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An Analysis of Two Dimensional Materials: Monolayer and Bulk

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AN ANALYSIS OF TWO DIMENSIONAL MATERIALS:

MONOLAYER AND BULK

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For my wife, who went to bed alone many nights this past year.

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I would like to acknowledge all the people that have believed in me and supported me. My family has been so understanding with how much I had to work, but few people (besides my wife) had to face more craziness than my advisor. Thank you all!

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ABSTRACT

Two Dimensional Materials has been the focus of much research in the past decade. We review 145 stable two dimensional materials in both bulk and monolayer. [4] We compare their final electronic properties and discuss the results. Specifically, we discuss notable materials that have transitions between bulk and monolayer. Additionally, we use both the bulk and monolayer data to search for structural trends that may be corralated with the electronic properties using machine learning techniques. We find that our machine was able to produce results that predict the basic electronic properties with approximately 65% accuracy.

CHAPTER 1

INTRODUCTION

Two Dimenional Materials have been a focus of the scientific community since the isolation of graphene from graphite in 2004. (cite) Interest in this class of materials streches as far back as the mid 20th century with the prediction of the existence of graphene to explain graphite's electronic properties. [2]

Now, the popularity of two dimensional materials has exploded as they can often present properties that differ from the Bulk material and open these materials to various applications, such as photovoltaics and semiconductor electronics. [1]

We used the structure data for 145 materals from Heine et al[4] and optimzied them using Crystal. Crystal was ideal for its capability to handle empty space in the material through its use of guassian atomic basis sets. We used this advantage to optimize the monolayer structures. Properties were also found using Crystal from the optimized materials.

1.1 Two Dimensional Materials: Definition

We define two dimensional materials as materials that are stable at one to a few atoms thick. Graphene falls under this definition as it is stable at one atom thick, but this defintion opens the class to many materials. Most notiably, Molybdinum Sulfide (MoS_2) is approximately three atoms thick in the monolayer, one molybdinum and two sulfur. MoS_2 is known for the interesting transtion from an indirect to direct semiconductor from bulk to monolayer. [3]

1.2 Machine Learning

Machine Learning allows for the discovery of trends and corralations through the use of various computational techniques. Researchers have been using machine learning for applications ranging from behavioral sciences to medicine. With bulk and monolayer two dimensional materials being so close in structure, the data affords opportunity to search for a corralation between changes in structure and electronic properties. We attempt to use machine learning to find corralations

between structural characteristics and electronic properties. An algorithum capable of discerning simple electrical characteristics from structure would be a useful, time-saving tool in applications such as electrical and material engineering.

CHAPTER 2

MONOLAYER AND BULK TWO DIMENSIONAL MATERIALS

We began by optimizing 145 two dimensional structures found in Heine et al [4]. From the optimized structure, we determine their band structure and basic electronic properties.

2.1 Methodology

Optimal structure and properties were found in Crystal. Crystal was preferred to other forms of material processing software for its treachment of atomic basis sets. Crystal uses guassian basis sets which allows for easy processing of empty spaces in materials. This afforded us the ability to compute the monolayer structure by optimizing the bulk material where the interlayer spacing was increased to approximately 100 Å.

2.2 Monolayer Versus Bulk

From Crystal, we take the most basic electronic information and can see notable changes at that level, as shown through a few key examples in Table 2.1.

These distinctions don't stop at the two more popularly known two dimensional materials, Graphene and MoS_2. Just taking from this small sampling, we see that there are significant energy

Table 2.1: Examples of materials' electronic properties

Material Name	Bulk	Monolayer
Graphene	Semiconductor	0 eV Band Gap
MoS_2	1.7 eV Indirect Band Gap	1.7 eV Direct Band Gap
$HfTe_2$	0.29 eV Indirect Band Gap	0.75 eV Indirect Band Gap
ZrS_2	1.57 eV Indirect Band Gap	2.43 Indirect Band Gap
TiS_2	1.2 Indirect Band Gap	1.9 Direct Band Gap
Fluorographene	5.4 eV Indirect Band Gap	5.4 Direct Band Gap

changes across most materials. Although the majority of occurances are not so significant as Graphene, there are changes seeming to arrive from structure change.

2.2.1 Material Changes from Bulk to Monolayer

Band Gap Transformation. In a majority of cases (as exemplified in Table 2.1), we see that the energy Band Gaps change in size. Looking specifically at Zirconium Sulfide, we see nearly an electron volt in change between the Bulk Band Gap and the Monolayer. This persisted in varying degrees across most materials, as is shown with the smaller change in Hafnium Telluride. Even these small changes are of serious interest as fractional differences in energy can move these materials across a spectrum of application.

Notably, in few instances, we see the change from Indirect to Direct semiconductor band gap. In Table 2.1, we include Titanium Sulfide and Fluorographene as examples of these occurances in the data. It seems that Molybdinum Sulfide, while having one of the most applicable changes, is not alone in this family of two dimensional materials. Titanium Sulfide and Fluorographene are certainly points for continued research.

2.2.2 van der Waals Interaction

In two dimensional materials, the interactions between layers in the bulk structure is attributed to van der Waals interactions. When speaking on heterostructures, where two unique layers are stacked, van der Waals forces are considered to be the dominate interaction between the two layers. [5] [7]

Structural Significance. As is apparent in the existance of heterostructures [5] [7], the structural relationship between layers in a bulk two dimensional material seem to have some effect on the electrical properties, whether due to van der Waals interactions or not. However, it is apparent that the monolayer structure does not have any van der Waals interactions.

Without the van der Waals interactions, we can assume that the electron orbitals that extend perpendicular to a layer may be responsible for the changes in electronic properties between the monolayer and bulk. This would only be true for compounds that have unpaired electrons present in the orbital. From Table 2.1, we find that this agrees for materials like WS_2 and Graphene, but not for MoS_2. Even further, we see no change for ZnO when it can have these same orbital relations.

CHAPTER 3

MACHINE LEARNING APPLIED TO MONOLAYER AND BULK MATERIAL

There are many types of Machine Learning Techniques and most can be generally catagorized into two types. In general, the goal of machine learning is to find the underlying function that may describe the relationship between data and certain classes that we wish to predict. In the case of Regression problems, the actual form of the function is attemped to be found. Classification problems are different in that we attempt to find functions that associate certain data points with one of various classes.

In our case, we attempt to use the structural data along with other easily attained features to discern whether the material is a conductor, insulator, or semiconductor. A machine that can identify if a material has certain basic electrical properties without the need to examine the band structure could be immensly helpful in academic and industrial research.

3.1 Feature Selection

In order for the machine to be impactful, we chose to focus on features that could be known without analyzing the band structure of materials. Table 3.1 shows a few data points with a few of our chosen features and their respective electronic classes. The additional features included the most basic form of electronic information, simply the total number of electrons in the compound and total number of valence electrons in the compound and per atom. For elemental compounds, such as graphene, the feature values are the same.

To optimize the machine's design, we employed feature selection through the creation of many machines each trained and tested with various levels of features. The machine that is evaluated at doing the best allows us to eliminate needless features.

Table 3.1: Examples of training data to be Inputed into the support vector classifier

Material Name	Form	Lattice Vector a	Lattice Vector b	Lattice Vector c	Angle α	Angle β	Angle γ
Graphene	Monolayer	2.45315	2.45205	19.97477	89.99	90.00	120.11
MoS_2	Bulk	3.12273	3.12247	15.20568	89.95	89.07	119.99
WS_2	Bulk	3.13511	3.13500	5.37281	90.00	90.00	120.01
$HfSe_2$	Bulk	3.68672	3.68668	15.18711	90.00	88.26	120.02
ZnO	Monolayer	3.25973	3.25975	19.97694	90.00	90.00	120.00

3.1.1 Support Vector Classifier

Support Vector Machines, or in our case Classifiers, are a type of machine learning technique that divide the data in the feature space using a hyperplane in that space. The feature space is a space of dimension equal to the number of features in the data. A Support Vector Classifier (SVC) finds a hyperplane in this space that divides the data into the respective classes. We chose to use a SVC as it is easy to train and scales well to higher dimensional data. This allows for our more simple feature selection. The difficulty is that it requires much data to train. We use 80% of the bulk and monolayer data to train the machine and 20% to test it.

We chose to use SVC from the Scikit-learn library in python. [6] SVC's require a kernel function to be the shape of the hyperplane. They also require the input of a penalty parameter for error. The penalty parameter determines how strict the precision of the hyperplane must be. In our work, we attempted many available kernel functions as well as many values for the penalty parameter.

3.2 Support Vector Machine Selection

Table 3.2 contains the information on the machines trained and how they scored.

Table 3.2: Accuracy scores from the 63 support vector classifiers with varied features for feature selection

Machine Label	Score (Mean Accuracy)
1	12.4%
2	12.6%
3	11.4%
4	12.2%
5	13.8%
6	12.4%
7	10.9%
8	18.5%
9	20.6%
10	22.3%
11	19.9%
12	17.5%
13	23.6%
14	25.1%
15	25.0%
16	22.6%
17	23.4%
18	25.2%

Table 3.2 Continued: Accuracy scores from the 63 support vector classifiers with varied features for feature selection

Machine Label	Score (Mean Accuracy)
19	22.6%
20	24.7%
21	20.1%
22	30.7%
23	20.4%
24	27.3%
25	25.0%
26	31.6%
27	32.0%
28	19.8%
29	18.0%
30	17.9%
31	29.2%
32	27.9%
33	21.6%
34	10.3%
35	22.5%
36	31.1%
37	17.1%
38	22.2%
39	11.0%
40	29.0%
41	18.2%
42	30.2%
43	42.9%
44	64.9%
45	29.3%
46	30.4%
47	47.3%
48	65.1%
49	30.9%
50	49.3%
51	40.2%
52	22.3%
53	22.0%
54	30.9%
55	42.5%
56	45.1%
57	46.7%
58	50.1%
59	49.8%

Table 3.2 Continued: Accuracy scores from the 63 support vector classifiers with varied features for feature selection

Machine Label	Score (Mean Accuracy)
60	50.7%
61	47.9%
62	39.6%
63	50.0%

The highest scoring machines in Table 3.2 are those associated with the features including either lattice vector a or b and angle α or β, but both included c, γ, and the basic electonic information. The ideal kernel function was found to be linear in the feature space and have a penalty parameter of 100.

3.3 Interpretation of Results

Since vectors a and b and angles α and β seem to be linearly dependent, feature selection finds that the best predictive result is found by not considering these features. Unneeded features can confound the results and dampen the predictive power of a machine. Excluding these features could have been expected, but they were included in the original analysis for completeness. Additionally, as the values for both the vectors and angles are not entirely the same, the small differences could have had a large impact on the results.

Our best result at 65% is a proof of concept that machine learning can be used to solve these types of problems. Specifically for the determination of these basic electronic properties from structure, more work and more advanced techniques will need to be employed to impove accuracy.

CHAPTER 4

FINAL DISCUSSION

4.1 Bulk Versus Monolayer

The analysis of the 145 structures supports the interesting phenomena that accompanys the transition of two dimensional materials from bulk to monolayer. van der Waals' forces are responsible for the connection between layers in these compounds. [5] [7] In the case of monolayer, the lack of van der Waals forces is, at least, partially responsible for the change in electronic properties as the transition is structural.

4.1.1 Further Study

Many things about two dimensional materials is not known. Research has been conducted in the creation of heterostructures and their properties. [5] [7] We plan to attempt to create all possible heterostructures from the 145 two dimensional materials in future works. Additionally, the transition state is not yet known. It is understood that there exists a electronic transition from bulk to monolayer for many materials, but at what amount of layers does the transition occur is not yet known. We will attempt to search for this in future works.

4.2 Machine Learning Applied to Two Dimensional Materials

As the transition from bulk to monolayer is structural, machine learning was employed to study the association between structure and electronic properties. As previously one would need to compute the band structure to find any useful information, a machine that can perform this task can be useful. We used a Support Vector Classifier to identify distinguishing features in the data and was able to predict electronic properties between three classes (Conductor, Insulator, Semiconductor) with approximately 65%. Further advancement could be done to improve the results.

4.2.1 Future Study

Many possible features were not included in this proof of concept. The goal of excerises in machine learning is to simplify the way we view a set of data. Through the identification of trends, we can open researchers to simply predict outcomes from their data. For our work, many new features could be included that would improve the predictive power of the machine, such as electronegativity. Additionally, to improve the versatility of the machine, structural information can be normalized and generalized. Ultimately, in machine learning, what matters is data. Though the collection of additional data points, through heterostructures and varied layer amounts for these materials, we can better the machines capability to locate the trends.

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BIOGRAPHICAL SKETCH

I received my undergraduate degree in Physics and Mathematics from Florida State University in 2016. At that point, I found more serious research interests in materials and enrolled in the Material Science and Engineering Program at Florida State University. I have learned much in that time and enjoyed researching this branch of two dimensional materials. I plan on continuing my education with pursuing a Doctorate degree in either Physics with a focus on Materials or in Material Science.