

Theory and Simulation of Lateral Heterostructures of 2D Materials

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2023 GQL IRTE Program Location: National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan

Primary Sources of Research Funding: 2023 Global Quantum Leap International Research Training Experience (GQL IRTE) Program

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Abstract:

The electronic structure of two types of lateral heterostructures — composed of MoSe₂ and WSe₂, and NbSe₂ and ReSe₂ — were analyzed, and band structure calculations were conducted on two types of heterostructure patterns for both compositions. Changing the MoSe₂ and WSe₂ heterostructures had minimal impact on the band gap. On the other hand, there was a noticeable decrease in the band gap when switching between the NbSe₂ and ReSe₂ heterostructures.

Summary of Research:

Two-dimensional (2D) materials are a class of compounds that have risen in popularity over the past half-century thanks to their extensive list of fascinating phenomena and wide range of tunable properties that make them excellent candidates for many applications: from biosensing to quantum computing. This work computationally explores the use of lateral heterostructures to engineer tunable properties in the band structure of these materials.

Methodology:

A vital step in creating heterostructures is determining what combinations of materials to use in each material system. There are many types of 2D materials with varying geometries and primitive unit cell sizes, so picking compounds in the same space group (geometry) that are close together in lattice constant and cell height prevents strain or defects (especially in experimental applications). This study focuses on two types of lateral heterostructure groups based on transition metal dichalcogenides (TMDs): the first composed of molybdenum diselenide and tungsten diselenide (MoSe₂ and WSe₂) and the second of niobium diselenide and rhenium diselenide (NbSe₂ and ReSe₂).

Each heterostructure is denoted as ABSe₄, where A and B refer to the different transition metals used. Two types of heterostructure

layouts were used: 1-1 (alternating rows of ASe₂ and BSe₂) and 1-1-2-2 (one row ASe₂, one row BSe₂, two rows ASe₂, and two rows BSe₂). Thus, all lateral heterostructures were designed to keep the same chemical ratio (one-to-one for each TMD) while changing their structure. By adhering to this format, this work aims to test how increasing the in-plane symmetry breaking affects the bands. Specifically, would an increase in symmetry breaking lead to more prominent relativistic effects?

To probe such questions, Density Function Theory (DFT) is used to calculate the band structure of the 1-1 and 1-1-2-2 layouts for the MoWSe₄ and NbReSe₄ heterostructures using the Quantum Espresso software, from which energies and band structures were obtained. All scalar calculations used the PBE functional, and all relativistic calculations used the LDA functional. Each computation had an energy cutoff of 50 Ry and cold smearing of 0.005 Ry. The SCF calculations had a different k-mesh for each heterostructure: 8X8X1 for the 1-1 structure and 6X6X1 for the 1-1-2-2 structure.

Each figure has the k-path and unit cell geometry displayed to the left of the band structure. The fermi energy of the relativistic calculations was set to zero with respect to the scalar fermi energy.

Conclusions and Future Steps:

Figure 1 details the 1-1 MoWSe₄ band structure. Since the fermi level is above the valence band and the band gaps of the scalar and relativistic calculations are below 2 eV (1.4697 eV and 1.3673 eV, respectively), the structure is a semiconductor.

Figure 2 describes the 1-1-2-2 MoWSe₄ band structure. Akin to the 1-1 structure, the fermi level is above the valence band and has scalar and relativistic band gaps below 2 eV (1.4778 eV and 1.3934 eV, respectively). However, compared to the 1-1 MoWSe₄ structure, the band gap of 1-1-2-2 MoWSe₄ is slightly larger across both calculations. Additionally, the trough of the

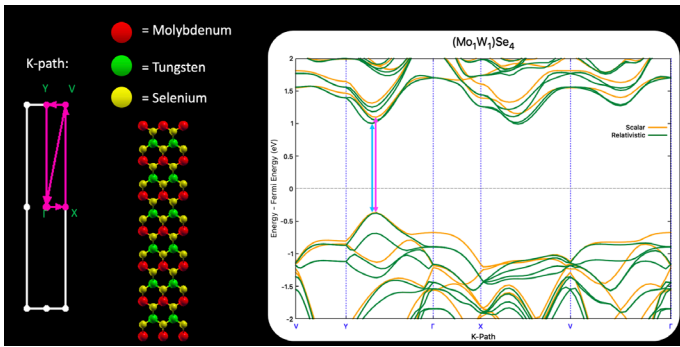


Figure 1: Band structure of 1-1 MoWSe_4 with unit cell and k -path.

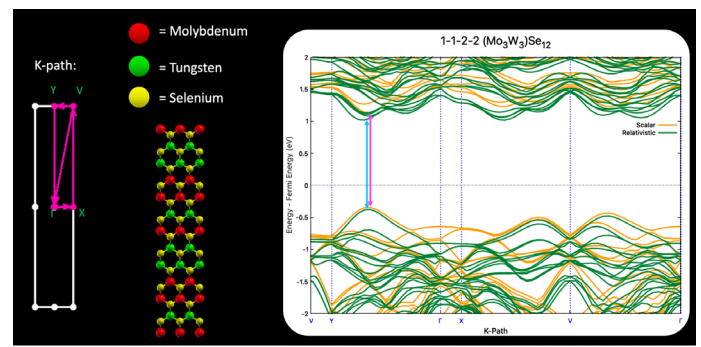


Figure 2: Band structure of 1-1-2-2 MoWSe_4 with unit cell and k -path.

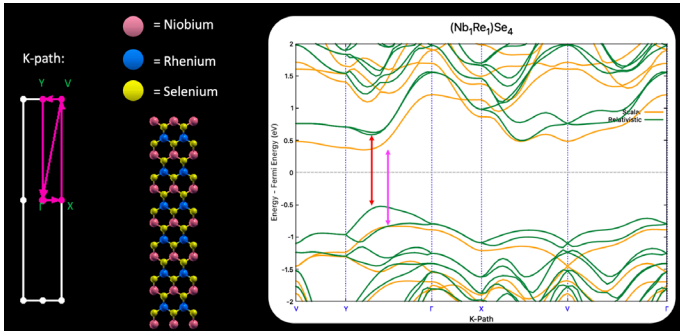


Figure 3: Band structure of 1-1 NbReSe_4 with unit cell and k -path.

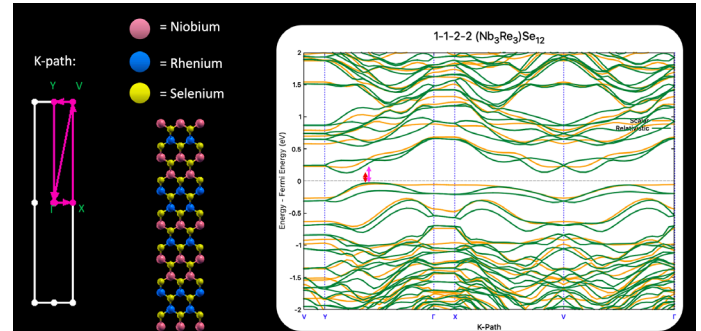


Figure 4: Band structure of 1-1-2-2 NbReSe_4 with unit cell and k -path.

conduction band has started shifting away from the peak of the valence band, so the band structure is morphing into an indirect band gap.

Figure 3 highlights the 1-1 NbReSe_4 band structure. Since the fermi level is above the valence band and the band gaps are less than 2 eV (1.1869 eV and 1.093 eV for the scalar and relativistic band gaps, respectively), the system is a semiconductor.

Figure 4 shows the 1-1-2-2 NbReSe_4 band structure, which is quite different from the 1-1 NbReSe_4 structure. For instance, while the fermi level of the system is above the valence bands, the band gaps themselves are more than half their values in the 1-1 system (0.4165 eV and 0.3705 eV for the scalar and relativistic band gaps respectively). As such, this system is closer to a semimetal than a semiconductor, as the original metallic properties of the heavy core atoms are gradually enveloping the system.

Overall, an interesting trend occurs between the 1-1 and 1-1-2-2 heterostructures. Larger heterostructures have a shift in the conduction band for relativistic calculations that widens the distance between the valence band maximum and conduction band minimum in k -space, thus creating a more indirect band gap. Considering that this effect does not occur with the scalar calculations, it seems plausible that there are increased relativistic effects in the system as heterostructure size grows.

In the future, more material compositions can be tested with varying chemical ratios to optimize for properties such as optical responsivity or electron mobility.

Acknowledgements:

I want to thank NIMS for hosting me and other REUs this summer; my mentor, Dr. Toshikase Kariyado, for his expert guidance and keen insight; and Dr. Lynn Rathbun and Professor Steven Koester for being excellent coordinators and allowing me to participate in this wonderful research experience.

References:

- [1] A. Jain, S.P. Ong, G. Hautier, W. Chen, W. Davidson Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson; Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater* 1 July 2013; 1 (1): 011002. <https://doi.org/10.1063/1.4812323>.
- [2] Ichinose, N., Maruyama, M., Hotta, H., Liu, Z., Canton-Vitoria, R., Okada, S., Zeng, F., Zhang, F., Taniguchi, T., Watanabe, K., and Kitaura, R. (2022). Two-dimensional atomic-scale ultrathin lateral heterostructures. <https://arxiv.org/abs/2208.12696>.