

Report on

Regeneration of the paper titled

“Tribo-piezoelectricity in Janus Transition Metal Dichalcogenide Bilayers: A First Principles Study.”

Building the Bilayer Structure

First, MoS₂ monolayer was built. Then another layer was added with a calculated interlayer distance to get the bilayer structure. A vacuum region of 2.5 nm in Z direction was added to avoid the effect of other periodic layers.

Monolayer

The monolayer was designed with the cell dimension depicted in the paper. ($a_1=a_2=3.234 \text{ \AA}$). Then “vc-relax” calculation was done to justify the value and got the almost exact result. Then “relax” calculation was done to compute the position of the atoms of the monolayer.

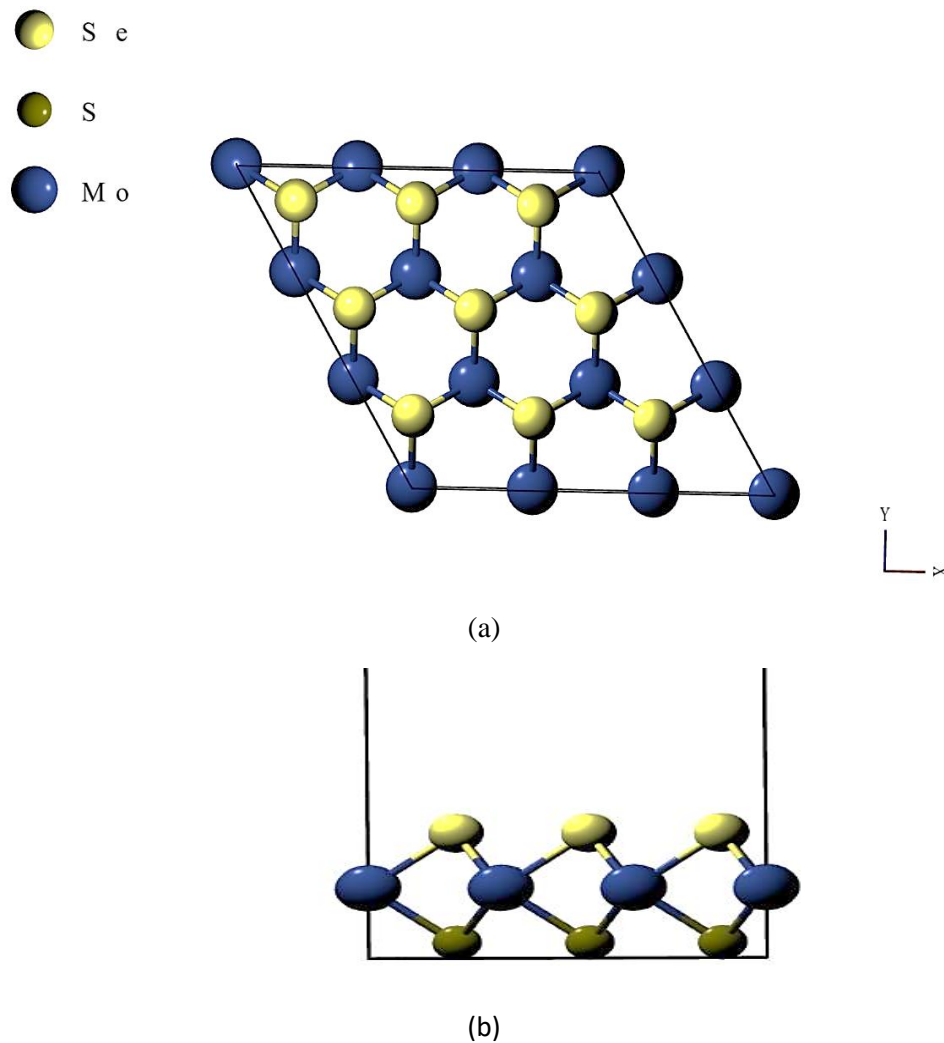


Figure 1: Relaxed MoS₂ monolayer. (a) Top view, (b) Side View.

A-B stacking

AB stacking is reported to be the most energetically stable stacking of the bilayer wherein A Mo atom of the top-layer is on top of the Se atom of the bottom layer. The equilibrium interlayer distance is described as 0.96 nm.

Equilibrium Interlayer Distance

The equilibrium interlayer distance is calculated in two steps. First step is changing the interlayer distance manually and getting a rough idea of the value and then in the second step, the roughly estimated value is used to do the “relax” calculation to get the exact interlayer distance. First, manually the interlayer distance is changed and corresponding energy is calculated for different distance. This gave a good approximation that the equilibrium interlayer distance is near 0.96 nm.

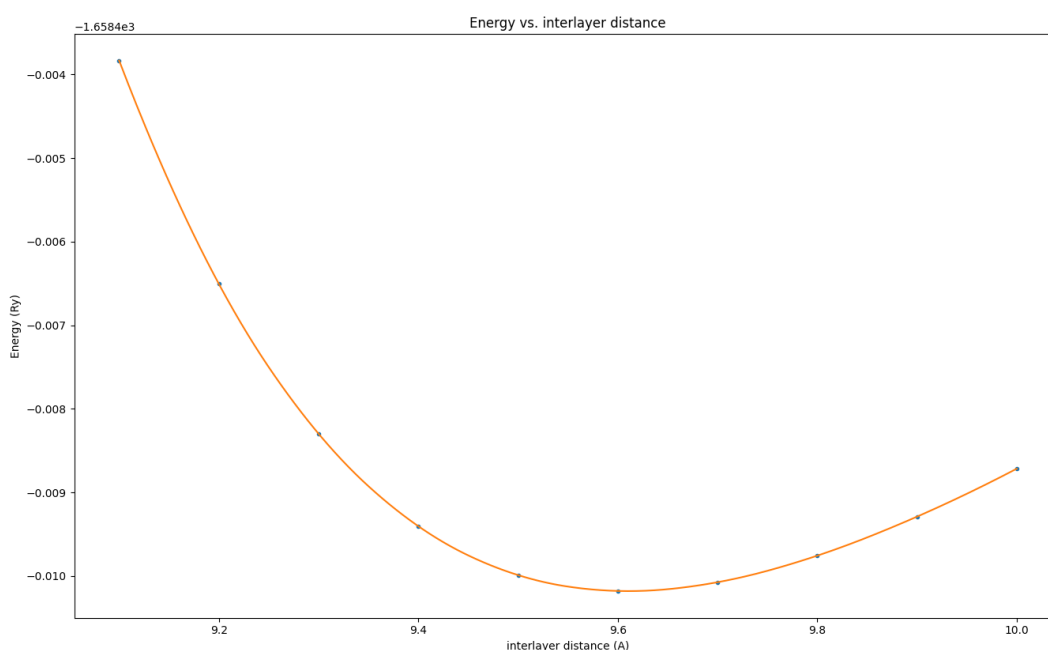


Figure 2: Energy vs. Interlayer distance of the bilayer indicates that when the distance is approximately 9.6 Å, the Energy is minimum.

Now, in the second step, keeping the interlayer distance fixed, the structure is relaxed to find the optimized position of the atoms of the bilayer in the XY plane. From this step, the XY coordinates of the atoms are kept fixed and the structure is relaxed in the Z direction. This gave the exact interlayer distance as **9.608738126 Å**, which is pretty close to the value shown in the paper.

Begin final coordinates

ATOMIC_POSITIONS (angstrom)

Se	0.000000000	1.867152000	3.240874323	0	0	1
Mo	0.000000000	0.000000000	1.534946682	0	0	1
S	0.000000000	1.867152000	0.000000000	0	0	0
Se	1.617000000	0.933576000	9.608738126	0	0	1
Mo	0.000000000	1.867152000	7.903713381	0	0	1
S	1.617000000	0.933576000	6.367479709	0	0	1

End final coordinates

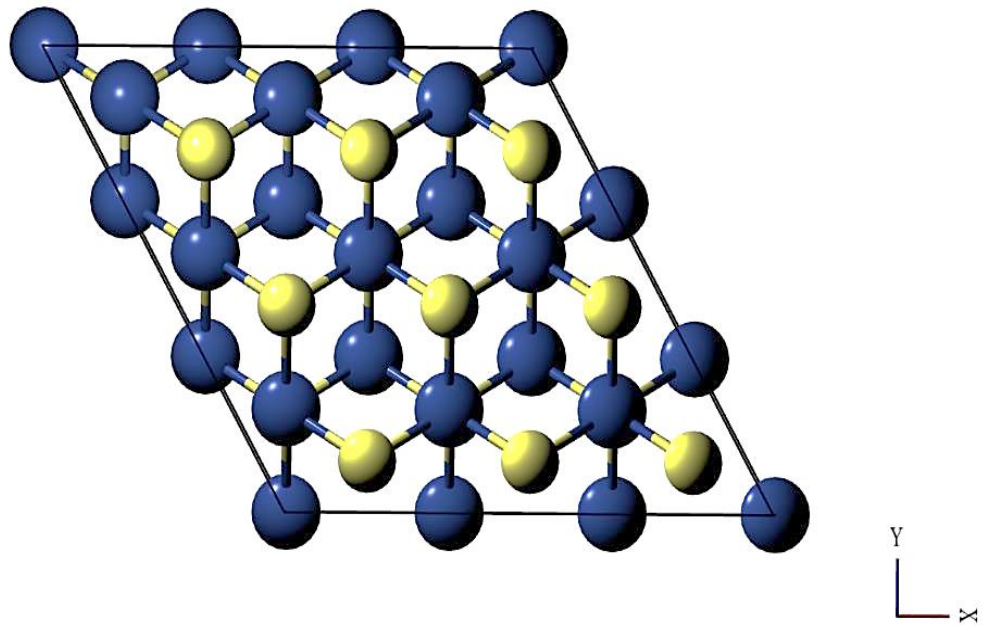
Figure 3: The final coordinates of the atoms in the AB stacking after relaxation in the Z axis.

Now, Finally the AB stacking is ready.

● S e

● S

● M o



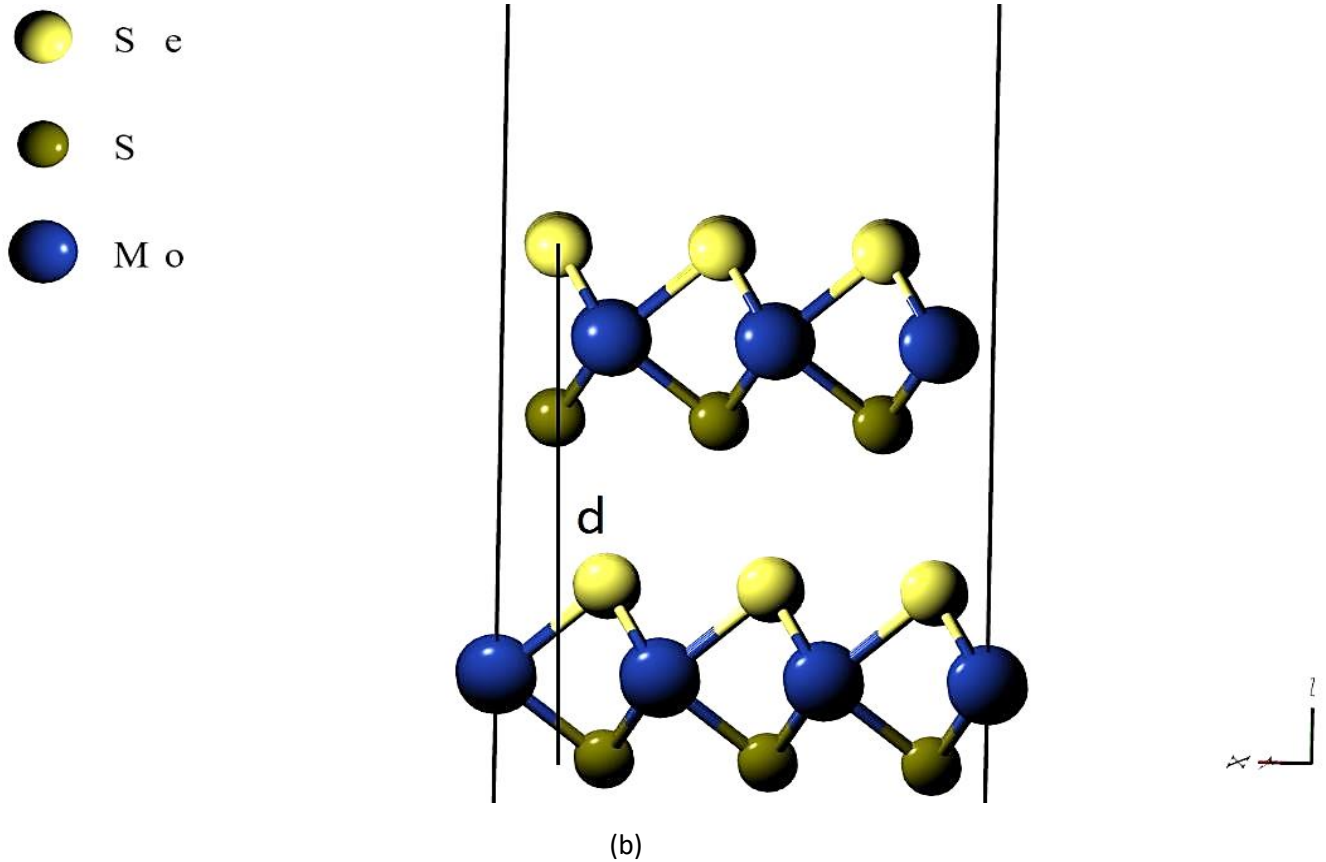
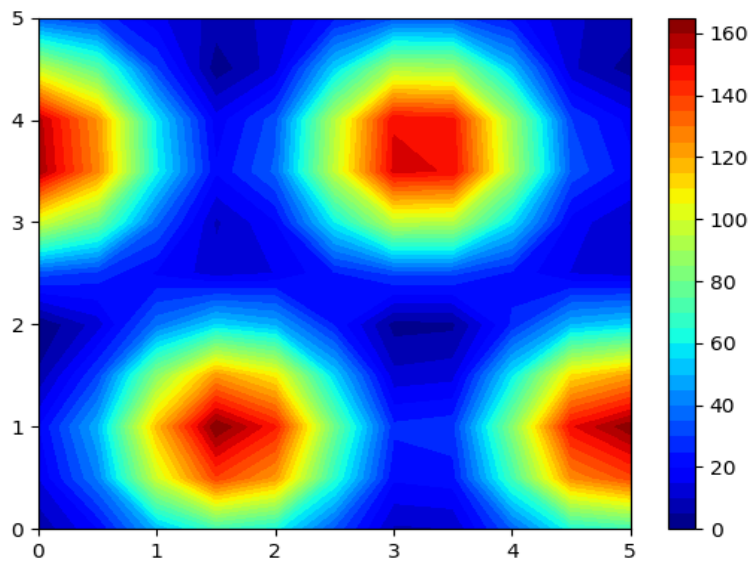


Figure 4: A-B stacking (a) Top View (b) Side View

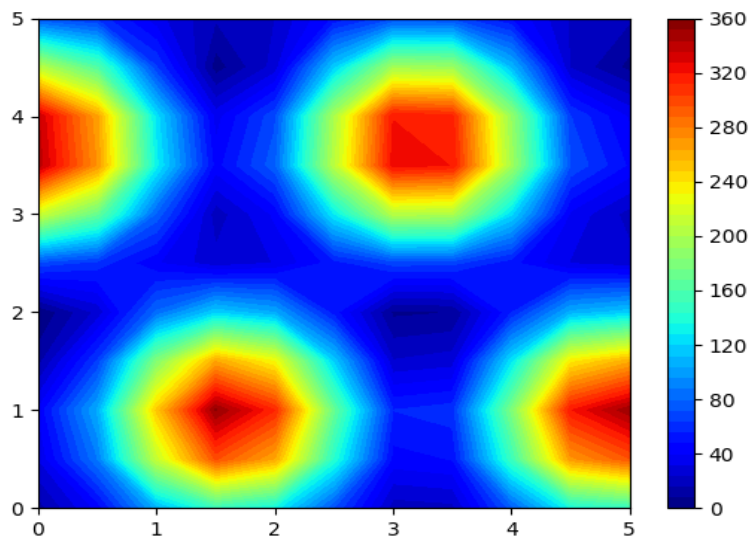
Potential Energy Surface (PES)

All the calculations are done using Projector Augmented Wave (PAW) method with the PBE exchange correlation functional. The influence of vdW interaction is considered by using "optB86b-vdW". Force conversion threshold is less than equal to 0.01 eV/nm. After structural relaxation, the top MoSSe monolayer is transversely sliding with respect to bottom layer and the whole system is relaxed again with the surface Se atom of the top layer and S atom of the bottom layer being fixed to maintain the **compression sliding** procedure. Cut-off energy is considered as **44 Ry (598 eV)** and k point sampled on **12×12×1** Monkhorst-pack mesh. PES is calculated by the formula

$E_{\text{PES}}(\mathbf{x}, \mathbf{y}) = E(\mathbf{x}, \mathbf{y}) - E_{\text{lowest}}$, Where, $E_{\text{PES}}(\mathbf{x}, \mathbf{y})$ is PES energy, $E(\mathbf{x}, \mathbf{y})$ is the SCF energy at (\mathbf{x}, \mathbf{y}) position of the top layer, and E_{lowest} is lowest energy of the system.



(a)



(b)

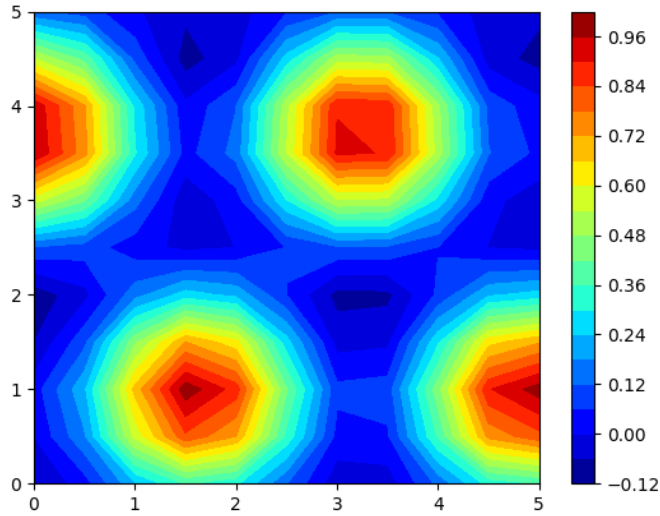
Figure 5: Potential Energy Surface (in meV), (a) for $d=0.96$ nm (b) for $d=0.93$ nm

polarization deviation surface (PDS)

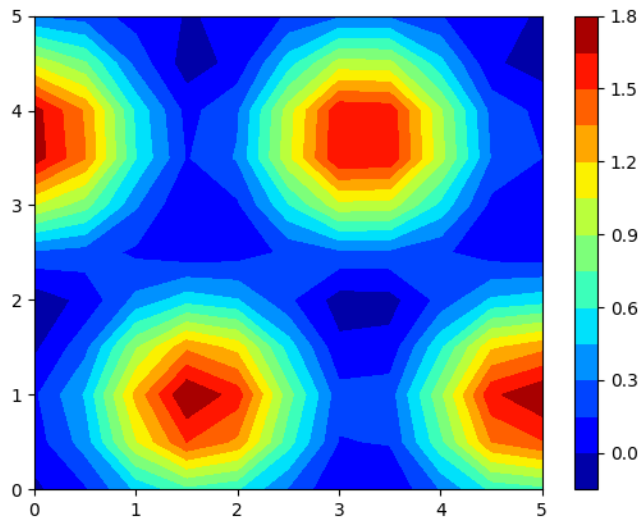
First, Vertical polarization P_d is calculated by

$$P_d = D/A, \text{ where, } D \text{ is vertical dipole moment and } A \text{ is area of the unit cell.}$$

Then PDS is constructed by , $\Delta P = P_d - P_{Fn=0}$.



(a)



(b)

Figure 6: PDS (in pC/m) of MoSSe Bilayer, (a) for $d=0.96$ nm (b) for $d=0.93$ nm.

For reference the PES and PDS surface from the paper is given here.

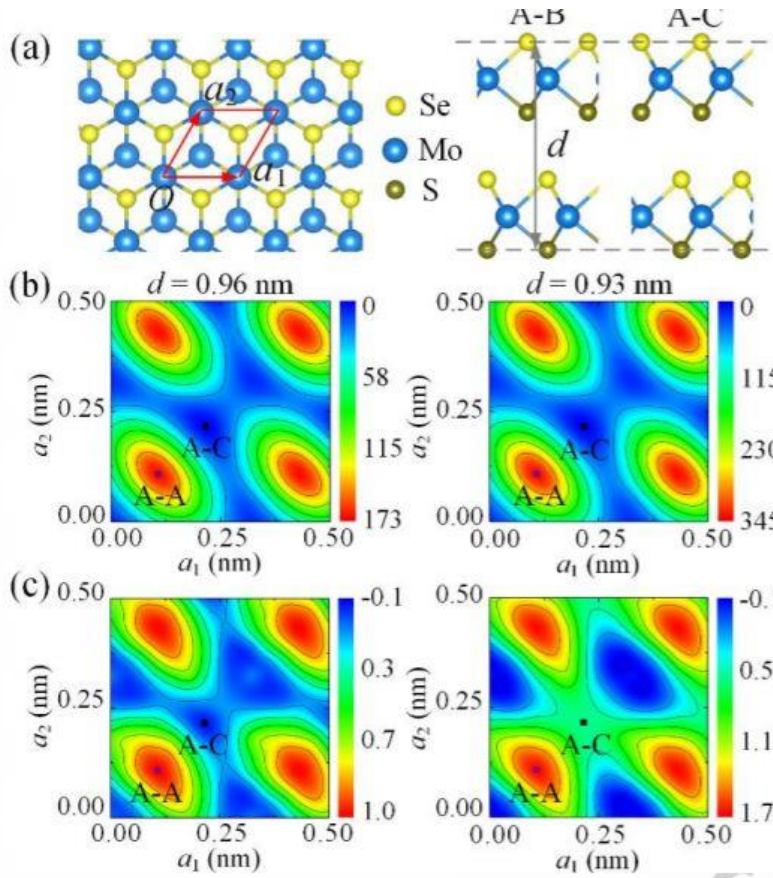


Figure 7: PES and PDS surface from the reference paper.

(Note 1: In the paper, the shapes found in the energy and polarization surfaces are elliptical, whereas in my work, the shapes found are more in circular shapes, otherwise, the energy and potential values comply with the paper. I tried with so many ways but I always get the circular shapes. At one point, I tried to increase the calculation number with different position of the top layer. I relaxed the system and calculated in every 0.5 Å sliding in both X and Y axis. So, I got 11 point in each axis, and had to calculate a total of $(11 \times 11 \times 2) = 242$ numbers of relaxation, SCF Energy and Dipole moment calculation to get those surfaces. Then it occurred to me, the reason behind this may be, when the top layer is transferred to different positions in XY plane, for a same distance the effect would be same on the other atoms for a single atom, so energy and polarization values will be symmetric for same distance in the left-right or up-down positions in the XY plane. So, a circular pattern is more probable than an elliptical one. Then I checked other papers regarding bilayer energy corrugation, all of them had these surfaces with the circular shapes.)

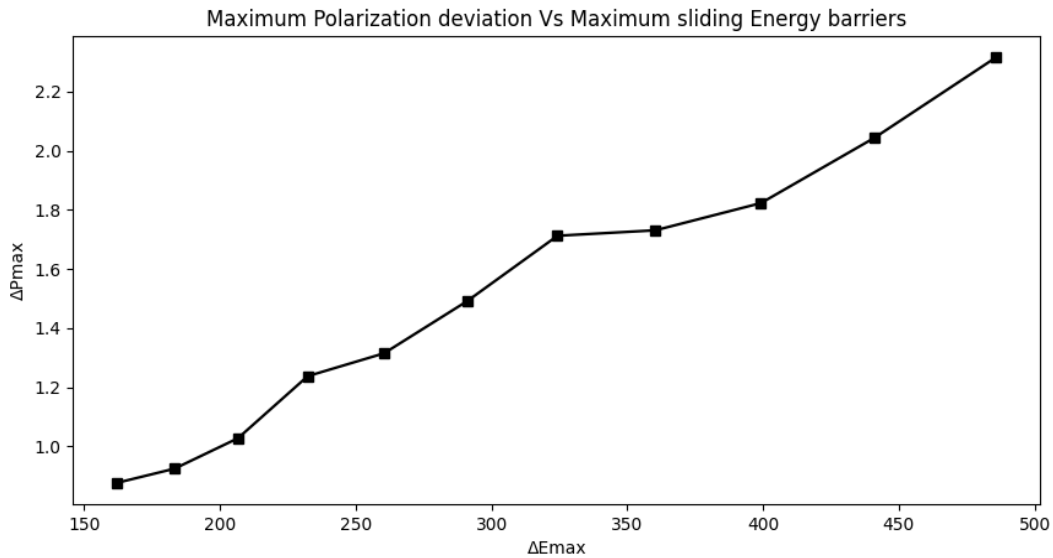
(Note 2: For vdW interaction, an algorithm “optB86b-vdW” is applied in the reference paper. As Mo is a transition metal, magnetization effect should be considered. But nothing is said about the calculation of magnetization effect of Mo in the reference paper and when I try to implement the magnetization effect, QE always shows an error. Quantum Espresso cannot implement “optB86b-vdW” and magnetization effect simultaneously. Also, it is not possible to calculate higher effects like Spin Orbit Coupling (SOC) with this “optB86b-vdW” algorithm.)

(Note 3: Theoretically, polarization has the unit of $\frac{charge}{(length)^2}$. But, in the reference work, pC/m is depicted as the unit of polarization. First, I was confused about the definition of polarization used in the work. It might be possible that, for 2D material dimension is different than that of a bulk material, that's why the unit is different. But I am not sure such definition exists for 2D material (or this is the right thing to do) as there is not enough information in internet or any other paper that I found of.)

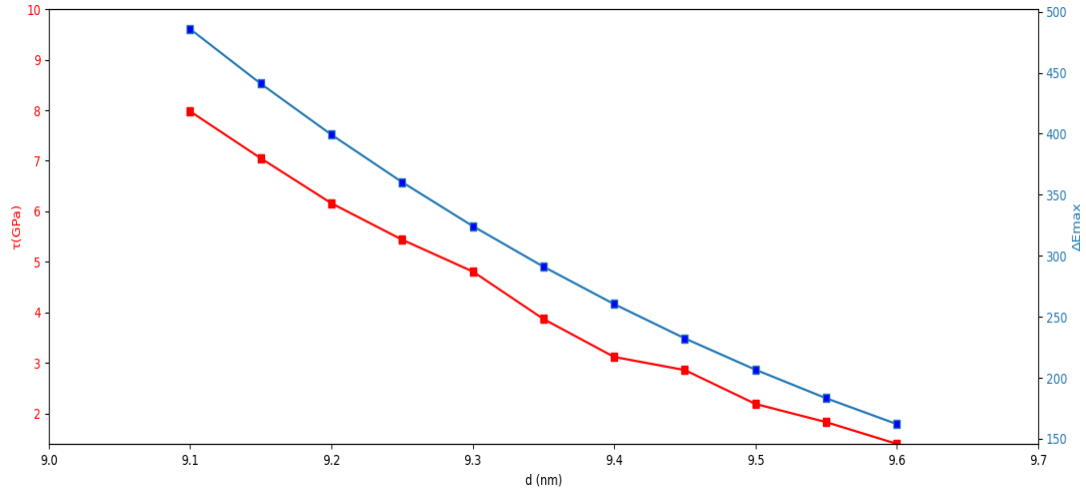
(Note 4: In Quantum Espresso, because of its periodic calculative nature, when there is a slab (non-periodicity in system boundary) of material, it is advised to consider a dipole correction. As I have calculated a 2D system, there is also discontinuation in the vertical axis. So, dipole moment correction should be considered, but nothing of this kind, is mentioned in the paper. Still, I have considered the dipole correction, while calculating polarization.)

Establishing the relation of Maximum polarization Deviation and Maximum sliding Energy Barrier

Maximum energy barrier is found at different interlayer distance is found by the difference of maximum energy (A-A stacking) and minimum energy (A-B stacking). Maximum polarization deviation is found by the maximum polarization difference at different height. The sliding energy corrugation ΔE in the PES of the MoSSe bilayer directly correlates with interlayer friction and resistance. Higher maximum energy corrugation or barrier ΔE_{max} indicates stronger interlayer friction. The maximum polarization deviation ΔP_{max} increases monotonically with the maximum energy barrier and the variation curve is approximately linear. To achieve larger vertical polarization needs more energy consumption on sliding friction.



(a)



(b)

Figure 8: Variations of (a) the maximum polarization deviations (in unit of pC/m) with the corresponding maximum sliding energy barriers (in unit of meV) when the interlayer distance decreases from 0.96 to 0.91 nm, and (b) the interlayer shear strength (red line with dots) and maximum sliding energy barriers (blue line with dots) with the corresponding interlayer distance.

For reference, the variation of maximum polarization with corresponding maximum energy barriers and interlayer shear strength vs. interlayer distance shown in the paper is given below.

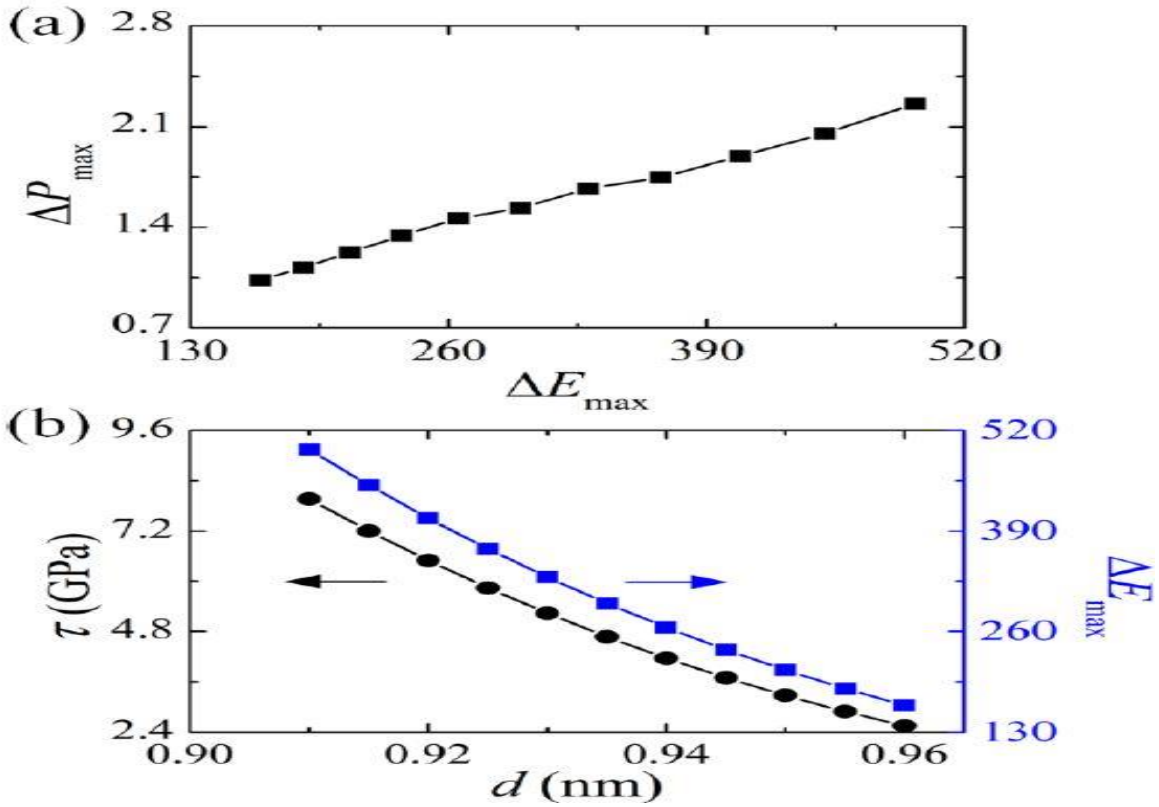


Figure 8: Figure described in the paper.

Charge Density Difference

To find the effect of Tribo-piezoelectricity charge density difference is calculated for 0.96 nm and 0.93 nm and for both A-B and A-A stacking. First, the system is relaxed, scf energy is calculated for bilayer, top layer and bottom layer separately and charge density is calculated.

Charge Density Difference for A-B stacking for 0.93 nm

Bilayer Charge Density

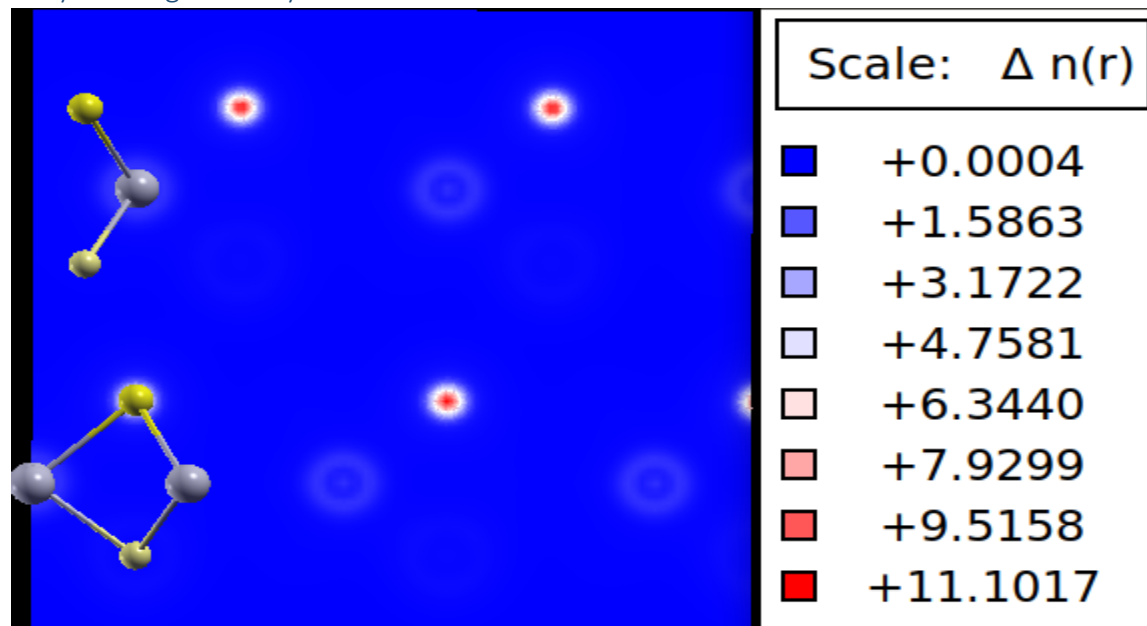


Figure 9: 2D projection of charge density for bilayer (ρ_{total}) of A-B stacking for 0.93nm.

Bottom Layer Charge Density

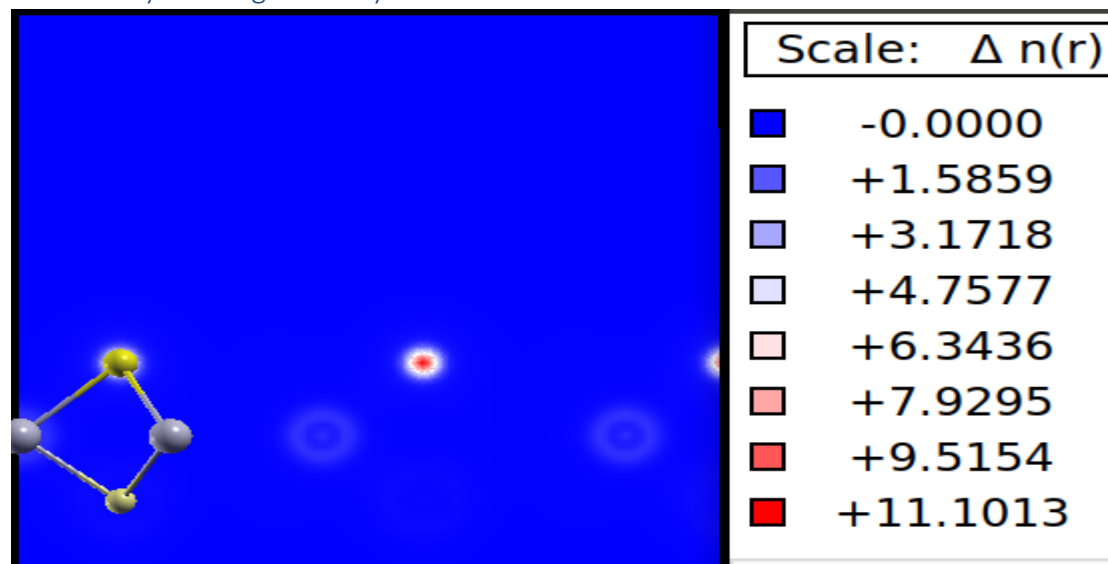


Figure 10: 2D projection of charge density for bottom layer (ρ_{bottom}) of A-B stacking for 0.93nm.

Top Layer Charge Density

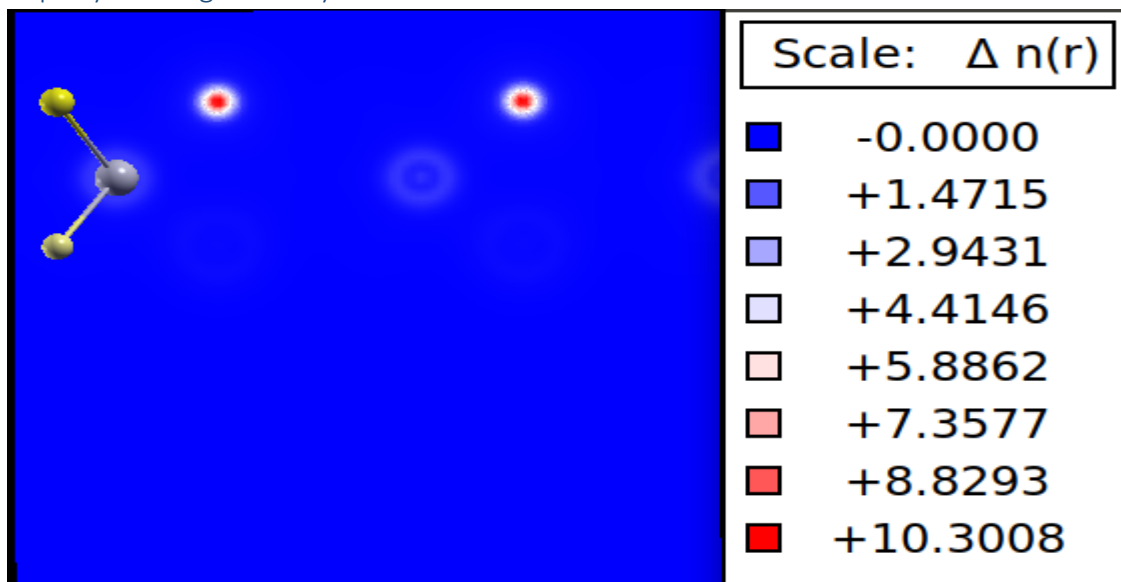


Figure 11: 2D projection of charge density for top layer (ρ_{top}) of A-B stacking for 0.93nm.

Charge Density Difference

Now that, we have ρ_{total} , ρ_{bottom} and ρ_{top} , we can calculate charge density difference for A-B stacking for 0.93 nm by subtracting ρ_{bottom} and ρ_{top} from ρ_{total} by this equation.

$$\Delta\rho = \rho_{\text{total}} - \rho_{\text{bottom}} - \rho_{\text{top}}$$

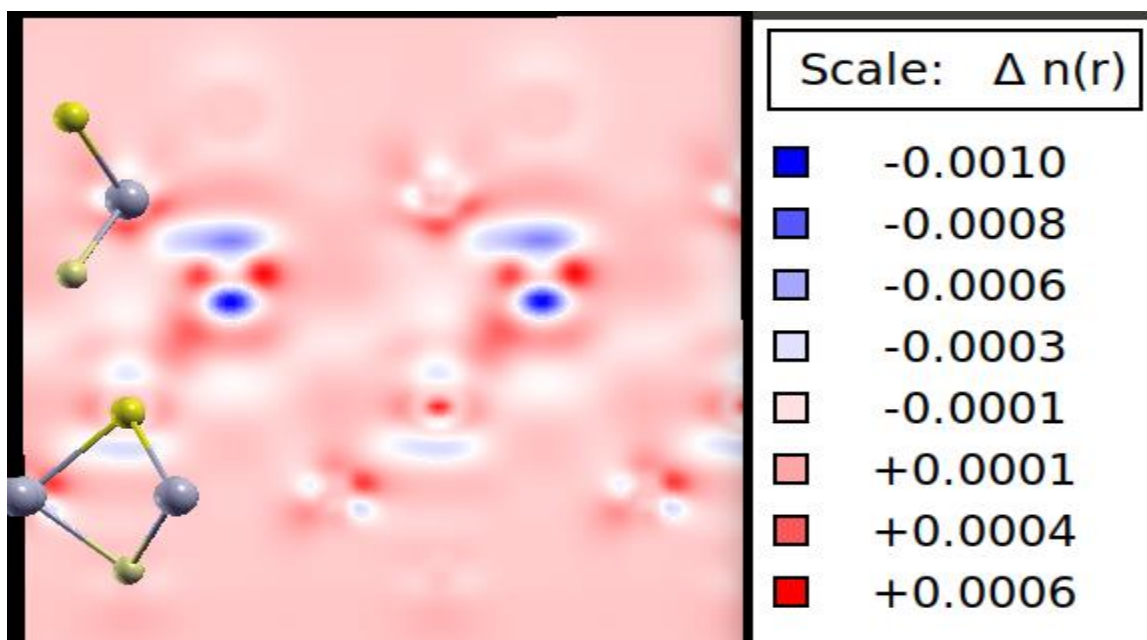


Figure 12: 2D projection of charge density difference ($\Delta\rho$) of A-B stacking for 0.93nm.

Similarly, all other charge density difference plot are built.

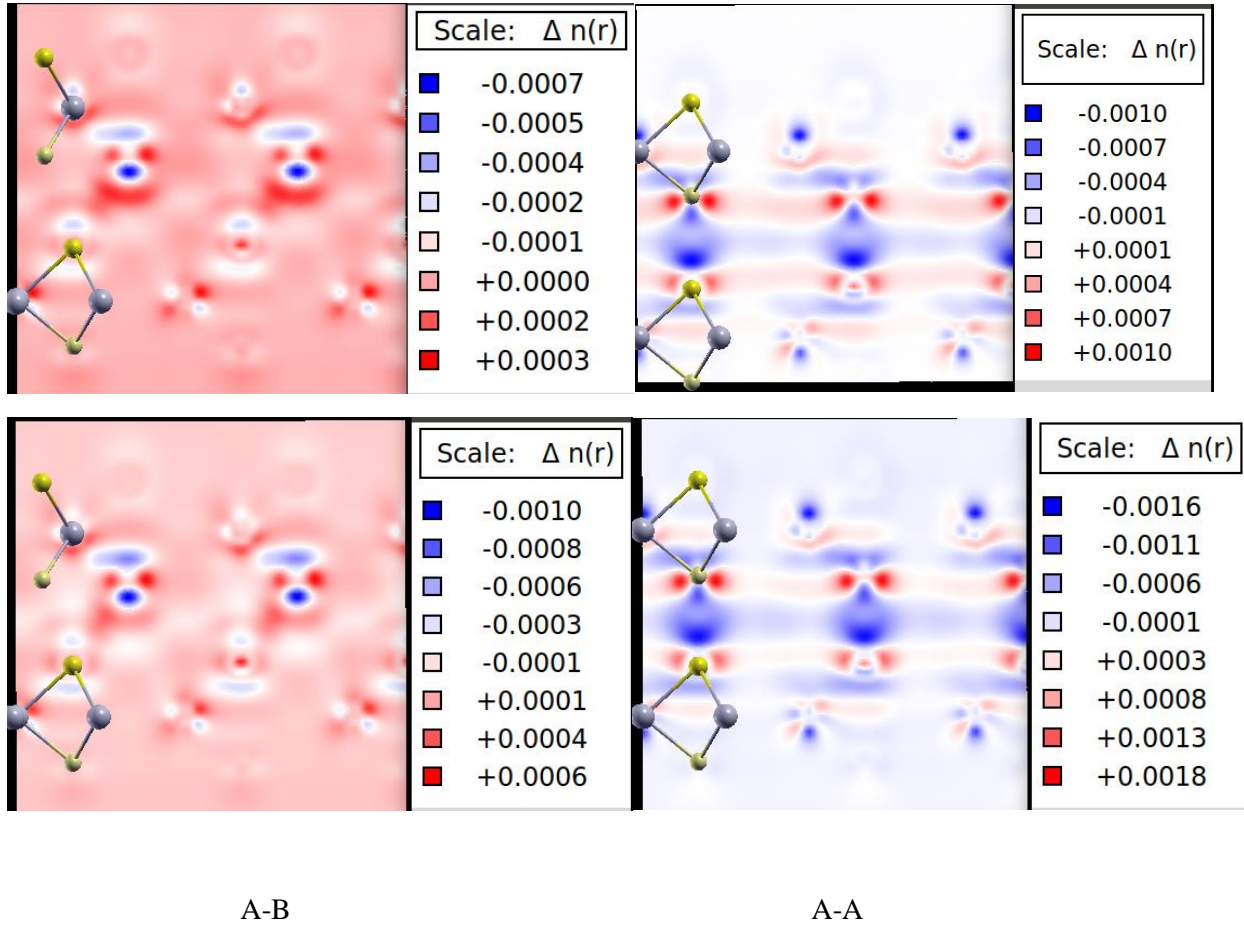


Figure 13: 2D projections of charge density differences (in unit $e/\text{\AA}^3$) of the A-B and A-A stacking MoSSe bilayers at $d = 0.96$ nm and $d = 0.93$ nm

For reference, the charge density difference plots given in the paper are given below.

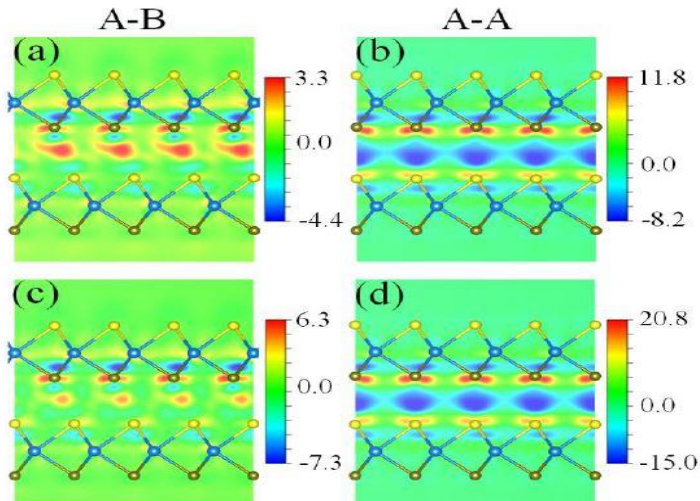


Figure 14: 2D projections of charge density differences (in unit $0.001e/\text{\AA}^3$) of the A-B and A-A stacking.

Electronic Band Structure Calculation

Electronic band structure for A-B stacking is given below.

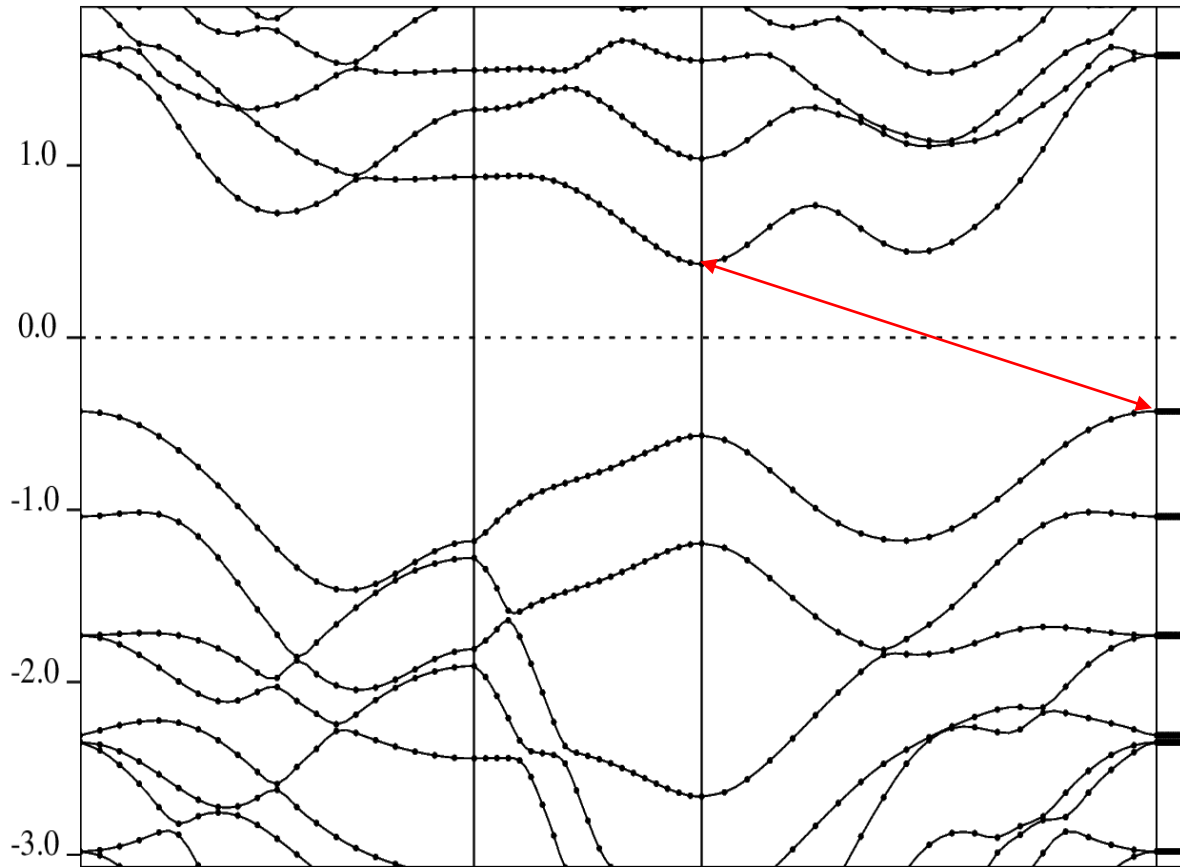


Figure 15: Electronic band structure of MoSSe bilayer A-B stacking. Indirect Band gap is found to be 0.8527 eV.

(Note: This paper doesn't include electronic band structure calculation of MoSSe bilayer. In fact no other band-structure of this bilayer has been published yet. So, to justify this work, I have calculated band structure of similar material structure (MoSe₂ bilayer and MoSSe monolayer) which have been published so that I can compare my work and justify.

MoSe₂ Bilayer

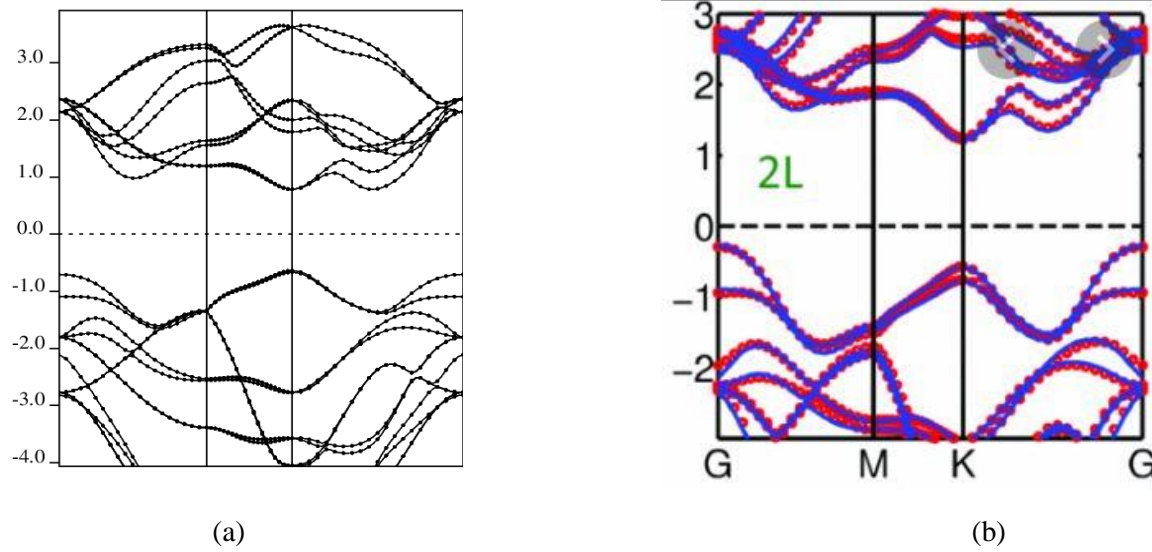


Figure 16: Electronic band structure of MoSe₂ bilayer (a) calculated structure (b) Structure published in paper.

MoSSe Monolayer

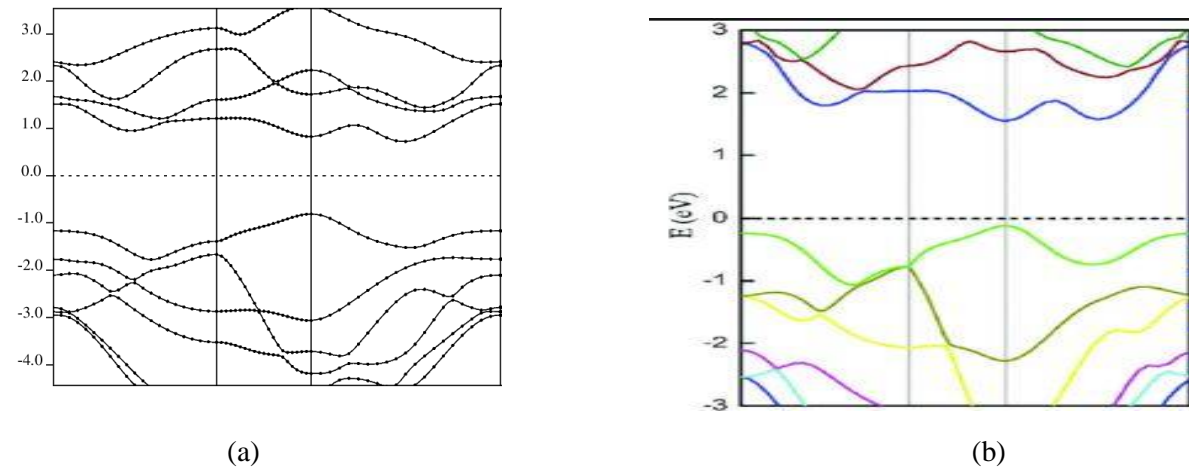


Figure 17: Electronic band structure of MoSSe monolayer (a) calculated structure (b) Structure published in paper.

As these two structures are similar to the published work, the methodology of finding the band structure can be assumed to be correct.)

Band Gap Engineering

Now band structure of different stacking at different interlayer distance is calculated to see the effect of structure of bilayer on the band diagram.

A-A Stacking at 0.96 nm interlayer distance

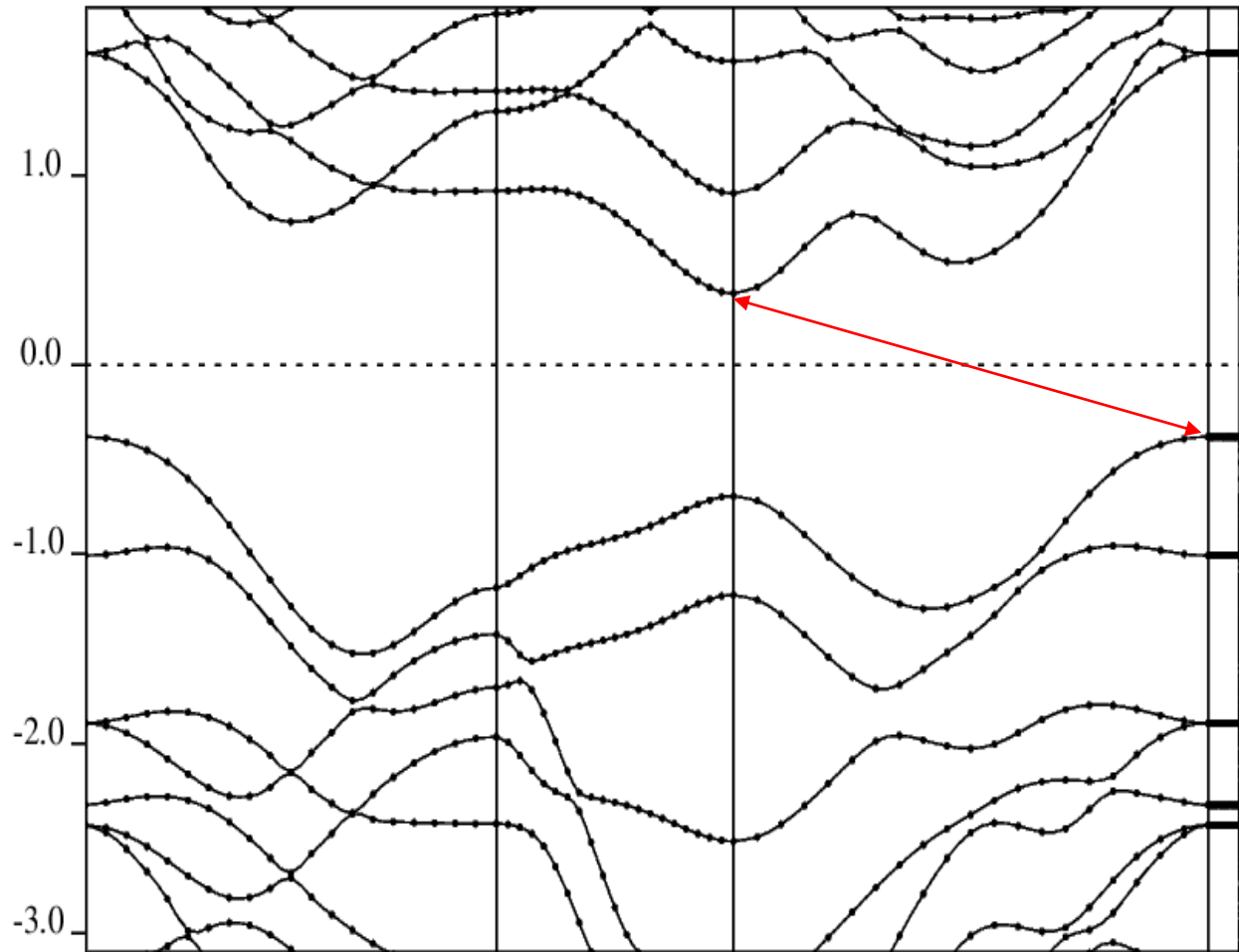


Figure 18: Electronic band structure of MoSSe bilayer A-A stacking with 0.96 nm interlayer distance. Indirect Band gap is found to be 0.7565 eV.

A-A Stacking at 0.94 nm interlayer distance

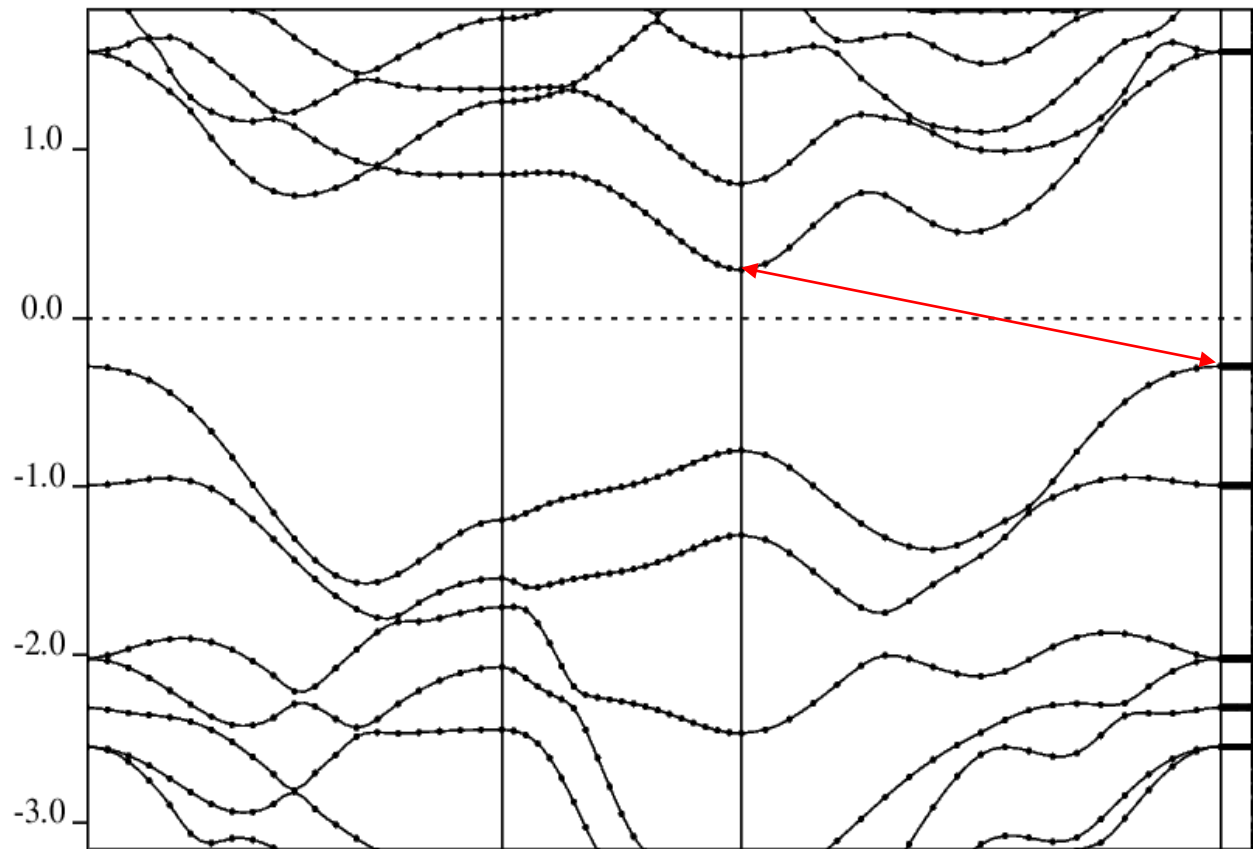


Figure 19: Electronic band structure of MoSSe bilayer A-A stacking with 0.94 nm interlayer distance. Indirect Band gap is found to be 0.5755 eV.

So, bandgap can be tuned by changing both the stacking and interlayer distance. It can be also noticed that, for monolayer the bandgap was direct, but for bilayer the bandgap is indirect.

Ideas for Work

Some potential key ideas for future works are listed below.

- i. The electronic and structural properties (band structure engineering etc.) calculation of the same MoSSe bilayer can be explored more.
- ii. The same work can be carried out with different TMD material bilayers like WSSe, MoSTe, MoSeTe, WSTe, WSeTe etc.
- iii. In the paper, “**Bandgap engineering of janus MoSSe monolayer implemented by se vacancy**”, vacancy defect of Se atom is used to tailor electronic bandgap of MoSSe monolayer. This idea can be implemented in our bilayer structure.
- iv. I also find this work very interesting- “**Band alignment of two-dimensional transition metal dichalcogenides: Application in tunnel field effect transistors**”- which could be further explored.