DFT study of electronic structure and absorption mechanism in 2D perovskite $(BA)_2PbI_4$

Jie-Ling Liou[1,2], Yang-Hao Chan[2], Hsu-Cheng Hsu[1]

1 Department of Photonics, National Cheng Kung University, 701 Tainan, Taiwan

2 Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

Abstract

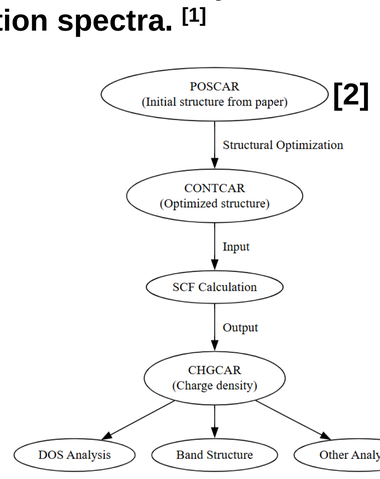
We investigate the electronic structure and optical properties of the two-dimensional perovskite $(C_4H_9NH_3)_2PbI_4$ (abbreviated as $(BA)_2PbI_4$) using density functional theory (DFT). Due to its strong UV–visible absorption, tunable band gap, and pronounced electron–phonon coupling, $(BA)_2PbI_4$ was selected as the simulation target. Compared with $(PEA)_2PbI_4$ containing 196 atoms, $(BA)_2PbI_4$ has only 156 atoms; since in DFT the computational cost roughly scales as N^3 with the number of atoms, larger systems quickly become very expensive, making $(BA)_2PbI_4$ more feasible. Calculations were performed with the GGA-PBE functional, a plane-wave cutoff of 500 eV, and an 8×8×3 k-point mesh, with structural relaxation converged to 10^{-9} eV. Element- and orbital-resolved analyses reveal that the Pb–I framework dominates states near the Fermi level, while absorption originates from I-5p to Pb-6p charge-transfer transitions. Spin–orbit coupling reduces the band gap, and the closer agreement without SOC is due to error cancellation rather than true physics. This work clarifies the band gap origin and absorption mechanism of $(BA)_2PbI_4$, providing theoretical insights into its optoelectronic performance.

Motivation

- **2D Ruddlesden–Popper perovskites exhibit strong UV–visible absorption, high EQE, tunable band gaps, and robust stability, with pronounced electron–phonon coupling—ideal for optoelectronics. To understand and engineer their response, I focus on the feasible n=1 system $(BA)_2PbI_4$: its smaller cell lowers DFT cost, enabling first-principles clarification of band-gap origin and absorption pathways.**

Methodology

- **DFT calculations were performed using VASP with the GGA-PBE functional. A plane-wave cutoff energy of 500 eV and an 8 × 8 × 3 k-point mesh were employed. Structural relaxation was carried out until the energy converged to 10^{-9} eV, followed by calculations of the electronic structure and optical absorption spectra. [1]**



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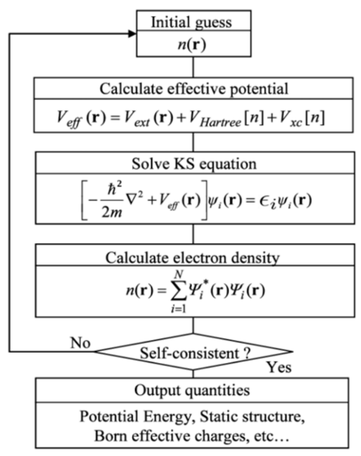
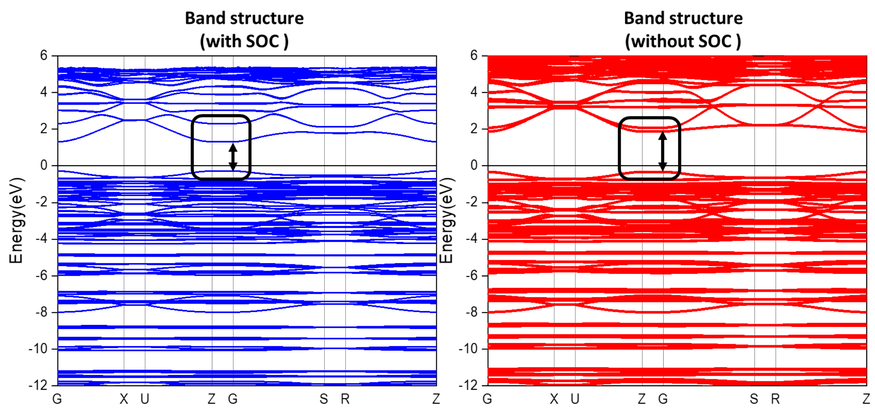


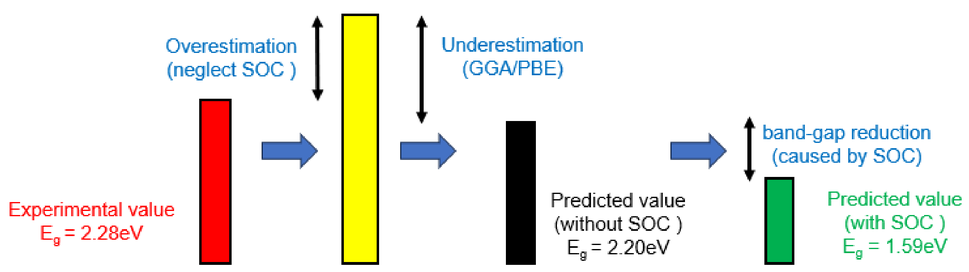
[3]

Effect of spin–orbit coupling on band structure

- **In $(BA)_2PbI_4$, the heavy elements Pb & I require consideration of spin–orbit coupling (SOC), which induces conduction band splitting and reduces the band gap (2.2012 → 1.593 eV).**

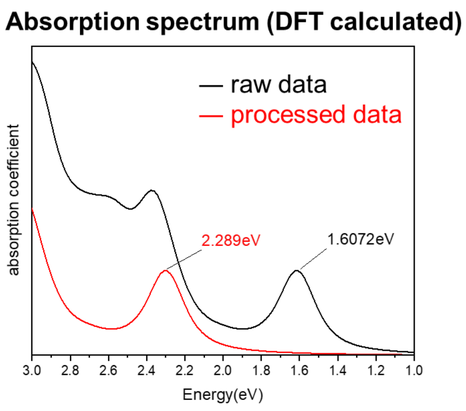


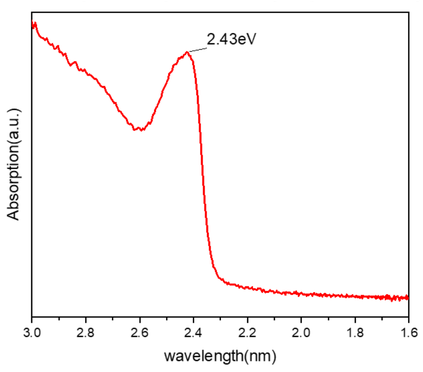
- **The ~2.28 eV experimental band gap of BA_2PbI_4[4] is seemingly matched without SOC due to error cancellation between GGA underestimation and SOC reduction, rather than true physics.**



Element-resolved band contributions

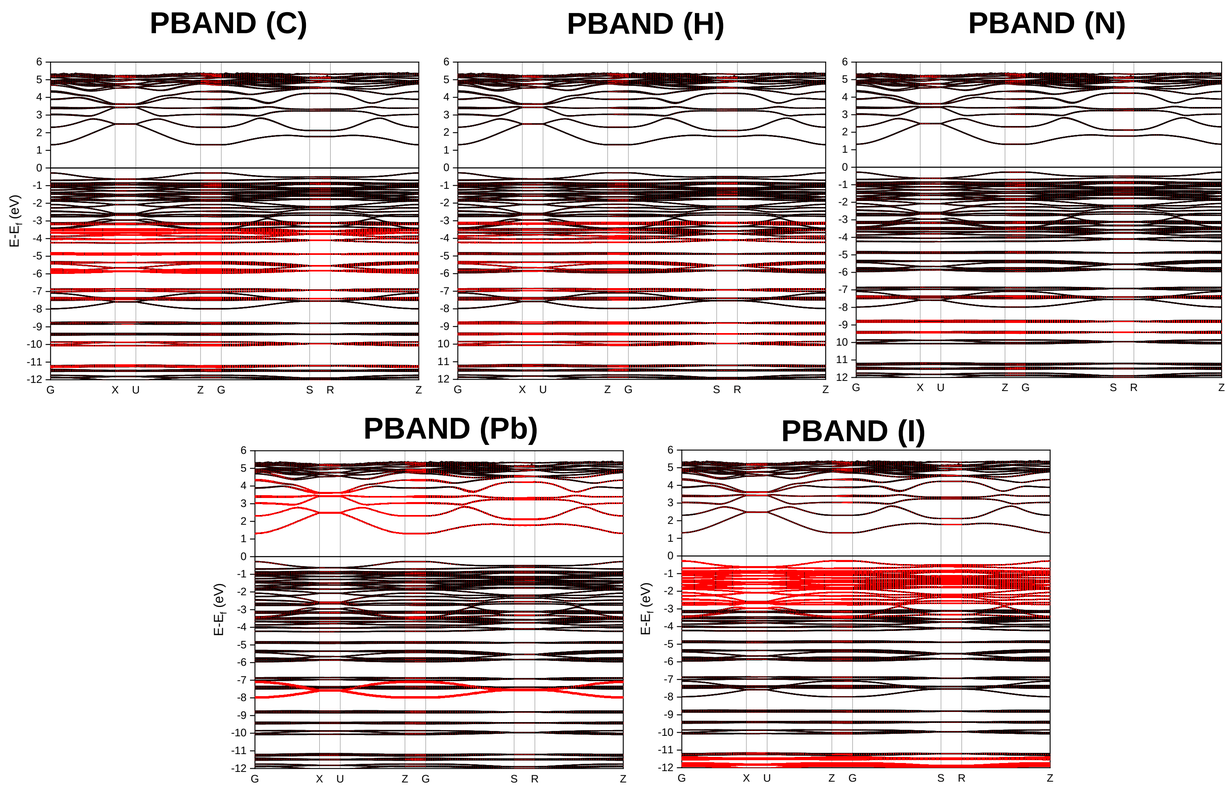
- **Without performing GW/BSE, the predicted values are aligned with the experimental ones by applying a scissor shift [5] (0.687eV).**





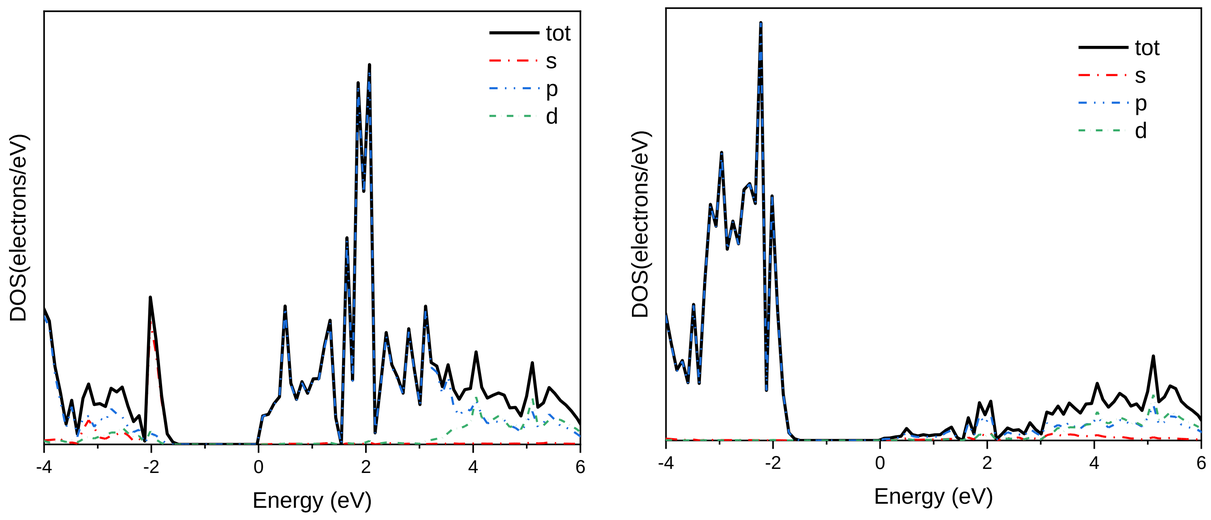
Element-resolved band contributions

- **Organic layer (C, N, H) forms deep states, serving structural and modulation roles rather than affecting electronic states near the Fermi level.**
- **Inorganic layer (Pb, I) contributes significantly to the bands near the Fermi level, indicating that the key electronic and optical properties are mainly determined by the Pb–I framework.**



Orbital-resolved absorption pathway

- **The host absorption of $(BA)_2PbI_4$ can be primarily attributed to charge-transfer transitions from the I-5p states in the valence band to the Pb-6p states in the conduction band.**



Future work

- **Future simulations will include phonon effects to explore the mechanism of phonon-assisted absorption.**
- **An experimental realization of BA_2PbI_4 will be attempted, with the aim of comparing the results to theoretical predictions.**

Summary

- **SOC reduces the band gap of $(BA)_2PbI_4$, and a scissor shift correction is needed to match experiments.**
- **DFT calculations reveal that the band gap arises mainly from charge-transfer transitions between the I-5p states in the valence band and the Pb-6p states in the conduction band.**

Reference

[1] Wang, V., et al. (2021). *Computer Physics Communications*, 267, 108033.
[2] Menahem, M., et al. (2021). *ACS Nano*, 15(6), 10153–10162.
[3] Rashid, M. A. (2024). An Introduction to Density Functional Theory (p. 13).
[4] Yuan, Y., et al. (2019). *Advanced Science*, 6(15), 1900240.
[5] Wang, C. Y., et al. (2019), *Journal of Physics: Condensed Matter*, 31(21), 214002.