Density Functional Theory (DFT) Investigation of Novel Materials for Applications in Sensing

Master's Thesis Computational Science and Engineering

Carried out at the Institute for Microelectronics TU Vienna
Supervised by Prof. Dr. L. Filipovic and Dipl. Ing. D. Waldhör

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Introduction

In my thesis, I applied Density Functional Theory (DFT) using Quantum ESPRESSO (QE)[2] and CP2K [4] to investigate the potential of two materials for sensing applications. One was a Metal-Organic Framework (MOF) which is a highly ordered crystalline coordination polymer with designable porosity and large surface areas, the other is the two-dimensional (2D) molybdenum disulfide (MoS_2).

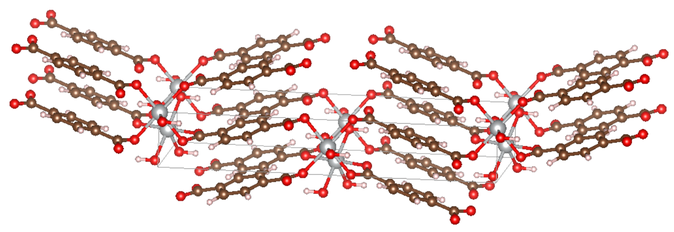

Figure: One of the investigated MOFs

Method & Implementation for MOF

Nickel-terephthalate MOFs (four isostructural variants) were studied with CP2K to predict stability and properties, but convergence was difficult, requiring long runtimes. The PBE functional underestimated the band gap, falsely implying conductivity instead of the expected insulating behavior. Switching to the PBE0 hybrid functional [1] resolved the band-gap issue, and duplicating the simulated cell into equally sized supercells improved convergence.

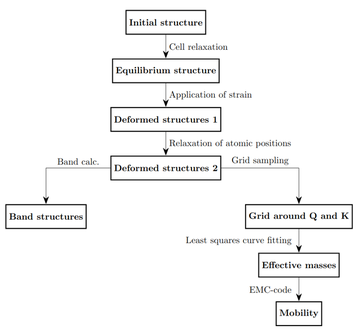

Figure: Workflow

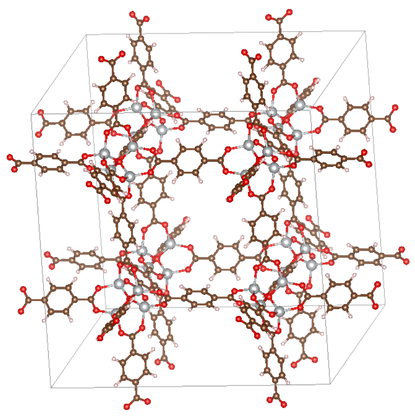

Figure: An alternative structure for the MOF

Method & Implementation for MoS_2

For the other material the aim was to investigate the response of MoS_2 monolayers to strain using Quantum ESPRESSO (QE). Because the choice of exchange-correlation functional, the used pseudopotentials, and the inclusion of spin-orbit coupling (SOC) influence the results of ab initio calculations, different combinations were investigated. This was the general workflow :

- **Structure Relaxation:** A cell relaxation was performed using a hexagonal unit cell with three atoms (a = 3.16 Å, c = 37.9204 Å), ensuring sufficient vacuum to treat the monolayer as 2D.
- **Strain Application:** Biaxial strain was applied by scaling the cell parameters with a strain factor.
- **Secondary Relaxation:** Only atomic positions were relaxed, keeping the cell parameters fixed.
- **Band Structure and Effective Mass Determination:** The strained structures were used to determine the band structure and calculate effective masses.
- **Mobility Calculation with the EMC Code:** Effective masses, non-parabolicity factors, and the K–Q valley energy difference were fed into the Ensemble Monte Carlo code [3] to determine carrier mobility.

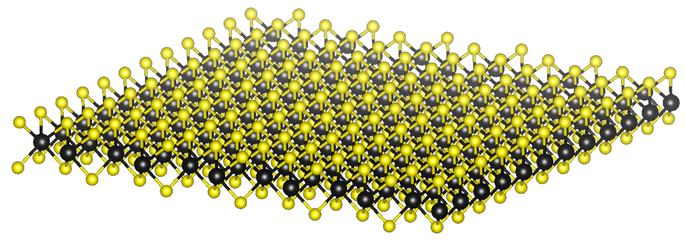

Figure: A molybdenum disulfide monolayer

Results and Discussion

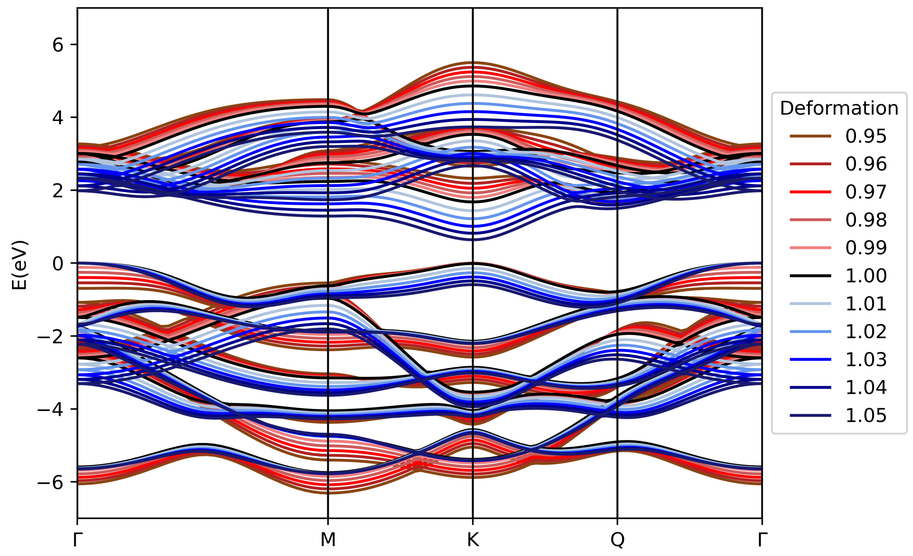

Figure: Influence of strain in the range ± 5 % on the band structure of the monolayer MoS_2 calculated with the PBE functional

Strain modifies the MoS_2 electronic structure, influencing the scattering mechanisms that limit carrier mobility. The second figure shows the resulting mobility under strain. In the Ensemble Monte Carlo simulations, electrons start with a certain energy distribution. To scatter between valleys, they must overcome the valley energy difference: small or negative differences lead to frequent scattering and reduced mobility, while larger differences reduce scattering and improve mobility. Eventually, when the valley separation is high, mobility is mainly limited by intra-valley or same-type valley scattering, which requires less energy.

Conclusions

Because the chosen ab initio approach was costly and prone to convergence issues, only structure optimizations of the MOFs were performed, not a full study of their surface properties and interactions. Strain effects on monolayer MoS_2 mobility were investigated via ab initio electronic-structure calculations; these parameters were then used in Ensemble Monte Carlo simulations of the Boltzmann Transport Equation. Results indicate tensile strain boosts mobility, while compressive strain lowers it. Experimentally, monolayer MoS_2 reaches about 200 $cm^2/(Vs)$ [5], much lower than predictions, likely because the model accounts only for Q- and K-valley scattering from optical and acoustic phonons, excluding other mechanisms.

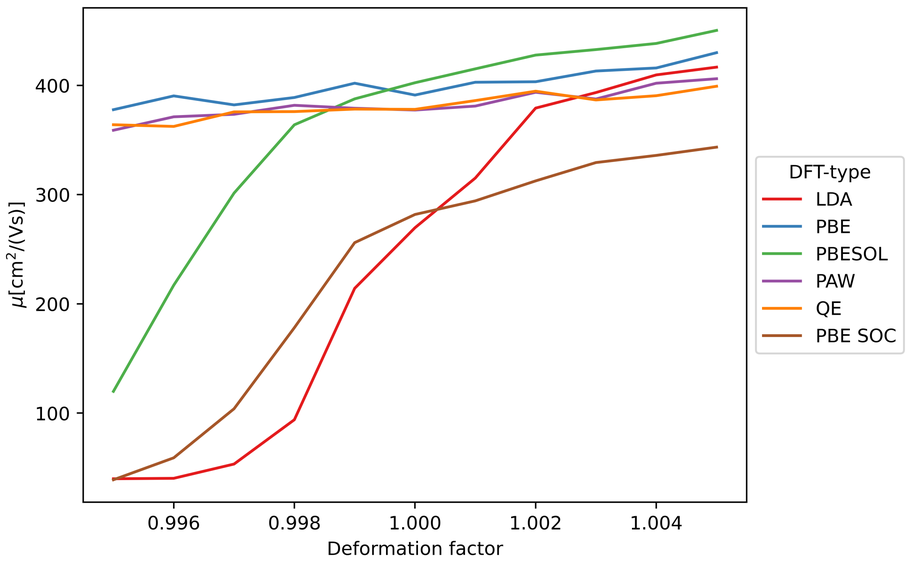

Figure: Influence of strain on the carrier mobility for all DFT-EMC calculations

[1] Carlo Adamo and Vincenzo Barone. "Toward reliable density functional methods without adjustable parameters: The PBE0 model". In: *The Journal of chemical physics* 110.13 (1999), pp. 6158–6170. DOI: 10.1063/1.478522.

[2] Paolo Giannozzi et al. "Advanced capabilities for materials modelling with Quantum ESPRESSO". In: *Journal of physics: Condensed matter* 29.46 (2017), p. 465901. DOI: 10.1088/1361-648x/aa8f79.

[3] Laura Gollner. "Development and Application of an Ensemble Monte Carlo Framework". Master's thesis. Vienna University of Technology, 2023. DOI: 10.34726/hss.2023.95902.

[4] Thomas D Kühne et al. "CP2K: An electronic structure and molecular dynamics software package-Quickstep: Efficient and accurate electronic structure calculations". In: *The Journal of Chemical Physics* 152.19 (2020). DOI: 10.1063/5.0007045.

[5] Branimir Radisavljevic et al. "Single-layer MoS_2 transistors". In: *Nature nanotechnology* 6.3 (2011), pp. 147–150. DOI: 10.1038/nnano.2010.279.