Electronic Structure of MoS_2

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Computational Solid State Physics

Abstract

The electronic structure of layered MoS_2 is studied through bandgap variation for 1-6 layers-thick crystal. The monolayer MoS_2 is studied via its band structure, the density of states, phonon mode frequencies, and effective masses.

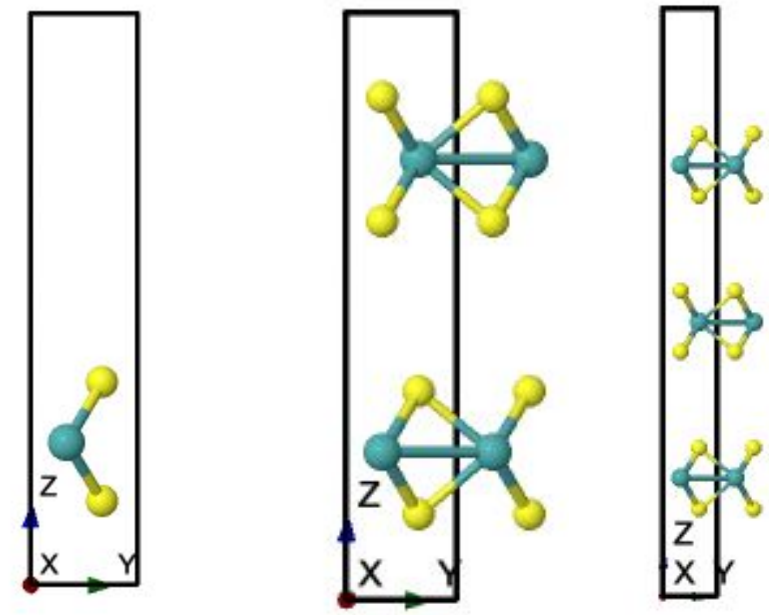
Introduction

Molybdenum Disulfide has been studied for its electronic structure and touted to be future replacements for silicon and graphene in nanoelectronics. The 2D layered structure offers flexibility in its usage in semiconductor applications, especially optoelectronic devices. The properties of MoS_2 are studied via simulations using Quantum-Espresso[1]. We carry out first-principles calculations to investigate the electronic structure of the monolayer case and the bandgap variation across layer thicknesses.

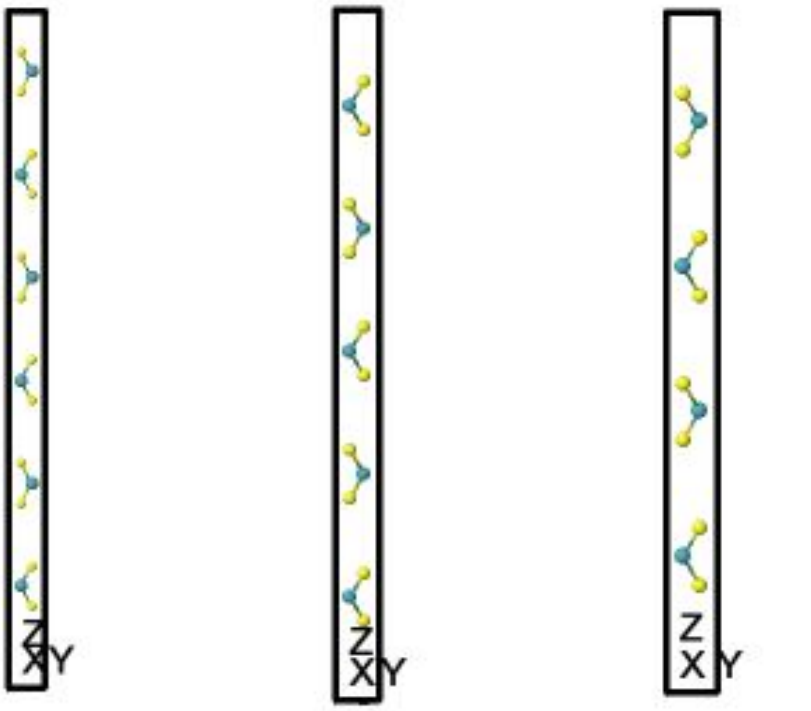
Crystal Structure

The monolayer MoS has a 2H (hexagonal symmetric) structure, with the two sulphur atoms sticking out of the plane in which the Molybdenum atom is situated. The bilayer is offset in accordance with the hexagonal structure of the lattice as shown below, keeping the bond-length of Mo-S constant. The gap between the layers is kept at a constant separation of 15 Angstrom. Additionally, the unit cells are scaled for each structure such that the periodic lattice does not affect the layers in the adjacent cell. The lattice constant (a) is kept constant at 6.0288 Angstrom. The following structures are obtained via the Quantum Espresso Input Generator[2].

[1] P. Giannozzi et al., J.Phys.:Condens.Matter 21, 395502 (2009)
http://dx.doi.org/10.1088/0953-8984/21/39/395502
[2] QE Input Generator



(a)Monolayer (b) Bilayer (c) 3-Layer



(d) 4-Layer (e) 5-Layer (f) 6-Layer

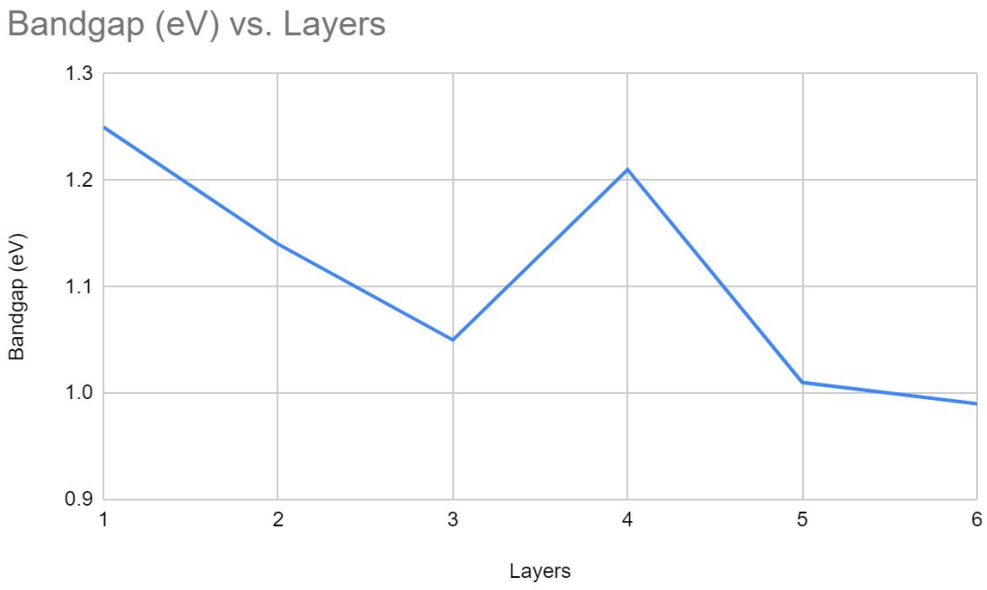
Figure 1: Unit Cells for all 6 configurations.

Computation

1. Band Gap Variation With Layers

The steps involved in calculating the bandgap are as follows

1. RELAX - Define the unit cell parameters for the Bravais lattice of MoS2. Run the relaxation routine on the cell to find the optimum parameters and atomic positions.
2. SCF - Using these positions, self-consistent field calculation is run to obtain the corresponding wave-functions for the material.
3. NSCF - Using a greater number of k-points, the non-self-consistent field calculation is run. We are essentially solving the **Kohn-Sham** equation. This builds upon the SCF calculations.
4. DOS (Density of states) - The density of states calculation helps in finding the variation in DOS, and hence also the band-gap.

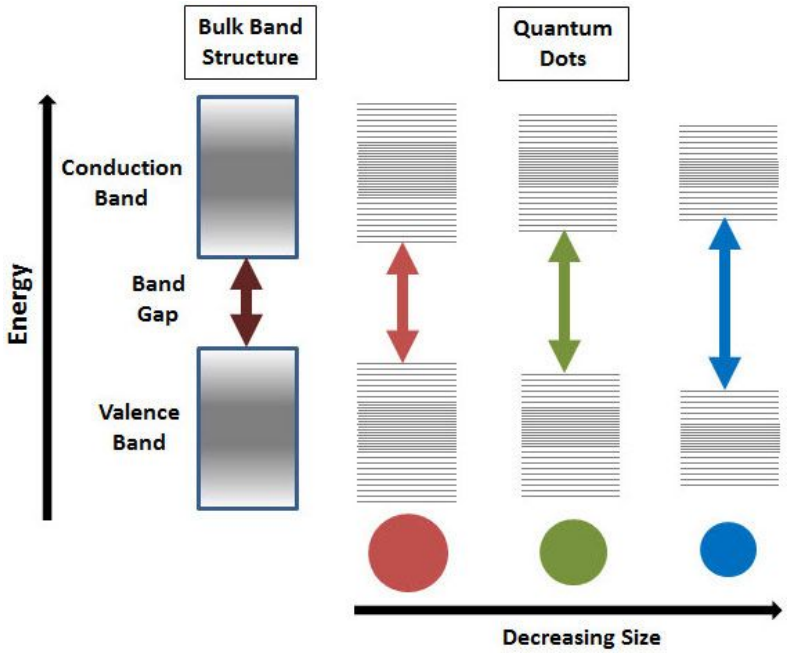


For all the calculations here, ultrasoft pseudopotentials are used, as provided by Materials Cloud[3].

[3] SSSP: G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet and N. Marzari, npj Computational Materials 4, 72 (2018). http://materialscloud.org/sssp

Quantum Confinement

In the case of nanostructures, the bandgap of the material may show an increase, as is seen with MoS_2. This is caused due to Quantum Confinement, where the particle-like layer approaches quantum scales and behaves in a probabilistic manner, as is typical. Hence, the energy levels are quantised, and the layer has an increase in its bandgap.



Quantum Confinement as seen in Quantum Dots[4]

[4] Sigma Aldrich - Quantum Dots

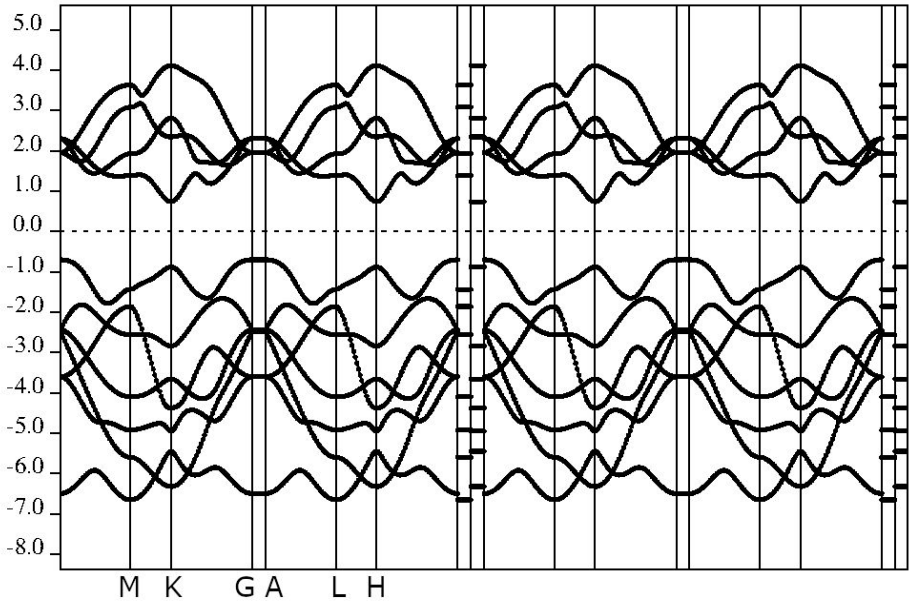
2. Monolayer Studies

The monolayer MoS_2 is studied through the following properties using Quantum Espresso.

2.1 Band Structure

Following the first three steps of the band-gap variation section, the following processes are executed.

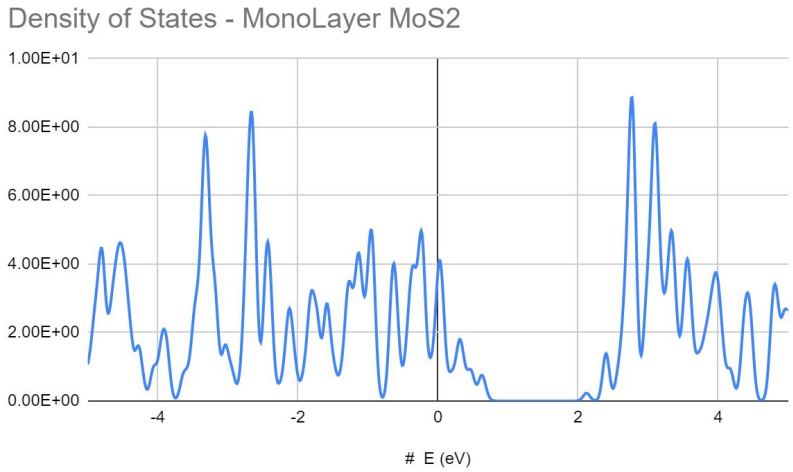
1. Generate the K-Points through the input-file. For the monolayer, 528 points were generated using the Seek Path tool.
2. The K-Points are used in the 'bands' input file and executed using pw.exe.
3. BANDS - Using bands.exe, the data files for the bands are generated.
4. PLOTBAND - Plotband.exe allows us to plot the band-structure, allowing for changes to the reference value (typically the Fermi-level), and the range of the energies.



Band Structure Obtained Through Q-E for MoS_2

2.2 Density of States

Using the steps laid out in the Band Variation calculation, we can apply the same to the mono-layer and find the density of states below.

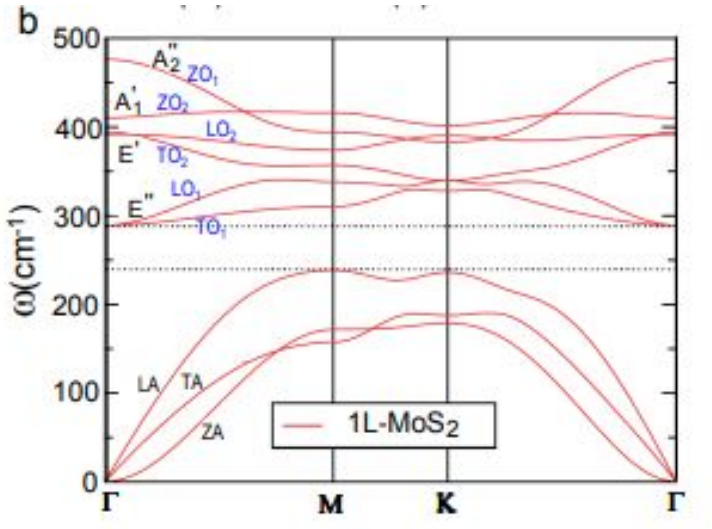


2.3 Phonon Mode Frequencies at Gamma Point

PH.X - The phonon calculation is run on the [0 0 0]/Gamma Point following the scf calculation. Nine frequencies are thus produced in the final output shown below, compared to reported values (at the Gamma Point).

```
**************************************************************************
    freq (    1) =      -1.533234 [THz] =     -51.143176 [cm-1]
    freq (    2) =       1.238517 [THz] =      41.312490 [cm-1]
    freq (    3) =       1.238517 [THz] =      41.312490 [cm-1]
    freq (    4) =       8.513076 [THz] =     283.965657 [cm-1]
    freq (    5) =       8.513076 [THz] =     283.965657 [cm-1]
    freq (    6) =      11.499053 [THz] =     383.567131 [cm-1]
    freq (    7) =      11.499053 [THz] =     383.567131 [cm-1]
    freq (    8) =      12.247754 [THz] =     408.541093 [cm-1]
    freq (    9) =      13.991065 [THz] =     466.691699 [cm-1]
**************************************************************************
```

(a) Simulated Frequencies



(b) Reported Values[5]

2.4 Electron and Hole Effective Masses

The charge carriers are awarded a certain weight in the potential field as they oscillate in the crystal. This is indicated by the effective mass which takes into consideration the convexity of the E-k curve.

$$m^* = \frac{\hbar^2}{2d.m_e}$$

where,

$$d = \frac{d^2E}{dk^2}$$

And m_e is the rest mass of the electron.

[5] *Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material* - Xin Zhang et. al

Discussion

The electronic structure of MoS_2 can be studied in great detail through the application of DFT. The material may lend use in various semiconductor applications in the future, and one of those is the LED[6]. The quantum confinement effect in the layered MoS_2 can be beneficial in energy-saving applications, thus. The input files for all the computational processes are uploaded here[7].

[6] *Calculation Study of Electric Properties on Molybdenum Disulfide By Using Density Functional Theory* - Diah Angraina Fitri, Acep Purqon.
[7] Github - CSSP