

5-2016

# Predicting Structures and Properties of Transition Metal Dichalcogenide Alloys Using Density Functional Theory

Lucas R. Bruzgulis

*University at Albany, State University of New York*

Follow this and additional works at: [https://scholarsarchive.library.albany.edu/honorscollege\\_nano](https://scholarsarchive.library.albany.edu/honorscollege_nano)



Part of the [Nanoscience and Nanotechnology Commons](#)

---

## Recommended Citation

Bruzgulis, Lucas R., "Predicting Structures and Properties of Transition Metal Dichalcogenide Alloys Using Density Functional Theory" (2016). *Nanoscale Science & Engineering*. 13.

[https://scholarsarchive.library.albany.edu/honorscollege\\_nano/13](https://scholarsarchive.library.albany.edu/honorscollege_nano/13)

This Honors Thesis is brought to you for free and open access by the Honors College at Scholars Archive. It has been accepted for inclusion in Nanoscale Science & Engineering by an authorized administrator of Scholars Archive. For more information, please contact [scholarsarchive@albany.edu](mailto:scholarsarchive@albany.edu).

*Predicting Structures and Properties of Transition Metal  
Dichalcogenide Alloys Using Density Functional Theory*

An honors thesis presented to the  
College of Nanoscale Science and Engineering,  
University at Albany, State University of New York  
in partial fulfillment of the requirements  
for graduation with Honors in Nanoscale Science  
and graduation from The Honors College.

Lucas R. Bruzgulis

Research Advisor: Bradley Thiel, Ph.D

May 2016

## ABSTRACT

Workflows for computationally simulating transition metal dichalcogenides using density functional theoretic methods and cluster expansion were established, as implemented in the Quantum ESPRESSO and Alloy Theoretic Automated Toolkit computer codes, respectively. Effects of energy cutoff values and k-point density on convergence of DFT results were investigated for the MoS<sub>2</sub> structure, and theoretic band structure calculations for MoS<sub>2</sub> and WS<sub>2</sub> were performed. The Mo<sub>x</sub>W<sub>(1-x)</sub>S<sub>2</sub> alloy system was also investigated using the maps code in the Alloy Theoretic Automated Toolkit in order to generate a composition vs energy plot. The application of Special Quasi-random Structures to further research into TMDC alloy systems and their order-disorder transformations is discussed.

## ACKNOWLEDGEMENTS

I'd like to thank Dr. Bradley Thiel for his help, support, and wisdom, as well as my research partner Udit Gupta who worked with me on this project.

# TABLE OF CONTENTS

Abstract .....	2
Acknowledgements .....	3
Transition Metal Dichalcogenides (TMDC's).....	5
Density Functional Theory (DFT) .....	6
Unit cell.....	7
Quantum ESPRESSO (QE).....	7
Calculation Parameters.....	8
Convergence .....	8
Band Structures of MoS <sub>2</sub> and WS <sub>2</sub> .....	10
The Alloy Theoretic Automated Toolkit (ATAT) .....	11
Cluster Expansion .....	11
Maps .....	11
Special Quasi-random Structures (SQS's) .....	13
Conclusions.....	14
References .....	15
Appendix.....	16

## TRANSITION METAL DICHALCOGENIDES (TMDC'S)

Transition metal dichalcogenides are a class of materials of the composition  $\text{MX}_2$ , where M represents Mo, W, Te, etc., and X represents S, Se, etc. They consist of hexagonal sheets of chalcogens (yellow) surrounding an inner layer of metal (green), as shown in Figure 1.

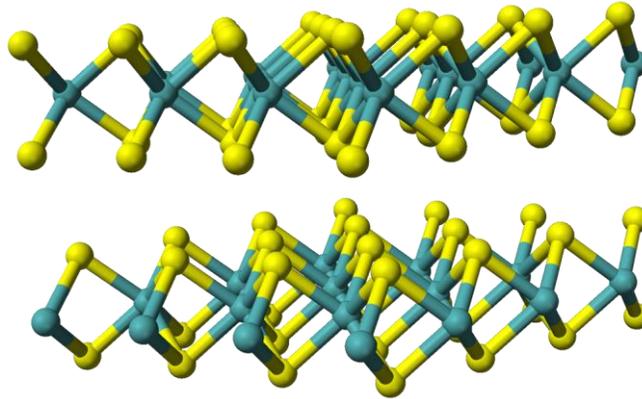


FIGURE 1: Bilayer TMDC<sup>1</sup>

Their structure provides extremely high conductivity in-plane, and very weak Van der Waals interactions across sheets, making them effectively stacked two-dimensional structures, possessing many of the same desirable physical and electronic traits as other two-dimensional materials such as graphene. TMDC's are being researched as potential next-generation semiconductor materials and alternatives to graphene. They demonstrate a transition from an indirect bandgap when in bulk form to a direct bandgap when in monolayer form, leading to the possibility of tuning their band gap and electronic properties by engineering their various possible alloys - either of the metals, chalcogens, or both. Engineering of the properties of these alloys may lead to the development of novel nanoscale semiconductor systems and devices - this research focused on establishing proper methods with which to computationally investigate these alloys in order to support further research into their synthesis, as experimental growth pathways are not yet well understood.

---

<sup>1</sup>"Molybdenite-3D-balls" by Ben Mills. Licensed under Public Domain

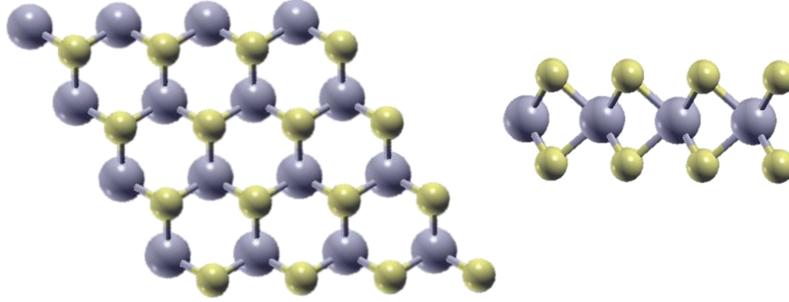


FIGURE 2: Alternate Views of the TMDC Structure[1]

## DENSITY FUNCTIONAL THEORY (DFT)

Density functional theory first-principles methods were used to predict the structure and electronic properties of monolayer TMDC alloys.

Hohenberg and Kohn laid the theoretical foundations of DFT in 1964, proving that the ground state electron density  $n(\mathbf{r})$  uniquely determines the potential of a system. This allows the potential of the system to be described by an electron density functional, assuming the Born-Oppenheimer approximation, and a ground state calculation. The Kohn-Sham equations, which describe a set of non-interacting electrons having the same density as the physical system under study, are then given by the following:

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r})$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

where  $v_s(\mathbf{r})$  is the potential,  $\mathbf{r}$  is the electron's position in space,  $v_{ext}$  is external potential,  $n(\mathbf{r})$  is the electron density,  $v_{xc}$  is the exchange-correlation term, and  $E_{xc}$  is the exchange-correlation function. The form of the exchange-correlation function is not generally known, and an approximation must be provided as one of the inputs to a DFT calculation. Expansion of the Kohn-Sham equations by a plane wave basis set turns them into a non-linear matrix eigenvalue problem, and DFT into a multi-variate minimization problem. Pseudopotentials then allow core electron states to be ignored in order to efficiently solve this problem, yielding the structure's total energy. This allows self-consistent calculations to minimize forces acting on atomic nuclei within the cell in order to arrive at the lowest-energy structural configuration. Calculating total energy requires a summation over points in k-space, which must be approximated by a discrete sampling - the number of k-points used is another of the many approximations necessary, including finite supercell size, finite number of plane waves, finite kinetic energy cutoff, and specified convergence criteria. If these approximations are carefully handled,

DFT can yield useful information on ground-state charge density, total energy, forces on nuclei, effective pressure and stress; minimum-energy structures, formation energies; molecular dynamics, reaction barriers and pathways, potential and free energy surfaces, and many other properties.

## UNIT CELL

In order to study systems which are not infinitely periodic, supercells must be constructed to artificially introduce large periodicities in order to approximate the behavior of an isolated system in that dimension. For two-dimensional structures, this involves a comparatively large artificial vacuum layer introduced into the unit cell of the structure, as indicated below for the Cartesian unit cell of MoS<sub>2</sub>:

3.15	0	0	
-1.575	2.72798	0	
0	0	<u>24.59</u>	
-0.000001575	1.818654243	3.07375	Mo
1.575001575	0.909325757	4.653780450	S
1.575001575	0.909325757	1.493719550	S

FIGURE 3: Unit cell of MoS<sub>2</sub> as represented in Cartesian coordinates in Angstroms (x,y,z), underlined has been artificially increased

## QUANTUM ESPRESSO (QE)<sup>2</sup>

Quantum ESPRESSO is an open-source implementation of DFT techniques and related codes made available under the GNU General Public License. The central component of QE is the PWscf module, which performs the self-consistent calculations much of the rest of QE requires to function. PWscf may perform several different types of calculations: 'scf' simply calculates the self-consistent solution for the energy of the input structure with no movement of the ion cores, and is required by many other modules of QE; 'relax' performs structural relaxation by calculating total energies and nudging ion positions until total energy of the cell is minimized without changing the overall cell parameters; 'vc-relax' is similar to 'relax', but also may vary overall cell parameters, however, 'vc-relax' was found to not support relaxation of structures in only two dimensions. More details on the operation and performance of QE codes may be found in its website, general documentation, and especially module-specific documentation.

Calculations were performed on a 64-bit Fedora 23 Linux operating system running on an Intel Core i5-6600K CPU. Quantum ESPRESSO version 5.3.0 precompiled binaries available in the standard Fedora updates repository were used. Precompiled parallel versions are also available but were not used, as no massively parallel systems were available to perform the computations.

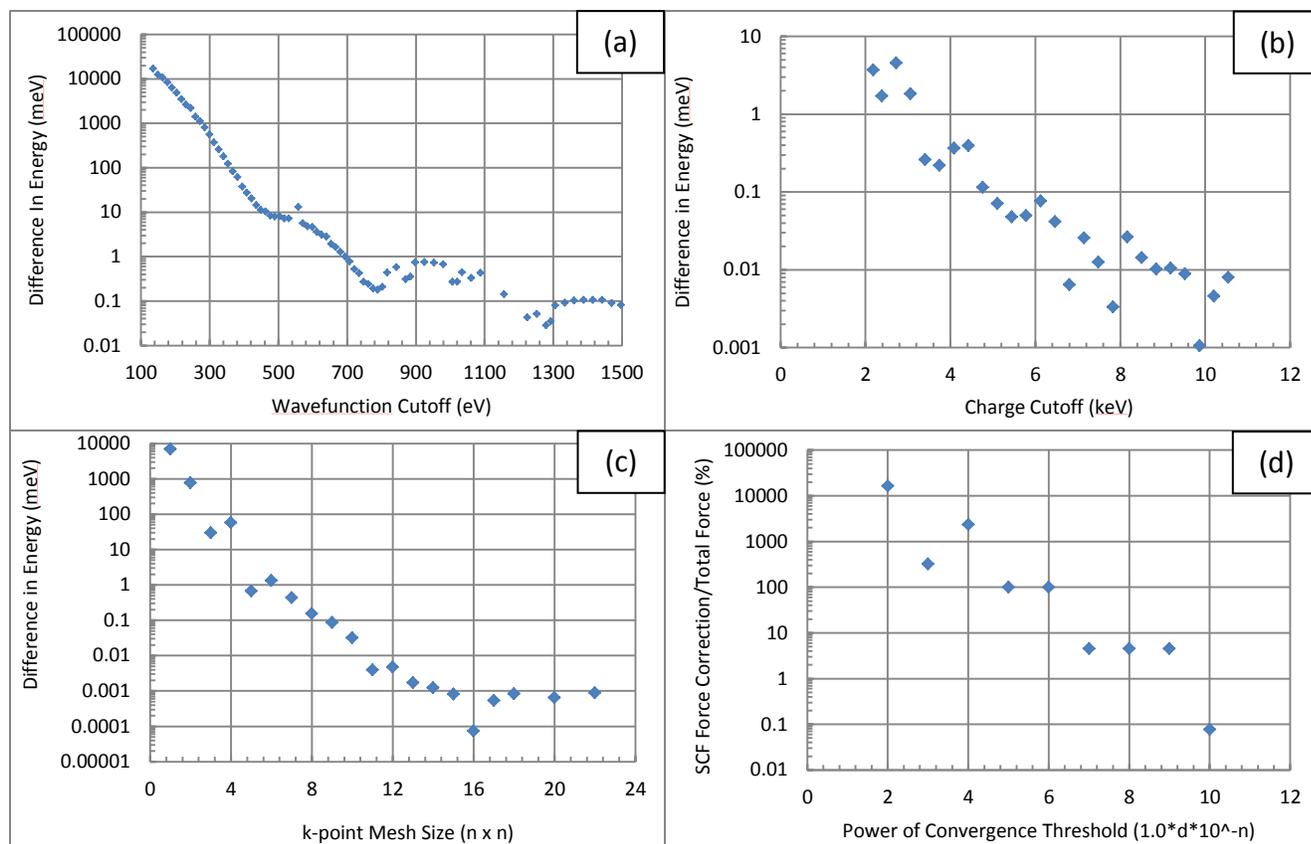
<sup>2</sup> <http://www.quantum-espresso.org/>

## CALCULATION PARAMETERS

In principle, an infinite number of plane waves are required to fully expand the Kohn-Sham equations; however, contributions from higher energy components become small, allowing any components above a chosen energy to be ignored - this is referred to as the wavefunction cutoff. In order to calculate the energy of a structure, the energy functional must be integrated throughout the structure. In practice, this is accomplished by numerically integrating at a sampling of points throughout the Brillouin zone. The choice of these points can affect the result significantly – if not enough points are taken into account, the total energy will be quite far from the true value, but if too many points are calculated, computational time required will soon outpace the incremental gains in accuracy each additional point contributes. These points are typically arranged in a simple equally-spaced mesh in k-space, according to the Monkhorst-Pack method. This parameter must also be tested to ensure enough detail in the energy functional is being taken into account during calculations. For materials with sharp discontinuities in band structure, a much denser k-point mesh would be required to accurately reproduce the effects. Charge cutoff refers to the ‘ecutrho’ input parameter for PWscf, which is the kinetic energy cutoff for charge density and potential – similar to the wavefunction cutoff for plane waves.

## CONVERGENCE

Convergence of DFT calculations to a final result is dependent on many different factors, but the most direct of these is the specified convergence criteria ‘conv\_thr’, which specifies the maximum squared norm of the difference between charge density in two consecutive iterations that must be satisfied in order for the self-consistent calculation to be considered converged. Proper convergence for the MoS<sub>2</sub> system was investigated by varying wavefunction cutoff, charge cutoff, k-point mesh, and convergence criteria in order to quantify their effects on the total calculated energy. This allowed for selection of optimized criteria for performing calculations on the monolayer TMDC’s under study in future computations. A wavefunction cutoff of 816.3416 eV, charge cutoff of 6530.733 eV, k-point mesh of 4 by 4 by 1, and convergence threshold of ‘1.0d-8’ were used as a standard for these calculations, otherwise only varying the parameter under test as shown in Figure 4.



**FIGURE 4:** Effects of computational parameters on convergence of the total energy for MoS<sub>2</sub>

**(a)-(b)** Absolute difference in total calculated energy for the MoS<sub>2</sub> structure vs cutoff values

**(c)** Absolute difference in calculated energy for the MoS<sub>2</sub> structure vs k-point mesh size (square mesh)

**(d)** Ratio of SCF force Correction to total force in structure as a percentage

When comparing energies as described in later sections, ranges were found to be on the order of meV, therefore, appropriate choice of these cutoffs to ensure enough accuracy to resolve these differences was essential to performing accurate computations.

## BAND STRUCTURES OF $\text{MoS}_2$ AND $\text{WS}_2$

A simple band structure calculation was then done for both the  $\text{MoS}_2$  and  $\text{WS}_2$  structures. (which were assumed throughout to have the same lattice constants) This involved a PWscf ‘relax’ calculation of their respective unit cells, each followed by a PWscf ‘bands’ calculation, which were then interpreted by bands.x and plotted using the plotband.x modules of QE.

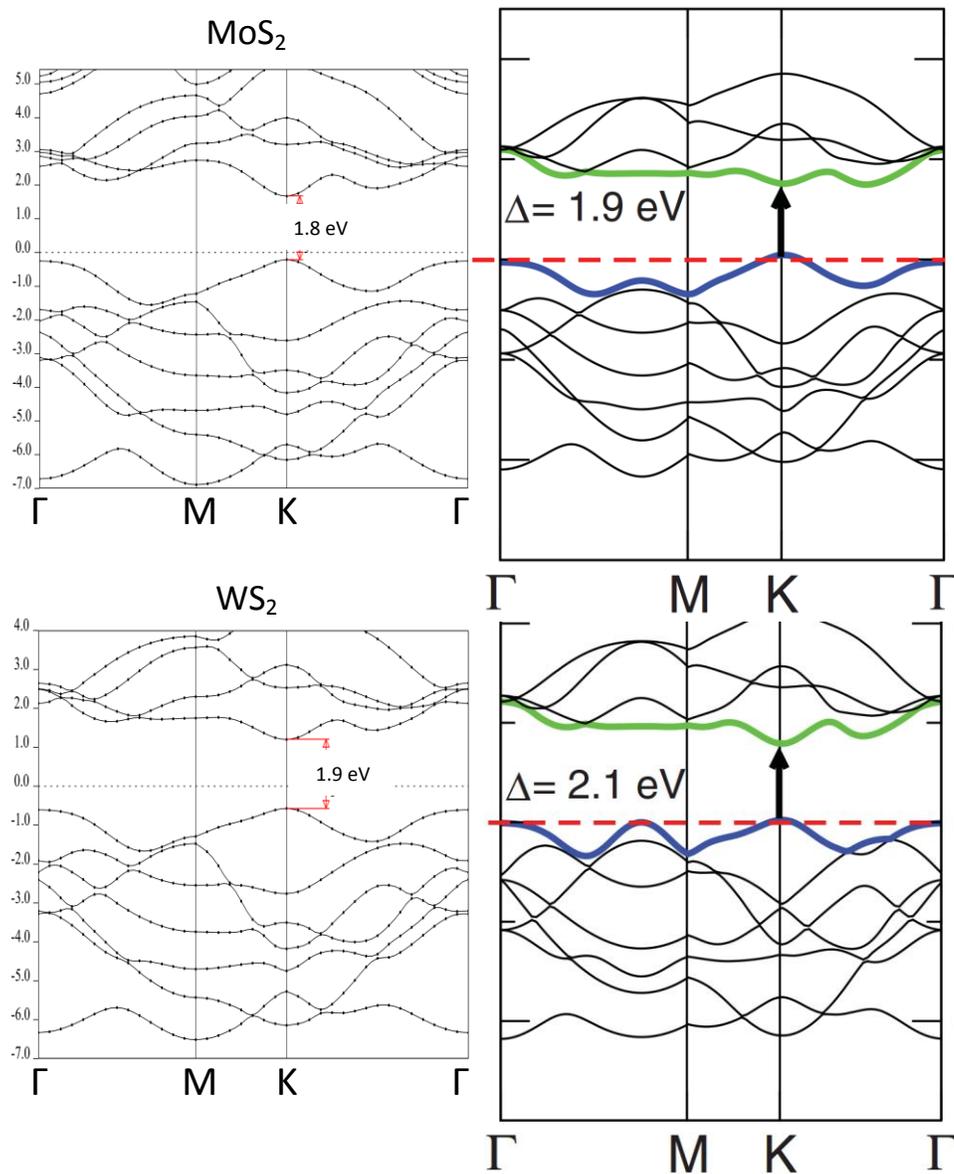


FIGURE 5: Calculated band structures of  $\text{MoS}_2$  and  $\text{WS}_2$ ,  $\text{ecutwfc}=60$  Ry,  $\text{ecutrho}=480$  Ry, pseudopotentials used: Mo.pbe-spn-rrkjus\_psl.0.2.UPF, S.pbe-n-rrkjus\_psl.0.1.UPF, W.pbe-nsp-van.UPF, compared with A. Kuc, et al. [2]

These band structures both prove that the implementation of QE was correct, and results are well in line with other studies on these systems, such as behavior near the K point - while at the same time show the differences in results most likely due to different pseudopotentials and computational parameters, such as behavior absent between the M and  $\Gamma$  points. As an early calculation, this served to also roughly indicate which pseudopotentials could be considered better, which was solidified by further research in the literature: for all subsequent calculations, Perdew-Burke-Ernzerhof (PBE) type functionals and Projector Augmented Wave (PAW) dataset pseudopotentials were chosen.

## THE ALLOY THEORETIC AUTOMATED TOOLKIT (ATAT)<sup>3</sup>

### CLUSTER EXPANSION

ATAT is a collection of tools related to cluster expansion and automating first-principles simulation of alloyed materials. The cluster expansion formalism allows a small number of known-energy configurations to be used to predict energies for any given atomic configuration by parametrizing the energy per atom as:

$$E(\sigma) = \sum_{\alpha} m_{\alpha} J_{\alpha} \langle \prod_{i \in \alpha'} \sigma_i \rangle$$

where  $\alpha$  is a cluster of  $i$  sites, as described in [32]. The coefficients  $J_{\alpha}$  represent the energetic interactions present in the alloy, and may be calculated from a small number of known configurations, which can be computed via first-principles. Using these known configurations, cluster expansion can allow ATAT to determine the energy of many other structures as well – which it does using the ‘maps’ module.

### MAPS

Maps can be interfaced with various first-principles codes in order to predict the energy of a range of alloyed structures, and in this case, the process was handled by a bash script called `runstruct_qe` which handles execution of Quantum ESPRESSO calculations on certain structures determined by maps. Once enough energies are known, maps can use these terms in cluster expansions in order to predict energies of other structures as well, making it much more efficient than simply calculating each structure individually directly from first-principles.[32]

---

<sup>3</sup> <https://www.brown.edu/Departments/Engineering/Labs/avdw/atat/>

Using a modified version of `runstruct_qe` (see Appendix), `maps` was then used to construct a composition vs energy diagram for the  $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$  system, using the following input lattice and the `-2d` runtime argument:

```
3.15 3.15 24.59 90 90 120
1 0 0
0 1 0
0 0 1
0.333333 0.666667 .125 Mo,W
0.666667 0.333333 .189255 S
0.666667 0.333333 .060745 S
```

This file is in a b c alpha beta gamma format consistent across ATAT, as described in its documentation. Ionic positions were from a previous structural relaxation calculation performed via QE. The Mo/W ion location specifies to `maps` which alloy to use for calculations. A multicomponent version of `maps` is also available in ATAT, which could be used for investigation of more complex tertiary TMDC alloys or beyond. Parameters for QE calculations called by `maps` were set in the modified `qe.param` file as follows:

```
ppMo Mo 95.95 Mo.pbe-spn-kjpaw_psl.0.2.UPF
ppW W 183.84 W.pbe-spn-kjpaw_psl.0.2.3.UPF
ppS S 32.06 S.pbe-n-kjpaw_psl.0.1.UPF
KPPRA 1000
CUT_WFC 65
CUT_CHG 500
PWCOMMAND pw.x
CONV_THR 1.0d-8
MIXING_MODE plain
MIXING_BETA 0.7
```

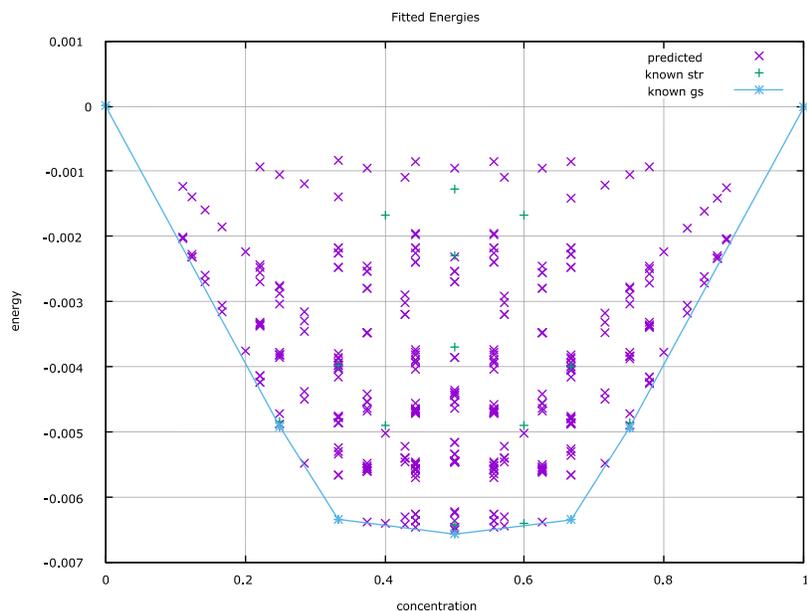
The pseudopotential for tungsten was retrieved from the THEOS database<sup>4</sup>, and others were on the pseudopotential download page for QE<sup>5</sup>. KPPRA refers to k-point density per reciprocal atom – other parameters are identical to the input parameters for QE discussed in the Calculation Parameters and Convergence sections above, except cutoffs are given here in units of Rydbergs.

With these parameters, `pollmach` was then run on `runstruct_qe` to handle communication with `maps` and automatically running the `runstruct` script in each folder generated by `maps` to calculate the energies of each structure – the entire process becomes automatic once both `maps` and `pollmach` are running. `Maps` will generate structures to have their total energy calculated, and use the information to infer energies of as many structures as are possible through cluster expansion techniques. `Mapsrep` was then used to plot the results generated by `maps` for the  $\text{MoS}_2$  system, shown in Figure 6.

---

<sup>4</sup> <http://theosrv1.epfl.ch/Main/Pseudopotentials>

<sup>5</sup> <http://www.quantum-espresso.org/pseudopotentials/>



**FIGURE 6: Composition vs Difference in energy in eV from a linear interpolation between pure compounds**

This plot was generated after calculations had been running for 113 CPU hours. Green crosses denote structures which have been calculated directly using DFT, while pink x's represent those obtained through cluster expansion of known terms. The energy range outlined here predicts that MoWS<sub>2</sub> will not display a miscibility gap, at least at low temperatures. Rather, the alloy should mix in order to minimize energy.

### SPECIAL QUASI-RANDOM STRUCTURES (SQS's)

In order to explore the implications of random vs ordered alloys, a representative structure is needed that will approximate the behavior of a fully random alloy. The Special Quasi-random Structures (SQS) method provides the mechanism necessary for generating such a structure, based on how many cluster terms it has in common with the fully random ideal case, which can be theoretically calculated. This allows a certain supercell to mimic the behavior of a random alloy while fitting within a finite supercell that can be solved via first-principles.

The monolayer TMDC alloy system could be further investigated by using the SQS tools available in ATAT to generate and then predict the energies of disordered structures and compare those to the energies found for ordered structures in order to shed light on order-disorder transformations. A limiting factor in research toward this goal was a lack of sufficient computational power, since in order to predict the energy of extremely disordered cells, necessarily larger supercells must be used, especially at extreme concentrations.

## CONCLUSIONS

Workflows for computational simulation of TMDC alloys via density functional theoretic methods using Quantum ESPRESSO and cluster expansion via ATAT were established and tested on the  $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$  system, proving the viability of these methods for further investigation of monolayer TMDC alloys and their various configurations and behavior. Conclusions that may be drawn from the tests performed include the fact that there should be no miscibility gap at low temperature for  $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$ , as well as the observation of a direct band gap for both monolayer  $\text{MoS}_2$  and  $\text{WS}_2$ . Appropriate cutoff values for the chosen pseudopotentials were also found, laying the foundation for future studies into ordered vs disordered TMDC alloy systems.

## REFERENCES

- [1] A. Kokalj, *Comp. Mater. Sci.*, **2003**, Vol. 28, p. 155. Code available from <http://www.xcrysden.org/>.
- [2] A. Kuc, N. Zibouche, and T. Heine, "Influence of quantum confinement on the electronic structure of the transition metal sulfide TS(2)," *Phys. Rev. B*, vol. 83, no. 24, p. 245213, 2011.
- [3] S. Ahmad and S. Mukherjee, "A Comparative Study of Electronic Properties of Bulk MoS<sub>2</sub> and Its Monolayer Using DFT Technique: Application of Mechanical Strain on MoS<sub>2</sub> Monolayer," *Graphene*, vol. 3, no. October, pp. 52–59, 2014.
- [4] P. W. Ayers, "Chapter 12: Density-Functional Theory," 2004, pp. 86–93.
- [5] K. Haule, "Density Functional Theory." 2009.
- [6] D. Roundy, "Density Functional Theory." 2005.
- [7] D. S. Sholl and J. A. Steckel, *Density Functional Theory : A Practical Introduction*. John Wiley & Sons, Inc., 2009.
- [8] A. P. Seitsonen, "Density functional theory in the solid state." 2009.
- [9] R. O. Jones, "Density functional theory: Its origins, rise to prominence, and future," *Rev. Mod. Phys.*, vol. 87, no. 3, 2015.
- [10] A. van de Walle, P. Tiwary, M. De Jong, D. L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, and Z.-K. Liu, "Efficient stochastic generation of special quasirandom structures," *Calphad Comput. Coupling Phase Diagrams Thermochem.*, vol. 42, pp. 13–18, 2013.
- [11] S.-H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, "Electronic properties of random alloys: Special quasirandom structures," *Phys. Rev. B*, vol. 42, no. 15, pp. 9622–9649, Nov. 1990.
- [12] P. J. Hasnip, "Electronic structure , plane waves and pseudopotentials." 2009.
- [13] E. S. Kadantsev and P. Hawrylak, "Electronic structure of a single MoS<sub>2</sub> monolayer," *Solid State Commun.*, vol. 152, no. 10, pp. 909–913, 2012.
- [14] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nat. Nanotechnol.*, vol. 7, no. 11, pp. 699–712, 2012.
- [15] G. Yizhi, "First principles study of charge density waves, electron-phonon coupling, and superconductivity in transition-metal dichalcogenides," Georgetown University, 2013.
- [16] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, and W. Tang, "First principles study of structural, vibrational and electronic properties of graphene-like MX<sub>2</sub> (M=Mo, Nb, W, Ta; X=S, Se, Te) monolayers," *Phys. B Condens. Matter*, vol. 406, no. 11, pp. 2254–2260, 2011.
- [17] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Phys. Rev. B*, vol. 59, no. 3, pp. 1758–1775, 1999.
- [18] S. Narasimhan, "How To Do Simple Calculations With Quantum ESPRESSO: I." .
- [19] K. Refson, "Introduction to DFT and the plane-wave pseudopotential method." 2014.
- [20] J. Kang, S. Tongay, J. Li, and J. Wu, "Monolayer semiconducting transition metal dichalcogenide alloys: Stability and band bowing," *J. Appl. Phys.*, vol. 113, no. 14, pp. 1–7, 2013.
- [21] Z. M. Wang, *MoS<sub>2</sub>*, vol. 21. Cham: Springer International Publishing, 2014.
- [22] A. van de Walle, "Multicomponent multisublattice alloys, nonconfigurational entropy and other additions to the Alloy Theoretic Automated Toolkit," *Calphad*, vol. 33, no. 2, pp. 266–278, Jun. 2009.
- [23] L.-Y. Gan, Q. Zhang, Y.-J. Zhao, Y. Cheng, and U. Schwingenschlögl, "Order-disorder phase transitions in the two-dimensional semiconducting transition metal dichalcogenide alloys Mo(1-x)W(x)X<sub>2</sub> (X = S, Se, and Te)," *Sci. Rep.*, vol. 4, p. 6691, 2014.
- [24] D.-A. Robinson and P. O. Conbhui, "Phonon Transport in Nanostructures," 2011.
- [25] L. Paulatto, "Pseudopotential methods for DFT calculations." pp. 1–17, 2008.
- [26] G. Kresse, "Pseudopotentials ( Part II ) and PAW," no. Part II. 2005.
- [27] P. Giannozzi, "Quantum simulations of materials using Quantum ESPRESSO." 2012.
- [28] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, "Special Quasirandom Structures," *Phys. Rev. Lett.*, vol. 65, no. 3, pp. 353–356, Jul. 1990.
- [29] G. Wang, C. Robert, A. Suslu, B. Chen, S. Yang, S. Alamdari, C. Gerber, T. Amand, X. Marie, S. Tongay, and B. Urbaszek, "Spin-orbit engineering in transition metal dichalcogenide alloy monolayers," *ArXiv e-prints*, vol. 6, pp. 1–9, 2015.
- [30] J. A. Reyes-Retana and F. Cervantes-Sodi, "Spin-orbital effects in metal-dichalcogenide semiconducting monolayers," *Sci. Rep.*, vol. 6, no. October 2015, p. 24093, 2016.
- [31] K. Burke, *The ABC of DFT*. Irvine, CA, 2007.
- [32] A. van de Walle, M. Asta, and G. Ceder, "The alloy theoretic automated toolkit: A user guide," *Calphad*, vol. 26, no. 4, pp. 539–553, Dec. 2002.
- [33] G. Kresse, "The PAW and US-PP database." 2005.
- [34] E. Pehlke, "The Plane-Wave Pseudopotential Method." 2006.
- [35] J. R. Chelikowsky, "The pseudopotential-density functional method applied to nanostructures," *J. Phys. D-Applied Phys.*, vol. 33, no. 8, pp. R33–R50, 2000.
- [36] H. P. Komsa and A. V. Krasheninnikov, "Two-dimensional transition metal dichalcogenide alloys: Stability and electronic properties," *J. Phys. Chem. Lett.*, vol. 3, no. 23, pp. 3652–3656, 2012.
- [37] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, and A. Kis, "Ultrasensitive photodetectors based on monolayer MoS<sub>2</sub>," *Nat. Nanotechnol.*, vol. 8, no. 7, pp. 497–501, 2013.

## APPENDIX

```
#!/bin/bash
# This bash script is for the interface between ATAT and Quantum-ESPRESSO v5.0
# The final result will be in eV unit
# Produced by GAO Zhe, Mater. Sci & Eng, Seoul Nat'l Univ., S. Korea
# Modified by L. Bruzgulis, CNSE, SUNY University at Albany, USA

# Set some calculation parameters here, which contents:
# cut-off energy for wave-functions and charge density;
# gaussian broadening parameter for smearing;
# especially, the directory where restore your pseudo-potential files.
# Definitely, you can directly set these and some other parameters
# in the input file-creating part.
#####
# Recommend from the official manual of Quantum-ESPRESSO:      #
# for Norm-Conserving pseudo-potential, the cut-off for charge #
# density does not need to be setted (or, 4 times of ecutwfc).  #
# But for ultrasoft pseudo-potential, set the cut-off for charge #
# density to 8~10 times of cut-off for wavefunctions.          #
#####
PseudoDIR=".../pseudopotentials"
ATAT_DIR=".../ATAT_binaries"

# Try to find the parameter setting file, which contents the
# information for species of elements
# If this file does not exist, the script will stop
ParamFile="qe.param"
if [ ! -e $ParamFile ]; then
  ParamFile="./qe.param"
  if [ ! -e $ParamFile ]; then
    ParamFile="../qe.param"
    if [ ! -e $ParamFile ]; then
      echo " Cannot find the param file qe.param, stop the code!"
      exit 1
    fi
  fi
fi

# Set the k-points density in reciprocal space
KPPRA=`grep "KPPRA" $ParamFile | awk '{print $2}'`
CUT_WFC=`grep "CUT_WFC" $ParamFile | awk '{print $2}'`
CUT_CHG=`grep "CUT_CHG" $ParamFile | awk '{print $2}'`
CONV_THR=`grep "CONV_THR" $ParamFile | awk '{print $2}'`
MIXING_MODE=`grep "MIXING_MODE" $ParamFile | awk '{print $2}'`
MIXING_BETA=`grep "MIXING_BETA" $ParamFile | awk '{print $2}'`

# Set the command to run pw.x, for example,
# if you wanna run it with 4 cores/cpus, set it
# as "$MPI_PATH/mpirun -n 4 $QE_PATH/pw.x"
PWCOMMAND=`grep "PWCOMMAND" $ParamFile | awk '{print $2}'`
echo "$PWCOMMAND"
# echo "set pw.x command"

# Create the fist part of input file for QE v5.0
cat > pwscf.in <<EOF
&control
  calculation = 'relax' ,
  prefix = 'pwscf' ,
  outdir = './temp/' ,
  pseudo_dir = '$PseudoDIR' ,
  disk_io = 'none',
/
&system
ibrav = 0 ,
```

```

ecutwfc = ${CUT_WFC},
ecutrho = ${CUT_CHG},
EOF

#echo "Find the atom number and elements number"
# Then, write them into the input file

NAT=`$ATAT_DIR/cellcvrt -f < str.out | tail -n +7 | wc -l`
NTYPE=`$ATAT_DIR/cellcvrt -f < str.out | tail -n +7 | awk '{print $4}' | sort -u | wc -l`
echo " nat = $NAT, " >> pwscf.in
echo " ntyp = $NTYPE, " >> pwscf.in

#echo "Create the temp input file, which corresponds to"
# the second big part. After creating, it will be
# attached follow the former one and deleted.
cat > pwscf.tmp <<EOF
/
&electrons
conv_thr = $CONV_THR,
mixing_mode = '$MIXING_MODE',
mixing_beta = $MIXING_BETA,
/
&ions
ion_dynamics = 'bfgs',
/
CELL_PARAMETERS angstrom
EOF
cat pwscf.tmp >> pwscf.in
rm -f pwscf.tmp

# Find and write the lattice vector information
cat str.out | $ATAT_DIR/cellcvrt -c -sig=9 >> cvrtstr.tmp
cat cvrtstr.tmp | head -6 | tail -n +4 >> pwscf.in

# Find and write the information for element type, mass
# and pseudo-potential files' name
echo "ATOMIC_SPECIES" >> pwscf.in
INT=1
while [ "$INT" -le "$NTYPE" ]; do
KIND=`pp`$ATAT_DIR/cellcvrt -f < str.out | tail -n +7 | awk '{print $4}' | sort -u | head -${INT} | tail -1`
grep "$KIND"$ParamFile | awk '{print " " $2, $3, $4}' >> pwscf.in
let "INT++"
done

# Find and write the atoms' position to input file
echo "ATOMIC_POSITIONS angstrom" >> pwscf.in
cat str.out | $ATAT_DIR/cellcvrt -c -sig=9 | tail -n +7 | awk '{print " " $4, $1, $2, $3}' >> pwscf.in

# Find the k-points mesh, the mesh will be created
# by Monkhorst-Pack method
echo "K_POINTS automatic" >> pwscf.in
nbat=`$ATAT_DIR/cellcvrt -pn < str.out`
echo " " `( echo $KPPRA $nbat | awk '{print $1/$2}' ; cat str.out | $ATAT_DIR/cellcvrt -f | head -3 ) | $ATAT_DIR/kmesh -q -r` 0 0 0 >>
pwscf.in

# Run pw.x for calculation
$PWCOMMAND < pwscf.in > pwscf.out

# Abstract the final total energy to "energy" file
# in the unit of eV
FERy=`grep '!` pwscf.out | tail -1 | cut -c 35-50`
FEeV=`echo "scale=15; $FERy*13.605698066" | bc -l`
echo "$FEeV" > energy

```