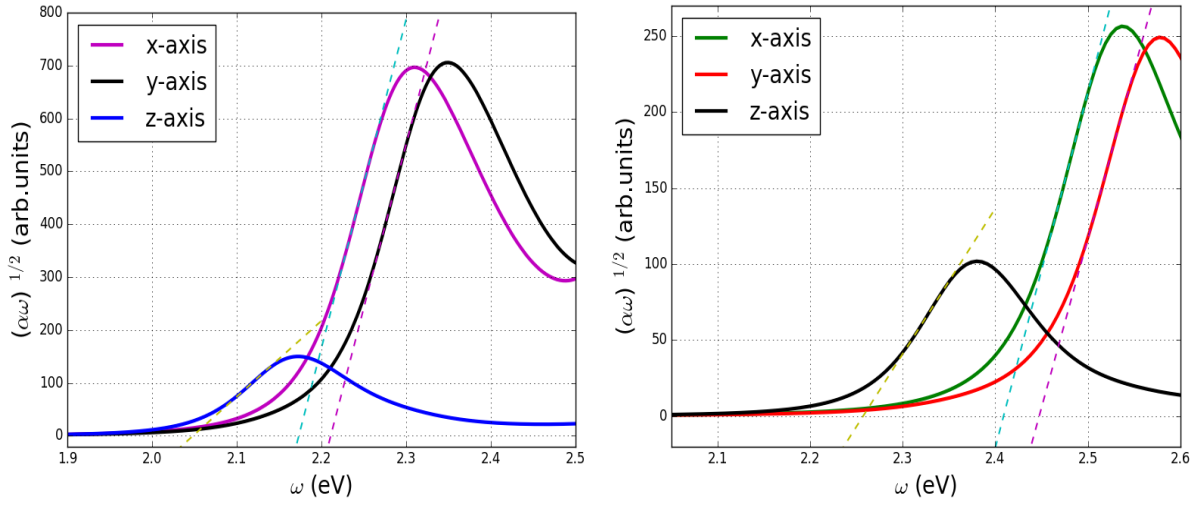
1. Introduction

Since the high power conversion efficiency of 16% to 21% [1, 2, 3, 4] was reported for mixed perovskites based solar cell (PSCs) from 2012 to 2015, metal halide perovskites have attracted the interest of researchers in the materials science community due to their excellent photovoltaic properties [5]. A prototypical example is $CH_3NH_3PbI_3$, which is readily available and inexpensive, easy to manufacture, has a very high diffusion length and high absorption coefficient, making it a promising material for commercialization. At low temperatures $CH_3NH_3PbI_3$ crystallises in an orthorhombic structure [6]. It undergoes a phase transition at 330.4 K to the room temperature tetragonal phase and above 330.4 K it has a cubic structure [7]. The objective of this work was to investigate the structural,electronic and optical properties of the room temperature tetragonal phase of $CH_3NH_3PbI_3$ using density functional theory (DFT) and post-DFT many-body perturbation theory.



(a) (b)

Figure 3. Optical band gaps obtained by Tauc plots for (a) HSE-GW-BSE and (b) hybrid TD-HSE calculations for $CH_3NH_3PbI_3$.

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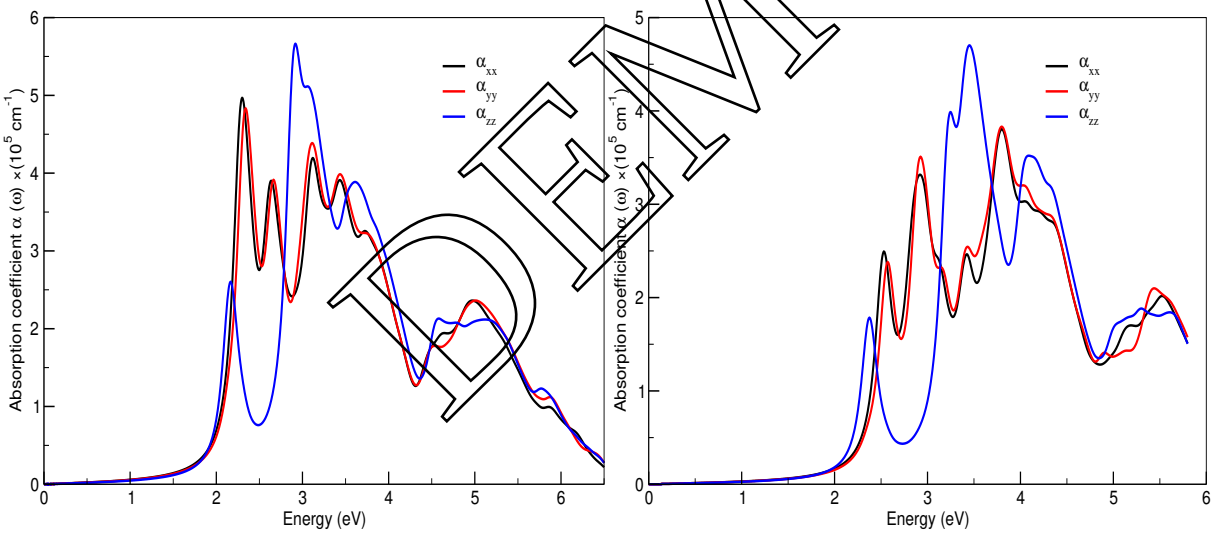

(a) (b)

Figure 4. (a) The absorption coefficient obtained by HSE-GW-BSE and (b) hybrid TD-HSE.

3.4. Conclusion

In summary, structural, electronic and optical properties of the organic-inorganic halide perovskites were investigated using Density Functional Theory. The PBE predicted structural lattice parameters and volume are in good agreement with experimental values. Electronic properties were studied by calculating the band structure, with and without SOC. The results show that tetragonal $CH_3NH_3PbI_3$ is a direct band gap semiconductor with at gap at Γ. Relativistic effects are important due the the presence of heavy Pb atoms. Optical properties

show anisotropy with peak absorption strength for polarization parallel to the *c*-axis.

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