Variations in the electronic and chemical properties of van der Waals heterostructures

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Abstract

In this thesis, a systematic study is performed on the formation of van der Waals heterostructures using dispersion-corrected density functional theory calculations within the generalised gradient approximation (GGA). Initially, an understanding of the current landscape of two-dimensional (2D) single layer materials was developed for a few selected compounds. Namely, graphene, boron nitride, metal dichalcogenides, and stanene are reviewed in the literature. Following the review, combinations of these materials are then modelled for bilayer and trilayer heterostructures, to understand the interactions and establish general principles for custom-designed van der Waal heterostructures.

In the stanene-graphene bilayer system, differences in physical and electronic properties from their pure counterparts could be observed. Electronic states correlated with variations in the buckling parameter of the tin layer reveal a competition between $sp^2$ and $sp^3$ hybridisation schemes. Observable changes in the layers are identified through their corresponding properties (i.e., buckling, buckling lengths, bond angles, charge transfer, electronic structures, electron densities, layer spacings, lattice parameters, orbital energies). A transition range of ~ 7% strain for the Dirac semimetal was demonstrated in single layer stanene. This transition can be controlled by strain/composition/stacking order to yield a metal-insulator transition in special circumstances in bilayer systems.

Investigations of trilayer combinations of stanene, graphene, and boron nitride in various stacking configurations revealed that asymmetric stacking of the layers resulted in increased interaction, while symmetrical stacking resulted in decreased interaction. The maximum binding energy (BE) difference was $\Delta BE = -16.073$ meV/Å². Stacking of the
layers results in two types of buckling, which can be classified into two major categories of configurations: they are either co-aligned or rotated. The rotated configurations generally show a more stable configuration. Furthermore, it was found that, for the BN/Stanene/BN trilayer combination of heterostructures, the electronic structure resembled that of the ideal stanene monolayer so that the electronic structure and Dirac dispersion of stanene are preserved.

Layer interactions in these 2D composites are more complex than for pure van der Waals forces. These interactions can yield emergent and unexpected behaviour. Ab initio calculations were deployed to rationalise the existing experimental results on few-layer MX₂ systems. It is found that the non-magnetic state of VSe₂ is energetically favourable by 0.225 eV/Atom. This result is in agreement with real sample measurements that showed non-magnetic favourability.

A common feature of all the diverse vdW heterostructures studied is that layer interactions play an important role. New states arise due to the mixed nature of bonding, which includes ionic and covalent contributions in addition to the conventional vdW interaction. Clearly, changing the layer compositions (i.e., metallic/insulator/semi-metallic/semiconductor, elemental/non-elemental, local dipoles, atom sizes), stacking order (i.e., stacking order, symmetric/asymmetric, buckling/planar), strain (i.e., compressive/tensile), and layer thickness offers a way to achieve atomic-scale engineering.
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Table of Contents

Certification ................................................................................................................................. 1
Abstract .......................................................................................................................................... 2
Acknowledgements ...................................................................................................................... 4
Table of Contents .......................................................................................................................... 5
1. Introduction ................................................................................................................................. 8
   1.1. Purpose of work .................................................................................................................. 8
   1.2. Outline .................................................................................................................................. 9
2. Literature Review: Single layer building blocks for van der Waals heterostructures ................................................................................................................................. 10
   2.1. Overview ............................................................................................................................. 10
   2.2. Motivation ........................................................................................................................... 11
   2.3. Two dimensional single-layered materials ........................................................................ 13
       2.3.1. Graphene ................................................................................................................... 13
       2.3.2. Boron Nitride ............................................................................................................. 19
       2.3.3. Stanene ...................................................................................................................... 23
       2.3.4. Transition metal dichalcogenide (MX$_2$) compounds ........................................... 29
   2.4. van der Waals (vdW) heterostructures ............................................................................. 34
       2.4.1. Heterostructures to van der Waals heterostructures .............................................. 34
       2.4.2. Bilayer heterostructures: .......................................................................................... 38
       2.4.3. Trilayer heterostructures ........................................................................................... 44
       2.4.4. Multilayer heterostructure ......................................................................................... 48
   2.1. Summary ............................................................................................................................. 50
3. Density Function Theory and computational methods .......................................................... 51
   3.1. Introduction ......................................................................................................................... 51
   3.2. First-principles calculations .............................................................................................. 52
3.3. Theoretical basis ............................................................................................... 54
  3.3.1. Many-Body Description ........................................................................... 54
  3.3.2. Born-Oppenheimer approximation ......................................................... 56
  3.3.3. Density functional theory ....................................................................... 57
3.4. Computational methods ..................................................................................... 69
  3.4.1. Basis sets ................................................................................................... 69
  3.4.2. Self-Consistency Field method ................................................................ 72
  3.4.3. Software and Hardware .......................................................................... 73
  3.4.4. Testing convergence ................................................................................ 73
  3.4.5. Structure optimization ............................................................................ 74
  3.4.6. Construction and calculation of heterostructure ................................... 75

4. Tuning the electronic structure in stanene/graphene bilayers using strain and gas adsorption .................................................................................................................. 78
  4.1. Overview ...................................................................................................... 78
  4.2. Introduction .................................................................................................. 79
  4.3. Results and discussion .................................................................................. 81
    4.3.1. Strain-structure relationship for monolayer stanene ............................ 81
    4.3.2. Lattice-strain in epitaxial matched stanene-graphene bilayers .......... 82
    4.3.3. Anisotropic H2O adsorption in the stanene-graphene bilayer .......... 95
  4.4. Conclusions .................................................................................................. 97
  4.5. Computational Methodology ........................................................................ 98

5. The effect of symmetrical and asymmetrical stacking in trilayer heterostructures of stanene with hexagonal boron nitride and graphene .......... 100
  5.1. Overview .................................................................................................... 100
  5.2. Introduction ................................................................................................ 101
  5.3. Results and Discussion .............................................................................. 104
    5.3.1. Chemical Structure ................................................................................ 104
    5.3.2. Electronic Structures ............................................................................. 111
Chapter 1

1. Introduction

1.1. Purpose of work

This work aims to probe the interactions within two-dimensional van der Waals heterostructures, following the work of previous discoveries in semiconducting heterostructures and 2D materials that are each individually of great importance and are awarded the Noble Prize in Physics in 2000[1] and 2010[2] respectively. Further interest in this field has been garnered with the recent developments in topological materials which were also awarded the Noble Prize in Physics in 2016[3]. Both heterostructures and 2D materials provide a fantastic platform for material design, where there are many new opportunities for the discovery of new novel effects and devices. Recently many new studies were performed regarding the synthesis and as well the modelling of these possible heterostructures as they offer a multitude of new quantum states including 2D superconductors[4], 2D spin gapless semiconductors[5], and 2D topological insulators[6]. Meanwhile, the primary driver behind the search for these new novel phenomena is for their applications in electronics in the semiconducting industry for more efficient and smaller devices. Due to the atomically thin nature of these new materials, the chemistry and physics are primarily dominated by interface-effects. This study aims to investigate some of the interface effects between the individual layers in heterostructures within the van der Waals interaction range as a step towards the rational design of new functionalities.
1.2. Outline

That chapters in thesis are arranged in the following manner:

- Chapter 2 provides a literature review of the current landscape of 2D materials with focus on the building blocks use in this thesis that is graphene, stanene, hexagonal boron nitride and MX$_2$ 2D materials.

- Chapters 3 provides an overview of the theory behind Density Functional and some of the techniques and tools used to model and analyse the structures in this thesis.

- Chapter 4 examines the effect of strain in the monolayer stanene and how it changes the stability and electronic structure in the bilayer stanene/graphene for various configurations and rotations.

- Chapter 5 examines asymmetric and symmetric layer compositional stacking in combinations of graphene, stanene, and hexagonal boron nitride in different trilayer configurations and their effect on the stability and electronic structure.

- Chapter 6 examines the 3D to 2D transition in single crystal VSe$_2$ and the effect on the stability, magnetism, and electronic structure.

- Chapter 7 provides a highlight of some of the main findings in each of the studies, along with prospects for further work.
2. Literature Review: Single layer building blocks for van der Waals heterostructures

2.1. Overview

There has been a rapid rise in research activities surrounding the topic of two-dimensional (2D) materials since the Nobel Prize was awarded in 2010 for the synthesis of graphene[2]. These discoveries and theories also directly led to the 2016 Nobel Prize for the discovery of topological phases of matter[3]. More recently there has been a focus on constructing novel van der Waals heterostructures by stacking multiple 2D materials. This chapter provides a literature review of the current field. Section 2.2 gives the motivation for the field of research by explained the technological relevance of these novel electronic materials. Section 2.3 briefly reviews the area of single-layer 2D materials with a focus on the building blocks used in this thesis, namely boron nitride, stanene, graphene, and transition metal dichalcogenides. Section 2.4 introduces heterostructures containing two or more layers, with the emphasis on combinations of BN, stanene and graphene, and the role of interface interactions leading to emergent van der Waals heterostructure phenomena.
2.2. Motivation

The continuous development that is going on in the field of condensed matter physics is one result of the ever-growing demand in the semiconducting and electronics industry for more efficient and smaller devices. With the predicted end of Moore’s law[7], and as the materials and fabrication technologies for miniaturisation reach their limits[8], new materials and technologies must be investigated[9-11]. The synthesis of the first 2D material, graphene[12], is one of the avenues that has opened a new way forward for the continued development of nanoelectronics. This synthesis subsequently inspired rapid growth in the development of many new 2D materials[13]. Now, with such a sizable arsenal of 2D materials, it was quickly realised that it would be possible to then use each 2D material as building blocks for new types of engineered composite nanomaterials[14], for example, 2D superconductors[4], 2D spin gapless semiconductors[5], and 2D topological insulators[6]. Due to the atomically thin nature of these new materials, the entire material is primarily dominated by interface-effects with highly susceptible properties. The material’s susceptibility to changes imposes limits on the ways that two layers can be stacked, based on the interactions between the layers. To make new heterostructure materials feasible and to enable the rational design of properties from first principles, it will be necessary to understand and model the types of interactions between the individual layers in heterostructures.
Depending on the type of interaction between the layers, a broad range of properties can emerge. Ultimately, it should be possible to select the desired properties by adjusting the layered composition, stacking order, strain, pressure, and temperature. Although *ab initio* calculations are a powerful technique in this field, more work is needed to establish the governing principles and fundamental theories that would allow rational materials design to help with atomic-scale engineering. Currently, it is necessary to evaluate each of the resulting properties on a case by case basis, and usually, it is still essential to perform an experimental synthesis to verify each property. To do this more efficiently, theorists must develop general rules guiding a more straightforward prediction of possible van der Waals heterostructures. It will only be possible to produce these general principles for heterostructures through investigating each case carefully with the goal of finding universal principles to apply on a wide range of materials.
2.3. Two dimensional single-layered materials

2.3.1. Graphene

2.3.1.1. Discovery of Graphene

The beginning of studies on graphene can be traced back to the English chemist Benjamin Collins Brodie who studied graphite through the oxidation of graphite which led to the determination of the atomic weight of graphite in 1859[15]. In the 20th century, with the introduction of X-Ray diffraction techniques in the 1912’s [16], the crystal structure of graphite was studied in 1916 by Kohlschütter and Haenni who also described what they called graphite oxide "paper" in 1918[17], which is a precursor of graphene. Theoretical studies into the electronic structure of both graphene and graphite appeared in a seminal paper by P.R Wallace in 1947[18]. With the development of electron microscopy techniques around that time[19], studies were put in place to fabricate and examine few-layered structures of graphite. The first images TEM images of few-layered graphite were published in 1948 by Ruess and Vogt [20]. After which an influx of studies began to populate the field, with first attempts at epitaxial growth[21] of graphene which, unfortunately, did not preserve the ideal electronic structure of graphene because of substrate-film interactions. Mechanical exfoliation was finally proved successful in 2004 by Novoselov and Geim[12] who went on to win the Nobel Prize for physics in 2010 “for ground breaking experiments regarding the two-dimensional material graphene”.

2.3.1.2. Structure of Graphene

Graphene is an allotrope of carbon, which consists of a nearly flat, single layer of carbon atoms in a hexagonal arrangement, as seen in Figure 2-1(a). The unit cell of graphene contains two carbon atoms in which, the carbon-carbon bond length is around 1.42 Å[22]. With only two carbon atoms in the lattice, the structure can be viewed as formed by two equivalent sub-lattices. The lattice symmetry of graphene is a six-fold symmetry with six mirror lines belonging to the P6mm 2D symmetry group. The lattice parameter of graphene is around 2.46 Å with minor buckling on the 0.01 Å order of magnitude, which is negligible and allows graphene to be defined as atomically flat, as shown in Figure 2-1(b).
2.3.1.3. The unusual electronic properties of graphene

\[ \hat{H} = \frac{\hat{p}^2}{2m^*} \]

Figure 2-2 Shown the various 3D HOMO-LUMO E-k diagrams that describes various different types of particles and the various forms of equation which model them, \( m^* \) refers to the effective mass, \( \hat{p} \) is the momentum operator, \( \hat{H} \) is the Hamiltonian, \( \sigma \) is the Pauli matrix, \( v_F \) is the fermi velocity and \( c \) is the speed of light. (A) Classical Schrödinger’s particle (B) Dirac particle, (C) Dirac particle in graphene with 2D pseudospin between the two sublattices (red and green). (D) Particles in bilayer graphene with pseudospin and left, right chirality (blue and yellow). Figure adapted from Ref. [23]

Since graphene is atomically flat and is only one atom thick, the modified dimensionality allows for fine tuning of the system’s band structure due to the two-dimensional confinement of the electron wavefunctions. The flatness makes the electronic structure susceptible to external electric fields, such as those provided by scanning probes in scanning tunnelling microscopy (STM)[24], and it displays sensitivity towards the proximity of the other materials on its surface[25]. The limited dimensionality also significantly reduces the amount of scattering within the material, and at the same time, it introduces new physics evident in its electronic structure which shows a linear-dispersion around the K-point, or so-called Dirac point, as represented in Figure 2-1 c).
Initial studies of graphene’s electronic properties were focused on discovering new physics through the use of the Dirac equation to generate new condensed matter phenomena. A summation of some of the new physics is provided in Figure 2-2. The most fascinating aspect of graphene is the physics of the electronic properties, which are unique and different from those of other known condensed matter systems due to the introduction of the massless Dirac fermion, which has been explored in numerous papers[26-28]. This uniqueness is first and foremost reflected in the unique band structure of graphene (Figure 2-1(c)), which shows that electrons propagating through its honeycomb lattice will lose their effective mass i.e., become massless or mass independent in that they have a linear dispersion. Consequently, the Schrödinger equation, which has been extremely successful in describing the quantum properties of materials, is less competent in modelling the graphene charge carrier with zero rest mass at energies near the Fermi level. Instead, this type of emergent fermionic quasiparticle can be better described using a Dirac-like equation. The massless charge carriers result in reduced scattering, so that the quantum effects in graphene are robust and can survive even at room temperature[29], which is one reason for the tremendous amount of interest in the fabrication of graphene. Graphene has also been recognized as a fantastic candidate for the exploration of fractional quantum Hall effect[30], which has ignited considerable theoretical interest due to the limited theoretical framework around the subject. Graphene has also been explored for a variety of other phenomena [31].
2.3.1.4. Synthesis and technologies of Graphene

The chemical, electronic, magnetic, optical, and phonon properties of graphene can be tuned through a variety of methods: these methods range from strain and deformation[33-38]; to surface and edge adsorptions[39-47]; to various defects[48-51]; to doping[52-55]; to edge and surface compensation[56-61]; and to varied edges[62].

There is a variety of methods for the synthesis of graphene. These mostly include mechanical exfoliation[12], chemical exfoliation[63, 64], chemical synthesis[65], chemical vapour deposition (CVD) through epitaxial growth[66], unzipping nanotubes[67], and microwave synthesis[68]. Mechanical exfoliation is the most prominent known synthesis method. Although the scotch tape method gives the best quality graphene crystals, commercialisation using this method has been difficult, as it does not scale efficiently for mass production.

Currently, chemical exfoliation[63] is deemed the most popular method for the synthesis of graphene due to its amenity to scaling for mass production. The chemical exfoliation

Figure 2-3 Realization and characterization a) shows a graphene crystal exfoliated using the scotch tape method on top of oxidized silicon substrate[23]. b) Shows atomically thin steps of mono-, bi- and tri-layers (red 1, purple 2 and green 3) on top of a SiC substrate[23], c) Atomic-resolution image of pristine graphene using high-angle annular dark field–scanning tunneling microscopy (HAADF-STEM); the scale bar is 1 nm[32].
of graphene is generally based on two principles: first breaking the van der Waals interaction and then using a density gradient to isolate the few-layer graphene that has been formed.

The characterisation of graphene is generally performed by first verifying the number of layers that have been stacked together, which can be done through atomic force microscopy (AFM) or electron microscopy techniques, and then verifying the structure, mostly through some form of TEM, as shown in Figure 2-3.

At present, much of the research and most applications for graphene have involved adapting graphene to existing applications and phenomena these are mainly $p$-$n$ junctions[69, 70], quantum point contacts[71], graphene-based quantum dots[71, 72] and nanoribbons[72-74].
2.3.2. **Boron Nitride**

![Figure 2-4](image)

Figure 2-4 a) Phases of boron nitride: hexagonal phase (h-BN), b) cubic phase (c-BN), c) wurtzite phase (w-BN).

### 2.3.2.1. Chemical and Electronic Structure

Boron nitride exists in three distinct possible configurations, the hexagonal phase Figure 2-4(a), the cubic phase Figure 2-4 b), and the wurtzite phase Figure 2-4 c). The hexagonal phase is the most useful for studying 2D materials because it can be reduced to the form of an atomic monolayer[75].

Following the development of graphene, enormous attention has been paid to 2D hexagonal boron nitride (hBN) due to its electrically insulating properties and the fact that it is the most stable of the boron nitride phases, which act as a counterpart to graphene. 2D-hBN materials are strongly covalent $sp^2$ bonded 2D layered insulators, consisting of hexagonal rings of alternating boron and nitrogen atoms, where each layer of hBN is weakly bonded vertically out of plane via van der Waals interactions. Within the plane of the hBN, the dominant force in bonding interactions is the covalently bonded and highly polarised boron and nitrogen sublattice. The structure of hBN is analogous to that of graphene with sublattices containing equal numbers of boron and nitrogen atoms alternatively arranged in a honeycomb configuration, as shown in Figure 2-5 (a). Like
graphene, it is extremely flat with negligible buckling, as shown in Figure 2-5(b). In bulk form, the van der Waals layered compound hBN is electrically insulating, so it has no free electrons. hBN has a hexagonal symmetry with lattice parameters $a = 2.5$ Å and $c = 6.66$ Å, with an interlayer spacing of 3.33 Å [76]. Due to the highly asymmetric nature of adjoining sublattices, the resulting electronic structure contains a large electronic band gap (3.6–7.1 eV) [77-80]. This feature survives when the dimensionality is reduced to single-layer form, still resulting in an insulating 2D material, as seen from its band structure (Figure 2-5(c)). The reduction of dimensionality, however, makes the material more susceptible to various changes compared to the bulk, such as through doping, substitution, functionalization, and hybridisation [81-86].

Figure 2-5 a) The BN lattice viewed along the c-axis; b) a side view of the BN lattice. c) Optimized band structure of BN. The dashed lines in (a) and (b) indicate the edges of the primitive BN unit cell. (Frank. F. Yun 2018)
Technological progress using hBN

As in the case of graphene, hBN characterisation is also performed by first verifying the number of layers, which can be done through AFM or electron microscopy techniques, then examining the structure, mostly through a form of TEM, as shown in Figure 2-6.

Inspired by the onset of enormous application potential, single- and few-layer hBN nanosheets have been successfully developed and investigated, with potential applications in transistor devices, photonic devices, dielectric tunnelling, and fuel cells[76, 87-91]. hBN is known for its resistance to mechanical strains and stresses, as well as its chemical inertness and large band-gap. It is because of these reasons hBN is a promising material for use as an encapsulation layer or as a substrate for two-dimensional heterostructured devices, as it provides an atomically smooth surface free of dangling bonds where all the interfacial charges is are naturally compensated. Consequently, hBN substrates for graphene do not affect the Dirac point and will not interact with bands arounds the fermi level and allows for improved mobility in graphene-based devices[92, 93]. (except for circumstances where special stacking alignments cause changes to the band structure)

Figure 2-6 a) Optical microscope image of hBN sheets on a SiO$_2$ substrate[76]. b) STM image of hBN on an Rh(111) surface with steps; the inset shows an enhanced image[76]. c) High-resolution TEM (HRTEM) image of monolayer hBN, with the inset showing an outline of the structure [76].
The stability and performance of 2D-hBN-based devices are of course highly dependent on the quality of the 2D nanosheets, which consequently requires careful control of the synthesis process. hBN has stimulated new strategies and innovation aimed at controlling the material growth processes and understanding the formation mechanisms.[94-96] Despite the great progress achieved so far, the current research into 2D-hBN still faces three major challenges: (a) growth of large-scale hBN with controlled layer quality and a corresponding transfer technique; (b) integration of 2D-hBN into other nanomaterials or nano-devices; and (c) effective modulation of electronic structures by other strategies (including energy bands and charge carriers) in 2D-hBN.

Although hBN is electronically insulating, the formation of the band gap is tunable through several strategies, depending on the desired properties, for example, by doping [81], substitution [82, 83], defects [84], and edge[85] and surface[86] functionalization. It is widely accepted that the equilibrium stacking order of hBN is AA’ stacking, that is, the boron atoms in layer A are directly above the nitrogen atoms in layer A’[97-100].
2.3.3. **Stanene**

![Stanene structure](image)

Figure 2-7 a) The stanene lattice viewed along the c-axis b) a side view of the stanene lattice c) the optimized band structure for stanene. The dashed lines in (a) and (b) indicate the edges of the primitive stanene unit cell.

### 2.3.3.1. Chemical and Electronic Structure

Stanene is a single layer allotrope of Sn in a hexagonal arrangement, as shown in Figure 2-7(a). The unit cell of stanene contains two tin atoms, with a relaxed bond length of approximately 2.8 Å and a lattice parameter of ~ 4.62 Å. Unlike graphene and hBN, stanene has considerable buckling, with the difference between the Z positions of the two Sn atoms being ~ 0.88 Å, and the bond angle between the Sn atoms being 110.653˚, as shown in Figure 2-7 b).

Although there is a difference between the sublattices in the Z position, the electronic properties are seemingly comparable to those of graphene, as stanene also exhibits massless Dirac fermions, as seen from the band structure in Figure 2-7(c). One notable
difference, however, is that Sn is a much heavier atom regarding atomic mass and there is a more significant spin-orbital coupling (SOC) effect on the free electrons in stanene. Given that experimental synthesis of stanene has proved to be difficult, there is currently great interest in the theoretical predictions. Structural predictions for free-standing monolayers of tin (that is, stanene) suggest that it will converge to a buckled honeycomb lattice[101, 102]. Similar to silicon and germanium, the two-level buckling causes some overlap of $\sigma$ and $\pi$ orbitals, stabilising the relatively weak $\pi-\pi$ bonding within the atomic plane. It can be noted that the crystal structure of buckled stanene is identical to bilayer and thin films of $\alpha$-Sn (111). The latter has been studied on a range of substrates[103, 104], and the key difference between the epitaxy of $\alpha$-Sn(111) and that of stanene is the exposed $p$ orbitals in the monolayer material. These orbitals account for the low-energy band structure of the material and are the source of the topologically non-trivial edge state. These subtle differences underpin the importance of thoroughly understanding the physical and chemical structure of novel 2D electron systems.

Figure 2-8 a) Atomically resolved STM image of stanene, b) height line profile across the red line in a); c) Large-scale STM topography of stanene film, and d) height line profile across the red line in c). Figure from Ref. [105]

2.3.3.2. Effect of spin-orbit coupling in stanene: a candidate for quantum spin Hall effects

The spin-orbit coupling (SOC) is weak in graphene and hBN because the elements involved are light. The heavier atomic mass of the tin atoms in stanene causes enhanced
spin-orbit coupling compared with carbon, silicon, and germanium. If SOC effects are incorporated into the stanene Hamiltonian, a significant gap of about 100 meV (for pristine stanene) [73, 74] to 350 meV (for chemically functionalized stanene) [73] is opened. Owing to this large opening of the band gap, stanene and its derivatives are expected to exhibit a high-temperature quantum spin Hall effect (QSHE) [73, 75, 76].

QSH insulators are a new state of matter with an insulating bulk state and conducting edge state [77, 78]. The edge states in QSH insulators are protected against backscattering through time-reversal symmetry, without back scattering it is possible to obtain dissipationless electron transport [77, 78]. Also, stanene has been theoretically predicted to exhibit other novel properties, such as near room-temperature quantum anomalous Hall effect (QAHE) [81], topological superconductivity [80] and possible enhancement of thermoelectric properties [79]. Such an abundance of new physics, if experimentally observed, can transform the current landscape of condensed-matter physics for future technologies.

Figure 2-9 a) Shows overlaid STM images with yellow sphere indicating Sn-A atoms in stanene on top of a grey Te in the Bi2Te3 substrate. b) Shows overlaid STM images with Sn-A(large) and Sn-B(small) atoms in stanene on top of a grey Te in the Bi2Te3 substrate. c) Show a side view of the atomic structure [105].
2.3.3.3. Technological progress using stanene

Experimental synthesis of stanene remained elusive until early 2015, when stanene was reported to be successfully grown on a Bi$_2$Te$_3$ substrate [82] using molecular beam epitaxy (MBE), as reported by Zhu et al.[105]. This is a major step towards the experimental study of stanene. The researchers synthesised monolayer stanene on the surface of a Bi$_2$Te$_3$(111) crystal under ultra-high vacuum (UHV) conditions by evaporating tin onto the surface at room temperature[105], as shown in Figure 2-8. The STM images in Figure 2-9 reveal the close-packed crystalline structure, but of only the buckled sublattice. Band structure calculations based on density functional theory (DFT) agree well with the angle-resolved photoemission spectroscopy (ARPES) measurements[105], as shown in Figure 2-10 near the Γ point in reciprocal space. The predicted topological band structure shown in Figure 2-7(c) near the K point (that is, a Dirac cone) was not observed experimentally. The authors describe the absence of these topological bands to the presence of adsorbates (for example, hydrogen), which modify the chemical structure of the unbonded $p_z$ orbitals responsible for those bands[105]. In any case, the absence of these topological states should be addressed to enable fundamental and technological applications of stanene. To this end, further experiments are needed to remove the adsorbates and to understand the nature of the interaction between stanene and its substrate. The former may be addressed through non-reactive encapsulation (that is, to exclude hydrogen), whereas the latter may be accomplished through more advanced characterisation (that is, cross-sectional microscopy, X-ray diffraction and spectroscopy, or Raman spectroscopy) and growth on additional substrates.
Although experimental work on 2D tin is relatively new, theoretical investigations into chemically modified allotropes are abundant. These studies have focused on the chemical saturation of the $p_z$ orbitals, which leads to stronger topological insulator characteristics by enhancing the magnitude of the band gap induced by spin-orbit coupling[106]. The stability of stanene when exposed to air has not been studied explicitly, but the high reactivity of these $p_z$ orbitals implies that stanene would not survive unaltered under ambient conditions without encapsulation. Several groups have included substrates in their calculations, effectively concluding that chemical interactions between the stanene and the substrate may resemble those between the stanene and the chemical functionalization in passivated monolayers[106, 107]. A particular case of functionalization arises from the addition of magnetic dopants, which would support dissipationless electronic transport and possibly enable robust quantum computing[108, 109]. These examples demonstrate how stanene may serve as a platform on which topological states can be chemically engineered and patterned through spatially selective
functionalization. Such patterning may be possible through scanning probe techniques such as STM, which have already been applied in the initial characterisation of stanene[105]. These techniques, in turn, would enable dissipationless (that is, low-power) electronic circuitry.
2.3.4. Transition metal dichalcogenide (MX$_2$) compounds

2.3.4.1. Chemical and electronic structure

Bulk phases of MX$_2$ (M, transition metal; X chalcogen atom) are often parent compounds to 2D MX$_2$ materials due to the layered structure of the bulk phase, which is often formed by stacking weakly interacting layers. Due to the weakly interacting nature of these layers, where the van der Waals interaction plays the dominant role, they are easily cleaved to form atomically thin sheets. Transition metal dichalcogenides exist in two fundamental phases: the H phase, as illustrated in Figure 2-11, which shows the chalcogenides within the same layer overlapping each other; and the T phase, which has the chalcogenides within the same layer but in alternate positions as shown in Figure 2-11. All stacking sequences in MX$_2$ compounds occur with a stacking order of (X-M-X). By using state-of-the-art first-principles calculations for structure optimisation, the phonon frequency, and molecular dynamics, Ataca et al. [110] were able to identify the existence of 52

Figure 2-11 (a) Top and (b) side views of the H (left) and T (right) phase atomic structures with lattice vectors $a$ and $b$; (c) contours show the total charge density. (d) Charge density illustration showing the charge density difference of charges (e) isosurfaces showing the charge density of $p$-$d$ hybridization at Mo–O bond. Figure adapted from Ref. [110]
different stable 2D MX₂ combinations of either the T or H phase, out of a possible 88. The key results of Ataca’s work are summarised in Figure 2-12.

The summarised chemical stability shows that 2D MX₂ compounds are only known to be unstable in several instances: these are TiO₂, CoO₂, CoS₂, CoSe₂, and NbO₂, as described by Ataca et al. [110]. For all other members, the composition exists in either the T or H phase or both in which one is stable the other is metastable.

Figure 2-12 Predicted stable transition-metal combinations by Ataca [110]. Metallic atoms are divided into 3d, 4d, and 5d groups. Each box indicates either gray (unstable), white-red (H is stable), white-green (T is stable, red-green (T is more stable than H), or green-red (H is more stable than T). (+), (*), and (***) indicate half-metallic, metallic, and semiconducting systems, respectively. Figure from Ref. [110]

The chemical bonding in both H and T phases are unlike the bonding in graphene, which consists of sp² hybridisation throughout the lattice. Instead, the H and T phases have a positively charged 2D hexagonal lattice of M atoms sandwiched between two hexagonal lattices of negatively charged X atoms, as seen in Figure 2-11. The electronic band
structures of the 2D MX₂ compounds shows that out of the 35 (if MoS₂ is included there is 39), as described by Acata et al., 16 show some form of band gap, while the other 23 appear metallic, with one showing half-metallic properties. 26 of the systems are only stable for either eight combinations of the T phase or 18 combinations of the H phase, leaving 13 metastable systems, with 11 of them having lower energy for the T phase and 2 of them lower energy for the H phase. This results in a total of 19 systems for the H phase and 20 systems for the T phase. 4d and 5d metals are components of 8 of 10 H phases and 3d metals are components of 17 of the 28 T phases.
Figure 2-13 The calculated electronic band structures of lower-energy stable MX$_2$ 2D materials, as predicted by Ataca et al. for all compounds except MoS$_2$. EF is the Fermi level as marked by the red dash-dotted lines. Nonmagnetic states only show blue lines. For magnetic structures, blue and orange represent spin-up and spin-down, respectively. [110]
2.3.4.2. Novel physics and applications

The calculated band structures shown in Figure 2-13 show possible electronic properties that can be of interest for use in nanoelectronics and sensor applications. Other applications of MX$_2$ materials include superconductivity, super-lubricants, solar converters and catalysts in redox-based reactions.

The uses for 2D MX$_2$ materials can be divided into two major types. The first class is for metallic 2D MX$_2$ materials, and the second is for insulating 2D MX$_2$ materials.

Metallic 2D MX$_2$ materials generally show a large $d$-orbital electron contribution to the density of states (DOS) near the Fermi level and a high total DOS at the Fermi level. The interest in metallic MX$_2$ comes from studies involving charge density waves (CDWs) and superconductivity[111]. As there is a competition between CDWs and superconductivity, the mechanism for the CDW and its direct relationship to superconductivity is still not well understood and shows many contradictory results [112, 113].

The second major class is the MX$_2$ semiconductors that have confined charges, i.e. localised electrons, and as such can be used to facilitate energy transfer between donor and acceptor interfaces, allowing for excitonic excitations. Such optical properties are well studied in these materials with a view towards catalysis applications.
2.4. van der Waals (vdW) heterostructures

A vast number of combinations of heterostructures are possible when stacking 2D materials, and many have been theorised and experimentally realised. In the interest of brevity, this section will focus on the combinations between graphene, BN, and stanene. Using these three combinations, the following sections in this thesis will show that it is possible to investigate certain fundamental interactions: interactions between two types of massless Dirac fermions between graphene and stanene; isolation of Dirac fermions (graphene/stanene) using BN; interactions between buckled and planar 2D materials; interaction between a supercell and a primitive cell in the Brillouin zone; and finally, how increasing the number of layers and stacking can change these interactions. To this end, Section 2.4.1 reviews the some of the current understanding in the literature on heterostructured materials. Section 2.4.2 reviews the literature concerning bilayer heterostructures of graphene, boron nitride, and stanene. Section 2.4.3 reviews the research on trilayer vdW heterostructures containing graphene and two other layers. Section 2.4.4 reviews the literature on many-layer vdW heterostructures.

2.4.1. Heterostructures to van der Waals heterostructures

Heterostructures are made of multiple layers of differing materials, in between each of the layers is what is known as a heterojunction, which, at its core, is an interface. Heterostructure effects have been studied since the development of the diode, with the use of $p$-$n$ junctions and depletion zones. The application of heterostructures has revolutionised various technologies such as the metal oxide semiconductor field effect transistor (MOSFET)[114]. It is clear that the interfacial interaction is important in heterostructures, and in particular, the nature of the out-of-plane bonding and electron interactions between the composite layers[115, 116]. To understand the van der Waals
heterostructures and what makes them different from other heterostructures, it will be necessary to briefly review the types of interactions and their respective interaction strengths. In terms of the intramolecular forces, one can distinguish five major types: ionic, covalent, metallic, dipole-dipole, and dispersion forces. Ionic bonding refers to the bond which occurs between two atoms with very different electronegativity, such that there is a net charge transfer between the atoms. Covalent refers to the bond which occurs between atoms with shared electrons, and metallic bonds refer to bonding which results in delocalized shared electrons. Dipole-dipole refers to the interactions that occur between the charged permanent dipoles of the molecules. van der Waals forces, also known as dispersion forces, originate from fluctuating dipoles because of electron motion that causes temporary changes in the interactions. [117, 118]

In general, the strength of the interactions can be arranged in the decreasing order as follows:

\[
\text{covalent > ionic > metallic > dipole – dipole > van der Waals}
\]

with the van der Waals interaction being the weakest type of interaction between materials, and it also has a subtler effect towards perturbing the electronic structure. Consequently, van der Waals heterostructures are expected to show quite different mechanical and electronic properties from strongly bonded ionic or covalent heterostructures.
Figure 2-14 Parameters of charge, orbital spin, the lattice, charge transfer, strain, symmetry breaking, electrostatic coupling, and frustration as the fundamental strategies to tune the interactions and properties that occur within bulk layered heterostructures. [118]

In strongly-bonded heterostructures, the interactions with the biggest impact are intramolecular, forces such as orbitals from covalent and metallic bonds and charge effects from the polarity of ions[119]. These lead to a rich set of interfacial phenomena as summarised in Figure 2-14.

The point that differentiates van der Waals heterostructures from conventional heterostructures is that, in the out-of-plane direction from the interface, the interaction is dominated by the van der Waals force. Consequently, there is a different set of emergent physical phenomena possible for this subset of heterostructures, in that the strong interactions described in Figure 14 are often moderated by the large interlayer spacing. A general summary of the possible types of heterostructures can be seen in Table 2-1 regarding strength.
Table 2-1 The possible combinations of in-plane and out-of-plane bonding interactions in all types of heterostructures.

<table>
<thead>
<tr>
<th>In-plane interaction</th>
<th>Out-of-plane bonding (Strong ↔ Weak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>Ionic</td>
</tr>
<tr>
<td>Ionic</td>
<td>Metallic</td>
</tr>
<tr>
<td>Metallic</td>
<td>Dipole-dipole</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>van der Waals</td>
</tr>
</tbody>
</table>

In practicality, it is hard to separate exactly which type of heterostructure a particular structure belongs to, as in most cases, there is a mix of interactions. Currently, one of the best ways to define which type of interaction is the primary interaction is by calculating the cohesive energies:

\[
E_{\text{Cohesive}} = \frac{E_{n \text{layer}} - E_{n-1 \text{layers}}}{\text{area}}
\]

Experimental evidence has revealed that the cohesive energy is in the range of 10-30 meV/Å² for van der Waals heterostructures depending on the size of the atoms[120], whereas it is much larger for non vdW heterostructures.
2.4.2. **Bilayer heterostructures:**

2.4.2.1. **Graphene/ hBN**

Figure 2-15 Graphene on hBN can form a Moiré pattern for graphene. A) Illustration of the exaggerated lattice mismatch of up to ~10%. B) Experimental data for the conductivity ($T = 150$ mK) near the charge neutrality of four heterostructure devices (A1, A2, B1 and B2), respectively. Left inset: schematic diagram of the measurement set-up and right inset: AFM image, respectively. Scale bar is three μm. C) Experimental resistance vs. gating voltage range. Figure adapted from Ref. [121]

Control of the gap formation in graphene-like electronic structures is an enticing prospect. Because of this, there has been a tremendous effort to find graphene-like insulating 2D materials. One of the first and foremost studied van der Waals heterostructures is the Graphene/hBN heterostructure, because of the small lattice constant mismatch of less than 2% [97]. 2D-hBN has thus been investigated as the ideal platform for future graphene electronics with superior performance and stability[122].
The properties of hBN make it possible to use hBN to tune the carrier mobility of other two-dimensional materials, such as graphene, MoS$_2$, and black phosphene. Depending on the layer configuration, it can reduce Coulomb scattering at interfaces, as well as protecting the materials from contamination, oxidation, and thermally/electrically induced degradation, as it is a highly stable structure.

Stacking between graphene and hBN can occur in three different ways: AA stacking of the layers, A (Carbon-Nitrogen) B stacking, and A (Carbon-Boron) B stacking. Depending on the way the structure is stacked, calculations have shown that gaps can be formed from the hybridisation of nitrogen and carbon orbitals[123].

Due to the chemical nature of the strong in-plane ionic bonds in hBN, it has strong resistance to oxidation and corrosion. This chemistry makes 2D-hBN a suitable candidate as a gate dielectric and capping layer to protect the active material element and the device as a whole from structural deformation and chemical degradation [92, 124]. hBN is fairly inert towards graphene unless placed at specific orientations [123]. Importantly, many of the gap tuning properties with hBN [123] can be achieved with bilayer graphene, for example, gap formation based on specific stacking orders[92]. A wide variety of work has been done to study the interactions within graphene/hBN heterostructures regarding their electronic structure, and tuning the electronic structure has been suggested using stacking, doping, strain, and defects [121, 125]. Experimental verification of some of these concepts is summarised in Figure 2-15(B, C).
2.4.2.2. Graphene/Stanene

While there is a large body of work studying the combination of graphene and hBN, fewer studies have been performed on combinations of graphene with other materials. One reason is that the large lattice mismatches with other materials result in Moiré patterns, which are difficult to describe in theory due to their irregular symmetries. The only methods suitable for finding the properties of these structures is the use of large supercells, which is computationally challenging and expensive. Recently, there has been a focus on the graphene/stanene system.

![Figure 2-16](image)

Figure 2-16 a), b), c), and d) Stanene/graphene bilayer structures calculated by Chen et al. and their corresponding band structures, e) shows the side view in which D is the interlayer distance, Δd is the buckling height. The C, upper Sn, and lower Sn are represented by grey, blue, and yellow, respectively. The lattice is defined by the red dashed lines. Figure adapted from Ref. [126]

Although this system has a larger mismatch (~5%) when compared to graphene, the structure of stanene is buckled, which allows for more structural tuning as the buckling allows a varied range of bond angles and bond lengths.

Recently, Chen et al. [126] studied the optical properties of such a system and found that, for certain stacking configurations, a gap can be formed in the bilayer electronic structure.
2.4.2.3. hBN/Stanene

Like the graphene/stanene systems, there have been relatively few studies on hBN/stanene systems. Wang et al. [127] produced calculations of stanene on various substrates, one of which was hBN, with the other being AlN (Aluminium Nitride) to study the quantum spin Hall effect. They predicted that using hBN as a substrate for stanene would be stable as shown in the phonon properties in Figure 2-17 c) and d) and that this system should preserve the electronic properties of the ideal stanene monolayer could be preserved in the bilayer and hence preserve the quantum spin Hall phase shown in Figure 2-17 f) for the edge estate. Their work gave insight into the effect of substrate strain on the electronic structure of the stanene/hBN heterostructure with Figure 2-17 b) vs c) showing that when there is a tensile strain, which moves the lattice parameter to $a = 4.72$ Å, it would transform the electronic state of the system from metallic for when $a = 4.35$ Å. 

Figure 2-17 Ab initio calculations performed by Wang et al.: a) Structure of the stanene/hBN heterostructure, $a = 4.35$ Å, b) the band structure for $a = 4.35$ Å; c) Phonon spectra of Sn; d) Phonon spectra of hBN; e) Electronic structure of hBN/stanene for $a = 4.72$ Å; f) Edge states for $a = 4.72$. [127]
Å to the QSHE state for when a = 4.72Å through the band energy changes at both the Γ
point and the K point shown in Figure 2-17 b) and c).

The change in the interlayer distance also has significance, as shown in Figure 2-18 d).
As variations in the interlayer distance, there is a defined change in the binding energy
that is typical of the interaction energy vs distance relationship shown for van der Waal
interactions as there is an increase in energy when the interlayer distance is decreased or
increase around a minimum that is around the 3-4Å range capable of being modelled by
the Lennard-Jones potential[128], further verifying the consistency of the modelling
method. This change in the interlayer distance also makes significant changes to the
electronic structures as shown in Figure 2-18 a), b) and c) the variations in the band
energies of the valence and conduction at the Γ and the K points of the band structures.

Figure 2-18 Band structures of the stanene/hBN system when lattice is fixed to a = 4.72 Å, while the
interlayer distance $d_2$ varied from (a) 2.70 Å, (b) 3.00 Å, and (c) 3.60 Å (d) shows the interlayer distance $d_2$
between stanene and the h-BN vs the binding energy per Sn atom with the lattice set to $a = 4.72$ Å from ref
[127]

The changes in the electronic structure through strain was also demonstrated on a slightly
rotated/translated structure shown in Figure 2-19 a), although this time with a minor
compressive strain of 1%. Which can tune the band gap from an indirect gap of 19 meV
to a direct gap of 66 meV, through the changes in the band at both the Γ point and the K point shown in Figure 2-19 b) and c).

Figure 2-19 a) shows a top view of the crystal structure of the stanene/hBN system, (b) shows band structure of the system without strain and (c) band structure of the system with a compressive strain of 1%.[127]

The ability of hBN to preserve the properties of stanene was also demonstrated by Wang, Liu et al. [120], who showed that, by using spin orbital coupling (SOC), it was still possible to open up a small gap in this structure, as shown in Figure 2-20.

Figure 2-20 Band structure of hBN/Stanene heterostructure: (left) with SOC, (right) without SOC from ref [120].
2.4.3. **Trilayer heterostructures**

2.4.3.1. **hBN/Graphene/hBN and Graphene/hBN/Graphene**

Figure 2-21 Band structures of trilayer heterostructures. Insets show the structures for the varying stacking configurations. a), b) and c) show (AB) stacking layers, d), e), f) show rhombohedral (ABC) stacking.[129]

There have been several reports on the trilayer structures of Graphene/hBN/Graphene and hBN/Graphene/hBN, and where their corresponding electronic structures were predicted [97, 129-137]. Ramasubramaniam et al. reported minor variations in the band gap depending on the stacking order shown in Figure 2-21 and that this variation was controllable through the use of an electric field shown in Figure 2-23.

Figure 2-22 (a) Shows the band structure of BN/graphene/BN stacked in the ABA configuration results in a gapped graphene (b) Shows the band structure of graphene/BN/graphene stacked in the ABA configuration with the overlapping Dirac points result in a gapped and a ungapped band. [129]
As a result of the inert nature of the interfaces between these two layers, studies were performed to confirm the ability to preserve the electronic properties of graphene[130]. It is seen that, in the bilayer system, there are specific stacking configurations which result in different electronic structures, as shown in Figure 2-22. Graphene/hBN/graphene ABA stacking results in a semi-metal, while BN/graphene/BN ABA stacking resulted in a gap, as shown in Figure 2-22(a). Zhong et al. [131] demonstrated that, depending on the stacking configuration, the system’s response in an electric field differs in how the band gap varies. This characteristic response to an electric field also has been experimentally observed by Quhe et al. [132].

Figure 2-23 a) Shows tuning of the band gap using in a varied electric field for bilayer BN/graphene (AB stacked), trilayer BN/graphene/BN(ABA-stacked) and trilayer graphene/BN/graphene (ABA stacked), (b) Shows tuning of the band gap in a varied electric field for graphene/BN/graphene three configurations AAA-stacked, ABA-stacked and ABC stacked. [129]
Kim et al. were able to demonstrate fluctuations in the band gap through increasing the number of layers shown in Figure 2-24. As a result, they demonstrated that the electronic structure is proportional to the thickness.[134] The thickness dependence was also noted by several other groups [135, 136].

![Figure 2-24](image)

Figure 2-24 Shows a thickness vs band gaps relationship of graphene(G)/BN/graphene(G), the black line indicate the BN/G/BN structure while the red line indicates the G/BN/G structures. As studied in ref[134].
2.4.3.2. hBN/Stanene/hBN

Studies on the hBN/stanene/hBN trilayer structure have so far only been performed by Wang et al. [120], who investigated the asymmetric bilayer structure compared with the symmetric trilayer structures. They showed that the hBN was able to preserve the electronic properties of the central layer. They also calculated the binding energy curves of silicene, germanene, and stanene, as shown in Figure 2-25.

Figure 2-25 (a) Shows the asymmetric bilayer structure all three monolayers (silicene or germanene or stanene)/hBN from the side and top views, (b) shows the symmetric trilayer structure of hBN/(silicene or germanene or stanene)/hBN from the top and side views, (c) shows the Brillouin zone for the resulting supercell. (d) shows the binding energy curves for silicene, germanene, and stanene on h-BN substrate, the labels $E_D$ and $E_d$ are the energy of the asymmetric heterostructures with the optimized interlayer distance $D$ and the stretched interlayer distance $d$.[120]
2.4.4. *Multilayer heterostructure*

![Diagram of multilayer heterostructures](image)

Figure 2-26 (a) B–C–C–B stacking, (b) B–C–C–N stacking, and (c) N–C–C–N stacking.[129]

There are only a few studies investigating heterostructures containing four or more vdW layers [135, 136, 138]. These studies mostly deal with how systems behave in the nanoscale environment and whether the electronic properties change or are preserved during transport [135, 136, 138].

![Graphene density of states](image)

Figure 2-27 Density of states of bilayer graphene (BLG) alone (a, b) and in BN/graphene/graphene/BN (c, d), arise from p_z orbitals projected on individual carbon in external fields of (a, c) 0 and (b, d) 2 V/nm. [129]
Ramasubramaniam et al. investigated a four-layer system of BN/graphene/graphene/BN as shown in Figure 2-26, in which their goal was to study the electronic structure of the centre bilayer graphene encapsulated by the hBN. They found that they were able to retain the free-standing properties of the bilayer graphene despite the changes in stacking order. They also demonstrated that it is possible to tune the gap up to ~0.2 eV using an external electric field. Remarkably, they proposed that this response to the electric field is independent of the stacking order, as shown in Figure 2-28, in which for bilayer graphene, the gapless phase remains constant, and only a minor gap is opened up for the B-C-C-N hBN/graphene/graphene/hBN structure. On comparing between the BLG and B-C-C-N hBN/BLG/hBN, it is clear that the change in the band structure remains similar.

![Figure 2-28 Band structure for (a) BLG (b) B−C−C−B, (c) N−C−C−N, and (d) B−C−C−N. Insets shows the band gap ($E_g$) and the gap at K ($\Delta_K$). Figure adapted from Ref. [129]](image-url)
2.1. Summary

The 2D materials family is an ever-growing family due to the increasing methods and techniques to produce atomically thin materials. With this increasing arsenal of new 2D materials, the range of possible van der Waals heterostructures is expanding exponentially, due to the increasing possible number of combinations and the variety of techniques available to assemble them. In this context, efficient theoretical techniques are required to predict useful combinations and isolate candidates for applications. Computational methods can be extremely helpful in the 2D van der Waals heterostructure discovery process because they can enable the exploration of a large number of materials theoretically at a rate much faster than is possible with experiment.

Furthermore, computer-based experiments have the potential to increase understanding of the physical and chemical interactions that occur at interfaces. A variety of challenges remain before it is possible to fully understand interfacial interactions, as there are so far no guiding principles for building useful 2D van der Waals heterostructures. The current approach is still a trial-and-error based approach based on case-by-case experimental synthesis or computational modelling. Hence, in this context, it will be useful to develop some guiding principles and common insights to predict whether electronic structure changes will occur when certain layer combinations are combined. Although tremendous progress has already been made in the past few years, much more work still needs to be done to address the following questions: how do properties depend on the layer stacking and interactions? What roles do composition and heterostructure symmetry play? How does layer thickness affect interactions and hence properties? What chemical routes can be used to isolate and preserve certain desired properties in custom-designed van der Waals heterostructures? This thesis is directed towards addressing these questions.
Chapter 3

3. Density Function Theory and computational methods

3.1. Introduction

In contemporary science, some consider there to be a new discipline alongside the commonly accepted experimental and theoretical branches of research. This emerging sub-discipline is usually known as the computational branch of science. A powerful application of using computational science is to model complex physical systems. This discipline allows researchers to explore material physics under conditions that are currently inaccessible using available experimental methods, for example, extremely high pressure and low-temperature environments. This discipline also allows a cheaper and faster solution to investigate many problems, which would be difficult to set up or would require complex experimental machinery. It is capable of giving better control over the variables in experiments that are highly sensitive to unwanted effects. When looking at smaller and smaller systems, the effect magnifies, since minor variation of a constant could significantly impact upon the reliability of the results. Thus, given the experimental challenges in researching atomically thin materials, computational methods have an important role to play in the discovery of new heterostructures. This chapter consists of the following section 3.2 describe the general theoretical framework underlying ab initio calculations using density functional theory (DFT). Sections 3.3.1-3.3.3 describe the more specific methods based on DFT or in conjunction with DFT. Section 3.4 describes the practical steps to construct a real-space model of a van der Waals heterostructure and
generation of input files suitable for VASP and CASTEP software codes and methods for analysis of results.

3.2. First-principles calculations

When modelling a solid-state or chemical system using various physics based methods, there are a variety of approaches to take, with a varying degree of accuracy in regards to the total energy of the system. The first are empirical methods, for example empirical molecular dynamics methods [139, 140]. These methods make use of pair potentials, many body potentials, and other generalised forces as force fields in particle-particle interactions. This method is by far the fastest method, but at the same time is the least accurate. Hence it is often used in large scale modelling in which it is not feasible to use other methods due to the amount of time it would take. The second type of modelling is the semi-empirical approach, which utilises the Hartree–Fock formalism [141], by applying approximations of parameters obtained from empirical data. As a result, it is significantly more efficient at treating large chemical systems. Semi-empirical methods can be based on two different outlooks, one group, which aims to fit the approximation parameters to experimental data [142], the other group aims to fit the approximation parameter to \textit{ab initio} results [143]. As a result, it is preferential for fitting data, but often the fitted approximation does not account for certain parameters and, as a result, these effects the accuracy of the result. The third type is the first principle calculations which can also be referred to as the \textit{ab initio} method, which covers methods such as Hartree-Fock [144-146], density functional [147, 148], and Quantum Monte Carlo[149]. The advantage of \textit{ab initio} techniques is that there are, in principle, no adjustable parameters. The disadvantage of such methods is that they are computationally the most expensive and become more expensive if there is more added accuracy to account for more non-local interactions as described in Figure 3-1. Consequently, \textit{ab initio} methods are usually
restricted to modelling small atomic-scale systems typically of less than 200 atoms. The work in this thesis focused on creating efficient models of two-dimensional heterostructures and applying *ab initio* techniques to these models.

Figure 3-1 Illustration of Jacobs ladder of chemical accuracy as described by Perdew[150].
3.3. Theoretical basis

3.3.1. Many-Body Description

Figure 3-2 Shows a model of the many-body system described by the full many-body Hamiltonian in Equation 3-4.

The primary task of *ab initio* theory is to find a full description of the many-body interactions of an N+ZN number of particles at a specific time between a system of N nuclei with coordinates \( R_N \) and mass \( M_N \), and a system of ZN electrons with coordinates \( r_n \) and mass \( m_e \). To first describe the total energy of a system (Hamiltonian \( \mathcal{H} \)), the use of the energy conservation law can be employed to help determine the interactions involved, in which \( T \) describes the kinetic energy and \( V \) describes the potential energy:

\[
\mathcal{H} = T + V
\]

Equation 3-1
In this case, firstly the kinetic energy description for both nucleus and electron (T), written within the Schrodinger description would be respectively:

\[
\sum_N - \frac{\hbar^2 \nabla_{\vec{R}_N}^2}{2M_N} \quad \text{and} \quad \sum_n - \frac{\hbar^2 \nabla_{\vec{r}_n}^2}{2m_e}
\]

Equation 3-2

while the potential energy would be interacting terms that are the Coulombic interactions between the nuclei (\(V_{n-n}\)), electrons (\(V_{e-e}\)) and between each electron and nucleus respectively (\(V_{n-e}\)).

\[
V_{n-n} = \frac{1}{8\pi\varepsilon_0} \sum_{A\neq B} \frac{e^2 Z_A Z_B}{|\vec{R}_A - \vec{R}_B|}
\]

\[
V_{e-e} = \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{e^2 Z_i Z_j}{|\vec{r}_i - \vec{r}_j|}
\]

\[
V_{n-e} = -\frac{1}{4\pi\varepsilon_0} \sum_{i,A} \frac{e^2 Z_A}{|\vec{R}_A - \vec{r}_i|}
\]

Equation 3-3

This gives the full Hamiltonian:

\[
\hat{\mathcal{H}} = -\sum_N \frac{\hbar^2 \nabla_{\vec{R}_N}^2}{2M_N} - \sum_n \frac{\hbar^2 \nabla_{\vec{r}_n}^2}{2m_e} + \frac{1}{8\pi\varepsilon_0} \sum_{A\neq B} \frac{e^2 Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} + \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{4\pi\varepsilon_0} \sum_{i,A} \frac{e^2 Z_A}{|\vec{R}_A - \vec{r}_i|}
\]

Equation 3-4

Which can also be simply written as:

\[
\hat{\mathcal{H}} = \hat{T}_n + \hat{T}_e + \hat{V}_{nm} + \hat{V}_{ee} + \hat{V}_{ne}
\]

Equation 3-5

It is then a highly complex problem involving \(N+ZN\) number of bodies, becoming very difficult to solve. Hence requiring appropriate approximations.
3.3.2. **Born-Oppenheimer approximation**

The Born-Oppenheimer approximation results from the fact that there is a large difference between the mass of the electron and mass of the proton/neutron, and because of this, there is a large difference in the time scale on which subatomic events take place. The difference in time scale makes the electron interaction seemingly instant when compared to the much larger atomic nucleus.

This approximation allows the reduction or elimination of certain variables as given in Equation 3-4. For the kinetic energy term as the nucleus does not move, the kinetic energy for the nucleus is zero and hence the

\[ \sum_N -\frac{\hbar^2 \nabla^2_{\vec{r}_N}}{2M_N} \]

Equation 3-6

term can be eliminated. The Coulombic interaction between the nucleus becomes a constant and hence the

\[ \frac{1}{8\pi\epsilon_0} \sum_{A \neq B} \frac{e^2 Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \]

Equation 3-7

term becomes a constant.
Finally, this leaves three terms, the kinetic energy of the electron ($\hat{T}$), the Coulombic potential between the electrons ($\hat{V}_{ee}$) and the Coulombic potential between the electron and the nucleus. As the nucleus does not move the interaction of nuclei can be regard as an external field acting on the electron ($\hat{V}_{ext}$). Which will give the form:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$  
Equation 3-8

### 3.3.3. Density functional theory

With the Born-Oppenheimer approximation, the complexity of the problem is greatly reduced and becomes tractable. In that, instead of dealing with a many body electron-nucleus system, it is now only a many electron system, and a constant field. Although this system is much easier to solve it is still far too complex for an exact analytical solution owing to the complexities required in the calculations of the kinetic energies ($\hat{T}$) and the electron-electron interaction energy ($\hat{V}_{ee}$). A very successful set of approximations to solve this problem is using the method now known as the density functional theory (DFT). The idea of using electron density to describe a system were first explored by Thomas and Fermi [151, 152]. In their approach the energy was calculated using the kinetic energy of a uniform electron gas as $\hat{T}$, coulomb interaction between the electrons-electron and electrons-nuclei as $\hat{V}_{ee}$ and $\hat{V}_{ext}$ all as an electron gas of a given energy. This theory became known as the Thomas-Fermi theory. Because of the large approximations made in the kinetic energy term $\hat{T}$ for Thomas-Fermi theory it gave relatively poor results[153, 154]. The work of Dirac extended the theory by adding the exchange energy of electrons which represented a significant improvement[155]. In its modern form, density functional theory allows the description of the ground state of a system using its charge density. As expressed by the following N particle system and the wave function $\psi(r_1, r_2, ..., r_N)$. 
\[ \rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 = \sum_{i=1}^{N} \int \psi^*(r_1, r_2, ..., r_N) \psi_i(r_1, r_2, ..., r_N) \, dr_1 \, dr_2 \ldots \, dr_N \]

Equation 3-9

This formulation of using charge density is obviously advantageous over using the wave functions, as it will reduce a system of 3N or more variables for wavefunctions to only 3 for using density. The basis of density functional theory, and its validity, rests on two powerful theorems developed by Kohn and Hohenberg. Using the Hamiltonian of the form:

\[ H = T + V_{ee} + V_{ext} \]

Equation 3-10

Where T is the kinetic energy term of the form:

\[ T \equiv \frac{1}{2} \int \psi_i^*(r) \nabla^2 \psi_i(r) \, dr \]

Equation 3-11

Where \( V_{ee} \) is the electron-electron interaction of the form:

\[ V_{ee}\equiv \frac{1}{2} \int \frac{1}{|r-r'|} \psi_i^*(r) \psi_i^*(r') \psi_i(r') \psi_i(r) \, dr \, dr' \]

Equation 3-12

\( V_{ext} \) is the electron-nucleus interaction with the interaction represented by unknown external potential \( v(r) \) of the form:

\[ V_{ext} \equiv \int v(r) \psi_i^*(r) \psi_i(r) \, dr \, dr' \]

Equation 3-13
3.3.3.1. Hohenberg-Kohn

The work of Hohenberg and Kohn[156] provided two fundamental insights, first it proved via *reduction ad absurdum* that each full many-body ground state gives a unique functional of the electron density. This is stated in Proof 1: *The external potential is uniquely determined by the ground-state density. Conversely, the ground-state density uniquely determines the external potential, within an additive constant.*

The first proof arises if through the assumption of two different Hamiltonians (\(\hat{H}\) and \(\hat{H}'\)), wavefunctions (\(\Psi\) and \(\Psi'\)), ground-state energies (\(E\) and \(E'\)) and potentials (\(V_{\text{ext}}\) and \(V_{\text{ext}'}\)), give rise to the same density \(\rho(\mathbf{r})\). It is then possible to formulate the following;

\[
E < \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle \\
E < E' + \int \rho(\mathbf{r}) [ v_{\text{ext}}(\mathbf{r}) - v_{\text{ext}'}(\mathbf{r}) ] d\mathbf{r} \\
E' < \langle \psi | \hat{H}' | \psi \rangle = \langle \psi | \hat{H} | \psi \rangle + \langle \psi | \hat{H}' - \hat{H} | \psi \rangle \\
E' < E + \int \rho(\mathbf{r}) [ v_{\text{ext}'}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r}) ] d\mathbf{r}
\]

Equation 3-14

By addition of \(E'\) and \(E\) will lead to an inconsistent:

\[
E + E' < E + E'
\]

Equation 3-15

From here it is possible to see that the two different potentials \(v_{\text{ext}}(\mathbf{r})\) and \(v_{\text{ext}'}(\mathbf{r})\) cannot give rise to the same electron density \(\rho(\mathbf{r})\). This indicates the fact that it is valid to use the electron density function as a variable to formulate the Schrödinger equation, and hence the name density functional theory (DFT).
Second, Hohenberg and Kohn proved through the variational principle that the it is possible to find the ground state density: the density that minimizes the total energy is the exact ground-state density.

The second proof arises from the fact as $\Psi$ is a functional of $\rho(r)$ hence, so must the kinetic energy and interaction energy. Therefore, it is possible to define:

$$ F[\rho(\vec{r})] \equiv \langle \Psi | T[\rho] + V_{\text{ext}}(r) | \Psi \rangle $$

Equation 3-16

Due to the importance of $F[\rho(r)]$ it is later known as $F_{HK}[\rho]$ a universal functional valid for any number of particles and any external potential, this functional if known would give the exact solution of the Schrödinger’s equation. With its aid it is possible to then use it to define the Coulomb repulsion $v_{\text{ext}}(r)$.

$$ E[\rho] \equiv F_{HK}[\rho] + \int v_{\text{ext}}(r) \rho(r) dr $$

Equation 3-17

Because of the long range of the Coulomb interaction, it is useful to separate the $F_{HK}[\rho]$ the classical Coulomb energy and write the total form for $E[\rho]$ as:

$$ E[\rho] = \int v(r) \rho(r) dr + \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|\vec{r} - \vec{r}'|} dr d\vec{r}' + G[\rho] $$

Equation 3-18

$G[\rho]$ is also a universal function like $F[\rho]$. The form of ground-state total energy $E[\rho]$, corresponding to a density giving is described below.

$$ E[\rho] = T[\rho] + V_{\text{ele}}[\rho] + \int v_{\text{ext}}(r) \rho(r) dr $$

Equation 3-19
To solve Equation 3-19 each of the terms must be defined. The first term, \( T[\rho(r)] \) is the kinetic energy, given by

\[
T[\rho] = -\frac{\hbar^2}{2m} \sum_i^N \langle \Psi | \nabla^2 | \Psi \rangle
\]

Equation 3-20.

Where \( n \) is the number of electrons, \( m \) is the mass of the electrons. The last term, \( V_{ee} \) is the electron-electron interaction given by Equation 3-21.

\[
V_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(r) \rho(r')}{|r - r'|} \, dr \, dr'
\]

Equation 3-21

In summary the theorem is divided into two fundamental parts; The Hohenberg-Kohn theorem shows that by using the ground state density, it is then possible to calculate the electronic properties of a system, although this does not yield a way of finding the ground state density.

### 3.3.3.2. Kohn-Sham

The work of Kohn and Sham [157] in 1965 expanded on Hohenberg-Kohn’s [156] previous work of density based and provided valuable insights into how to obtain the ground state density. By assuming that a fictitious system of non-interacting electrons \( V_{nle}[\rho(r)] \) that move under a KS potential \( V_{KS}[\rho(r)] \) that gives the same density as the real system of interacting electron \( V_{ee} \) moving under a real potential \( V_{ext} \). Where \( E_{xc} \) contains all the difference between non-interacting and interacting systems and \( T_{nl} \) is the kinetic energy of non-interacting electron,
\[ H = T + V_{ee} + V_{ext} \]  
Equation 3-22

\[ H = T_{ni} + V_{ni,ee} + V_{ext} \]  
Equation 3-23

\[ H = T_{ni} + V_{ni,ee} + \frac{\Delta T_{ni} + \Delta V_{ni,ee} + V_{ext}}{E_{xc}} \]  
Equation 3-24

\[ H = T_{ni} + V_{ni,ee} + V_{ext} + E_{xc} \]  
\[ \frac{1}{V_{KS}} \]  
Equation 3-25

\[ E_{xc} \] complicated term composed of kinetic energy correction due to interaction for e, self-interaction correction, and exchange and correlation effects. The Hohenberg-Kohn ground state energy can be written in the form:

By using the single particle non interacting Schrödinger’s equations with wavefunctions \( \psi_i \) as described in Equation 3-26, where, and density \( \rho(r) \), where \( N \) is the number of electrons.

\[ \rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 \]  
Equation 3-26

Kohn and Sham were able to derive the necessary equation using this idea of non-interacting systems and find the forms for the various density-based ground state energy descriptions.

\[ T_{ni}[\rho(r)] = \sum_{i=1}^{N} \int \psi_i^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi_i(r) dr \]  
Equation 3-27

\[ V_{ni,ee} = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' \]  
Equation 3-28
\[ V_{KS} = V_{ext}(r) + V_{ni,ee}(r) + E_{xc}[\rho] \]

Equation 3-29

Here \( E_{xc} \) is the exchange-correlation energy functional. The full form of this potential is unknown due to the unknown exchange and correlation contributions. With the assumption that \( E_{xc} \) is known it is possible to write the energy functional as:

\[ v_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \]

Equation 3-30

\( v_{xc} \) can only be obtained if \( E_{xc}[\rho] \) is known which will result in the exact total energy of the form:

\[
E = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \psi_i^* \nabla^2 \psi_i \, dr - \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr' + V_{xc}[\rho] - \int v_{xc}(r)\rho(r) \, dr
\]

Equation 3-31

If the orthonormal wavefunctions is:

\[
\int \psi_i^*(r)\psi_j(r) \, dr = \delta_{ij}
\]

Equation 3-32

Then it is possible to define a density function of the wavefunctions:

\[ \Omega[\psi_i] = E[\rho(r)] - \sum_i \sum_j \epsilon_{ij} \int \psi_i^*(r)\psi_j(r) \, dr \]

Equation 3-33

Minimization of \( \Omega[\psi_i] \) with respect to \( \psi_i^*(r) \) results in the Kohn-Sham form:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r)
\]

Equation 3-34

The complicated \( E_{xc} \) term is composed of kinetic energy correction due to interaction for electrons, self-interaction correction, and exchange and correlation effects. They can be split into two terms the exchange (\( E_x \)) and the correlations (\( E_c \)).

\[ E_{xc} = E_x + E_c \]

Equation 3-35
3.3.3.3. Exchange-Correlation Potentials

The $E_{xc}[\rho]$ function is the exchange-correlation potential. This potential is vital towards the accuracy of the DFT calculations in which there are many variations, e.g. Generalised Gradient Approximations (GGA) and Local Density Approximations (LDA). Depending on the form in which this exchange correlations potential takes there are various degrees of accuracy and at the same time increase in computational cost. This is described in Figure 3-1, which is suitable guide for the many types potential available.
3.3.3.3.1. Local Density Approximation

On the bottom of the ladder in Figure 3-1 is the Local Density Approximation (LDA). It was introduced by Kohn and Sham [157] similar to the Thomas-Fermi-Dirac model. It assumes that the density is treated as a uniform electron gas that does not change in density and that the exchange correlation energy $E_{xc}$ is same throughout the uniform electron gas. Hence, this approximation is only suitable for systems in which there are minor variability in the density. The exchange-correlation energy $E_{xc}$ using density $\rho(r)$ can be given by Equation 3-36, where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy for each particle in an uniform electron gas of a constant density $\rho$.

$$E_{xc}^{LDA} = \int \rho(r) \epsilon_{xc}(\rho(r)) dr$$

Equation 3-36

The exchange-correlation potential is then given in Equation 3-36:

$$v_{xc}^{LDA}[\rho(r)] = \frac{\delta E_{xc}^{LDA}}{\delta \rho(r)} = \epsilon_{xc}(\rho) + \rho(r) \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho}$$

Equation 3-37

Equation 3-37 can then be substituted into Equation 3-29 to solve the equation for the ground state density. For calculations involving LDA, to determine the exchange-correlation energy for a uniform electron gas of a constant density. It will be necessary to split $\epsilon_{xc}[\rho(r)]$ into exchange $\epsilon_x[\rho(r)]$ and correlation $\epsilon_c[\rho(r)]$ potentials. The exchange potential can be given by functional:

$$\epsilon_x[\rho(r)] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \rho(r)$$

Equation 3-38

[155] The values for $\epsilon_c[\rho(r)]$ are not known are can be paramterized from methods such as quantum Monte Carlo[158, 159].
3.3.3.2. \textit{Generalized Gradient Approximation}

Above LDA on the ladder in Figure 3-1 is the Generalized Gradient Approximation (GGA) which has dependence on the density gradient of the electron and better captures situations where there are swift changes in density as compared to LDA. GGA are semi local functionals of the form Equation 3-39 and meta-GGA are just the second derivative of $\rho(r)$ of the form Equation 3-40 and/or with kinetic energy densities $\tau(r) = \frac{1}{2} \sum_i |\psi_i(\rho(r))|.$

\begin{equation}
E_{xc}^{GGA} = E_{xc}[\rho(r), \nabla \rho(r)] = E_x[\rho(r), \nabla \rho(r)] + E_c[\rho(r), \nabla \rho(r)]
\end{equation}

Equation 3-39

\begin{equation}
E_{xc}^{\text{meta-GGA}} = E_x[\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \tau] + E_c[\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \tau]
\end{equation}

Equation 3-40

There are a wide variety of implementation using the GGA methods. Examples of GGA can be separated into the exchange $E_x$ (Becke86/88\cite{160, 161}, PBE\cite{162}) and correlation $E_c$ (PW86/91\cite{163, 164}, PBEsol\cite{165}, LYP\cite{166}) potentials. While fully defined $E_{xc}$ are also available (XLYP\cite{167}, VV10\cite{168}).

Using the gradient density method various other accurate method have been implemented these are the meta-GGA($E_x$(BJ06\cite{169}), $E_c$(B95\cite{170})) and fully defined(TPSS\cite{171, 172}) and Hybrid Functional(X3LYP\cite{167}/B3LYP\cite{173}, HSE03/06/12/sol\cite{174-177}) methods.
3.3.3.3.3. Van der Waals corrections

Almost at the top of the ladder in Figure 3-1 is exchange correlation functional that include dispersion corrections. Dispersion forces such as van der Waals are of great important in many organic and layered structures. However, they are not built into the standard DFT description.

A variety of approaches have been taken to allow the modelling the vDW forces due to the mixing of functionals between the short and long-range interactions as shown in
Figure 3-3. They can be class into four classes as shown in Figure 3-4, these are non-local vdw-DFs[179, 180], semi-local HF-DF/meta-HF-DF approximations[181, 182], DFT-D which are atom-pairwise interaction potential corrected DFT[183-185], and Dispersion Correcting Atom Centered One-Electron Potentials(DCACP[186]) or variants[187, 188]. Currently the most accurate correction for layers systems has been DFT-D corrections and out of the D/D2/D3 D2 is currently the most common[120, 184]. In this thesis, DFT-D2 methods were tested and used.

DFT-D can be described as a semiclassical addon to the DFT method, in which the dispersion energy ($E_{disp}$) can defined by Equation 3-41.

$$E_{disp} = -\frac{1}{2} \sum_{AB} \frac{C_{6}^{AB}}{R_{AB}^{6}} f_{dmp}(R_{AB}) \left( \frac{C_{8}^{AB}}{R_{AB}^{8}} f_{dmp}(R_{AB}) \right)$$

Equation 3-41

$R_{AB}$ is the distance of the atom pair AB, $C_{6}^{AB}$ is the isotropic dipole-dipole dispersion coefficient for AB, $f_{dmp}$ is a damping function, inclusion of the $\frac{C_{8}^{AB}}{R_{AB}^{8}} f_{dmp}(R_{AB})$ term is DFT-D3 and without it is the DFT-D2 method. $C_{6}$ coefficients are derived from each pair of atoms with Equation 3-42 which is a modified Casimir–Polder formula. These dispersion coefficients are computed through time-dependent (TD)DFT.

$$C_{6}^{AB} = \frac{3}{\pi} \int_{0}^{\infty} \frac{1}{m} \left[ \alpha^{A \times n}(i\omega) - \frac{n}{0} \alpha^{X_{o}}(i\omega) \right] \times \frac{1}{f} \left[ \alpha^{B \times k}(i\omega) - \frac{k}{l} \alpha^{Y_{i}}(i\omega) \right] d\omega$$

Equation 3-42

where $\alpha^{X_{o}}(i\omega)$ are the values for the molecule, $m, n, j, k$ are stoichiometric factors, and $\alpha^{A \times n}(i\omega), \alpha^{B \times k}(i\omega)$ are their respective molecule $A_{m}X_{n}$ and $B_{j}Y_{k}$.
3.4. **Computational methods**

3.4.1. **Basis sets**

In real materials, bulk single crystals are periodic systems of a near infinite size of atoms. But to be able to solve such a system it must be reduced from an infinite system to a finite system. Hence, the periodicity of the materials is used in which, the system is broken up into unit cells that are repeated periodically towards all directions. To model this periodic nature, periodic function can be used.

### 3.4.1.1. Plane waves

The periodic ions will also have periodic external potential acting on the electrons. To model this system the use of the Bloch’s theorem[189] can be applied. Bloch’s theorem uses the periodicity to produce wavefunctions equal to the number of electrons in the unit cell. The wavefunction solution of the Schrödinger equation using a periodic potential is described in Equation 3-43.

$$
\psi_i(r) = e^{ikr}f_i(r)
$$

Equation 3-43

$e^{ikr}$ describes the wave, while $f_i(r)$ describes the periodic unit cell, the periodic unit cell part can be expanded to give Equation 3-47. Where $G$ is the reciprocal lattice vector given by defined as $G \cdot l = 2\pi m$, where m is an integer and l are the lattice vectors.

$$
f_i(r) = \sum_G c_{i,G} \times e^{iG \cdot r}
$$

Equation 3-44
The electronic wavefunction hence can be written as described in Equation 3-45 which is the sum of plane waves.

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,k+G} \times e^{i(k+G) \cdot \mathbf{r}}$$  
Equation 3-45

When used for DFT calculations Equation 3-45 can be inserted into Equation 3-34 and used with Equation 3-29 to obtain the form in Equation 3-46 as described in [190].

$$\sum_{\mathbf{G}} \left[ \frac{\hbar^2}{2m} |k + G|^2 \delta_{gg} + V_{ext}(G - G') + V_{ee}(G - G') + E_{xc}(G - G') \right] c_{i,k+G} = \epsilon_i c_{i,k+G}$$  
Equation 3-46

Through Fourier transformations Equation 3-45 can be converted from real to reciprocal space. The set of plane waves is within a sphere in this reciprocal space represented by $E_{cutoff}$, for all values of $\mathbf{G}$. The introduction of a plane wave energy cut off limits the basis set to a definable size, however it also limits the plane waves high kinetic energy although this does not affect the result as plane waves with small kinetic energy are of more importance. So, the convergence of the calculation with respect to $E_{cutoff}$ as described by Equation 3-47 will be necessary to determine the amount of plane waves to take into consideration. The convergence of the $E_{cutoff}$ is further discussed in Section 3.4.4.

$$\frac{\hbar^2}{2m} |k + G|^2 < E_{cutoff}$$  
Equation 3-47
3.4.1.1. Projector-Augmented-Wave method

The need for pseudopotential arises from the fact that core electrons are of less importance as they see a weaker potential than the full Coulomb potential and so can be approximated through a potential which can be added to $V_{\text{ext}}$ in the KS functional. The PAW method introduced by Blöchl[191] combines the ideas from pseudopotential methods and LAPW(Linearized Augmented Plane Wave) and has similarities to the ultrasoft pseudopotential method[192, 193]. The PAW method a linearly transforms the pseudo to an all electron wave function then derives the PAW total energy by applying this linear transformation to the Kohn-Sham functional. For a more complete formalism refer to [191].
3.4.2. **Self-Consistency Field method**

Self-consistency is used in DFT to find the electron densities by converging the eigenvalue first introduced by Hartree-Fock for HF equations. A summary is given in Figure 3-5.

![Diagram of the SCF method used to converge the KS Hamiltonian](image)

Figure 3-5 Diagrams of the SCF method used to converge the KS Hamiltonian, in which the closeness of the densities should be specified to allow convergence otherwise will convergence will not be achieved.
3.4.3. **Software and Hardware**

In this thesis calculations are performed with the assistance of the CASTEP (version 3.1)[194], Dmol3 (version 8.0)[195], and VASP(version 5.4.4)[192, 196-200], quantum chemistry software packages. Using the 4x AMD Opteron 6174, 2x AMD Opteron 6174, and 2x Intel Xeon E5-2699V3 supermicro HPC’s, as well as allocations on the RAIJIN cluster provided by the National Computational Infrastructure (NCI).

3.4.4. **Testing convergence**

Testing convergence refers to the convergence of two parameters, these are the Energy-cut off and the K-point mesh. Section 3.4.1.1 describes s parameter E-cut which controls the number of plane waves accounted for within the basis-set expansion, of course the most accurate would come from accounting for all plane waves. However, due to limitations in calculation hardware and accounting for the fact that the electronic energy converges with a number of plane waves it is possible to approximate the point in which the plane waves of higher energy than the cut off energy has almost no interaction.

The second parameter of significance is the K-point sampling within the Brillouin zone, like the energy cut off the most accurate would arise from the maximum number of k-points in the Brillouin zone. Due to limitations in calculation hardware and accounting for the fact number of k-points also converges with the electronic energy, hence at a certain k-point density it can be approximated that there would not be any unexpected changes in the charge density and the potential, so that at that point it would be equivalent to the maximum number of k-points i.e. reached convergence. There multiples algorithms in generating the k-points used the in the calculation, the most popular being the Monkhorst Pack[201].
To find the converged parameter for the cut-off energy and the number of k-points. Two sets of convergence tests should be performed, the first by increasing the number of k-points, while fixing a cut off energy to see at which point the convergence occurs for the k-point vs Energy. The second by increasing the number of plane waves increasing the cut off energy, while fixing a set of k-points to see at which point the convergence occurs for the cut off energy vs Energy. To ensure the further reliability of the calculations and to reduce to overall error, the convergence points can then be used to then be used to find a new convergence.

3.4.5. **Structure optimization**

As DFT fixes the position of the ions hence calculations involving DFT do not minimize the ion positions. Hence it is necessary to use certain schemes to achieve minimization of the ion positions to find the lowest energy positions for the system with respect to KS Hamiltonian. The various methods used in this thesis are the Conjugate Gradient Method[202] and BFGS algorithm[203].
3.4.6. *Construction and calculation of heterostructure*

The previous sections gave a brief overview of the DFT methods used in this thesis. This section discusses the methods used to construct and interpret models of the van der Waals heterostructures

3.4.6.1. **Lattice rotations and translation**

Alignment of heterostructures play an important part in 2D materials, hence when performing calculations, specific rotations should be considered. When building heterostructures, the lattice symmetry of each layer must match accordingly. When aligning between a supercell and primitive cell or layers of different supercell sizes, it is necessary to consider possible rotations of the supercell. In two dimensions these can be modelled by transforming the co-ordinates using the following linear algebra:

3.4.6.2. **Translation**

Can be performed simply by adding the translated position:

\[
\begin{bmatrix}
T_x \\
T_y
\end{bmatrix}
\]

3.4.6.3. **Rotational matrix**

\[
R_\theta = \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}
\]

Equation 3-48

3.4.6.4. **Reflection matrix**

\[
X - axis \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, Y - axis \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, X = Y \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}
\]

Equation 3-50
3.4.6.5. Example input files for VASP

This section an example of the input files needed for VASP to calculate a van der Waals heterostructure, INCAR, POSCAR, KPOINTS.

```ini
#*******************************************************************************
# START INCAR
#*******************************************************************************
PREC = Accurate
ENCUT = 500.000
IBRION = 2
   NSW = 200
ISIF = 2
NELMIN = 2
EDIFF = 1.0e-05
EDIFFG = -0.02
VOSKOWN = 1
NBLOCK = 1
NWRITE = 1
NELM = 100
   ALGO = Normal (blocked Davidson)
IVDW = 1
   LVDW = .TRUE.
VDW_S6 = 0.75
VDW_SCALING = 0.75
   ISPIN = 1
INIWAV = 1
   ISTART = 0
ICHARG = 2
   LWAVE = .FALSE.
LCHARG = .FALSE.
ADDGRID = .FALSE.
ISMEAR = 1
   SIGMA = 0.2
LREAL = .FALSE.
RWIGS = 0.77 0.75 0.82 1.41
#*******************************************************************************
# END INCAR
#*******************************************************************************

#*******************************************************************************
# START KPOINTS
#*******************************************************************************
Automatic mesh
0
Gamma
   4   4   1
   0.  0.  0.
#*******************************************************************************
# END KPOINTS
#*******************************************************************************
```
(Sn B3 C6 N3)2 (P1) ~ 415 minimized: S3-5L-AB-BNCSnBN-AB-BN1 (VASP)
1.0
4.29360000 0.00000000 0.00000000
-2.14680000 3.71836667 0.00000000
0.00000000 0.00000000 50.00000000
12 6 6 2
Direct
0.66801109 0.99881558 0.31736365
0.00140350 0.66550119 0.31736697
0.33471831 0.33221262 0.31736259
0.00135855 0.33214771 0.31734928
0.33468054 0.99880793 0.31735306
0.66801001 0.66548984 0.31734821
0.66796499 0.99874268 0.62243341
0.33465197 0.33217835 0.62243017
0.00141201 0.66550530 0.6224394
0.00140451 0.33222284 0.62240246
0.66805020 0.66550973 0.62241635
0.33474020 0.99886103 0.6224170
0.00154722 0.99901866 0.37971399
0.33490212 0.66567357 0.37973653
0.66828288 0.33241218 0.37972744
0.66822103 0.33239338 0.68475225
0.00158769 0.99905586 0.68478325
0.33496116 0.66579723 0.68474090
0.33490544 0.33240328 0.37963242
0.66826878 0.99902109 0.37963475
0.00158227 0.66570396 0.37963160
0.00161546 0.66579873 0.68470891
0.33496852 0.33243007 0.68471149
0.66825737 0.99908817 0.68470839
0.33353307 0.66648005 0.51866423
0.66657496 0.33343716 0.48412107

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Chapter 4

4. Tuning the electronic structure in stanene/graphene bilayers using strain and gas adsorption

4.1. Overview

Epitaxial growth of stanene monolayers on graphene substrates is an attractive synthesis route for atomically-thin electronic components, however, it remains unclear how such composites will tolerate lattice strain and exposure to ambient atmosphere. Using density functional theory, the work in this chapter identified several epitaxial configurations for the stanene-graphene bilayer system and determined the effect of strain and water adsorption. In addition to previously reported co-aligned bilayers, a second family of low energy structures are identified here, involving rotation of one layer by thirty degrees. The band structures of the rotated configurations exhibit a fully metallic interface, whereas the co-aligned structures are poised at the transition between semi-metallic and semiconductor characteristics. In general, the electronic states are directly correlated with differences in the buckling parameter of the tin layer assigned to the competition between \( sp^2 \) and \( sp^3 \) hybridization schemes. This can be controlled by strain to yield a metal-insulator transition in special circumstances. For the equilibrium structure, \( H_2O \) preferentially adsorbs on the stanene layer, and the system remains metallic with a mixture of Dirac and parabolic bands at the Fermi surface.
4.2. Introduction

Over the past decade, the quest to discover materials with superior properties has unveiled a treasure trove of two-dimensional crystals that form in honeycomb lattices. The prototypical material in this family is the now-famous carbon allotrope, graphene, which consists of a single layer of \( sp^2 \) hybridised atoms\(^{204, 205} \). The strong interplay between the chemical and the electronic structure in the carbon honeycomb lattice leads to a band structure with regions that are linearly dispersive. Consequently, electrons behave as so-called Dirac fermions obeying the relativistic equation at low energies, yielding many appealing electronic and chemical properties, for example, rapid charge transport, semimetallic conductivity and low resistance states\(^{12, 18, 26, 39} \). Furthermore, zero gap\(^{206} \) 2D materials with Dirac dispersion are very sensitive to adsorbed molecules and offer potential as ultra-sensitive gas sensors\(^{40} \). Collectively these properties have stimulated immense international efforts to mass-produce sheets of graphene in recent years.

Despite its overall utility, however, graphene does not have an intrinsic band-gap, posing a severe limitation for applications requiring tunable semiconducting characteristics (e.g. photocatalysis, field effect transistors, Quantum Spin Hall Insulators). This has motivated a parallel search for closely-related 2D materials which possess a Dirac electronic structure but enable tunable conductivity via spin-orbit or charge-transfer gaps. The growing list of candidates now includes hydronated-borophene\(^{207} \), silicene\(^{208} \), germanene\(^{209} \) and stanene\(^{105} \).

Recently, stanene (a honeycomb monolayer of Sn) has attracted special interest owing to its outstanding electronic properties supported by the strong spin–orbit coupling (SOC)
which enables significant gap formation, and potentially generates robust 2D topological insulating states ideal for quantum transport[106, 210]. Compared to graphene, planar stanene is a less stable chemical structure, and to account for the instability, Sn atoms adopt a buckled form of the hexagonal honeycomb. The buckling in stanene results from the preference of $sp^3$ hybridization over $sp^2$ which lowers the bond angles from $120^\circ$ and increases bond lengths. Furthermore, unlike graphene, it has not been possible to produce stanene simply by mechanical exfoliation. Instead, pioneering experiments have relied on epitaxial growth of stanene sheets on Bi$_2$Te$_3$ (0001) and Ag(111) substrates[105]. It is noteworthy that such substrates produce a large lattice mismatch of 6.68% compared to the hypothetical equilibrium lattice of freestanding stanene, and substrate-induced charge transfer also affects electronic structure [105]. Consequently, two grand challenges remain, namely: i) to realise quasi-free-standing versions of stanene with a structure close to that of the ideal monolayer ii) to electronically or chemically passivate the composites to survive in ambient atmosphere. To this end, one potential avenue is to exploit freestanding graphene as a substrate, since the predicted lattice mismatch is significantly smaller at 5.01% and graphene is chemically stable. More generally, it is also the subject of fundamental curiosity to clarify whether the interplay of Dirac states in graphene and stanene will produce new exotic phenomena, or just act as a weakly-interacting van-der-Waals (vdW) composite that is merely the sum of its parts.

A recent density functional theory (DFT) theoretical study of the bilayer stanene/graphene system provided an introductory overview of the properties, together with the striking revelation that a gap can be formed[126]. Further theoretical and experimental exploration is needed, however, to clarify the effect of lattice strain, and whether gap formation is universal for all epitaxial configurations, or if it depends on the level of misalignment between the sub-layers. It also remains unclear whether the special
electronic features can survive when exposed to the ambient atmosphere. To address these questions, this section is divided into three sections. In the first section, clarification of the general effect of lattice strain on a hypothetical monolayer of free-standing stanene was given, providing a general framework to understand lattice-strain effects. In the second section, examination of the graphene-stanene bilayers with various configurations and strain was performed. In the final section, an analyse of the electronic structure change from H$_2$O molecular adsorption was performed.

4.3. Results and discussion

4.3.1. The strain-structure relationship for monolayer stanene

Compared to graphene[37, 211] there are relatively few studies on effect of strain on the electronic structure of stanene. It is, therefore, useful to clarify the effect of strain in this new material and identify the range of lattice parameters where the semi-metallic Dirac dispersion exists before discussing the more complicated bilayer system. Figure 4-1 shows the effect of strain on the chemical and electronic structure of a hypothetical freestanding stanene monolayer when the lattice constants were clamped at fixed values between 4.4 to 5.0 Å, while allowing the internal atomic positions to relax. Clearly tensile or compressive strain modify the buckling height of the stanene sublattices (Figure 4-1 a, c, e). The Sn-Sn bond length in Table 4-1 shows a relationship with the area of the plane and the buckling distance, which can be easily understood because, as the area of the plane shrinks, the Sn-Sn bond must move out of the plane, which increases the buckling distance. Figure 4-1 summarises the resulting cohesive energy, buckling parameter and bond-angle for different lattice constants. As expected, the maximum in the cohesive energy occurs as the equilibrium lattice constant 4.609Å in good agreement with past works[120, 126, 212]. However, the buckling and bond-angle parameters show three distinct regions of behaviour labelled in Figure 4-1(i) as Regions (1), (2) and (3).
Furthermore, the inset illustrates that each of these regions possesses a characteristic electronic band structure. In Region (1), for compressive strain for \((a < 4.55 \, \text{Å})\), the stanene is metallic, and semi-metallic character is lost because the Dirac point at K-point is below the Fermi level. For Region (2), between 4.57 to 4.75Å, the system is a pure Dirac semimetal with the Fermi level at the K-point, and no overlapping bands at the Γ point. This corresponds to the lowest energy configuration. Consequently, the calculated band structure agrees well with past reports[213]. Beyond this point, in Region (3), tensile strain result causes the Γ-centred bands to cross the Fermi level, such that the system becomes a multi-band conductor with both Dirac and parabolic valleys. It is important to note that the equilibrium Region (2) is narrow, and electronic structure of stanene is rather delicate so that a strain of 5% can easily lead to a transition into either Region 1 or 3. This provides an important guideline to understand the following results on the graphene/stanene bilayers.

4.3.2. \textit{Lattice-strain in epitaxial matched stanene-graphene bilayers}

Five symmetric combinations of the matching honeycomb lattices were constructed to investigate the stanene/graphene bilayer, as shown in Figure 4-2 and labelled S1-S5, in order of increasing lattice constant. Only the final structures are shown in the Figure 4-2 together with the resulting band structures after ionic relaxations and lattice optimisations were performed to minimise energy and the internal atomic co-ordinates. Structure S1 and S2 correspond to a rotation of the graphene sub-lattice of 29.8 degrees with respect to the stanene lattice. Although the rotated bilayer structures (S1 and S2) are clearly viable structural configurations, this is the first time these have been proposed for this system. Meanwhile, Structure S3-S5 are close related to the previous models proposed in Ref [126], where the hexagonal lattice vectors are co-aligned for the graphene and stanene.
Structures in the two families (S1-S2) and (S3-S5) differ only by an additional translation of one lattice with respect to another. To evaluate the interaction between the layers of graphene and stanene, the binding energies were calculated for the bilayer, in terms of the binding area per area $E_{\text{b/area}}$ and $E_{\text{b/Sn}}$ using the formulas:

$$E_{\text{b/area}} = \frac{(E_{\text{GSn}} - E_{G} - E_{\text{Sn}})}{A}$$

$$E_{\text{b/Sn}} = \frac{(E_{\text{GSn}} - E_{G} - E_{\text{Sn}})}{n}$$

Where $E_{\text{GSn}}$ is the enthalpy energy of the bilayer, $E_{G}$ is the enthalpy energy of monolayer graphene, $E_{\text{Sn}}$ is the enthalpy energy of monolayer stanene, $A$ is the 2D area of the (001) plane across the unit cell and $n$ is the number of Sn atoms in the supercell.
Figure 4-1 The relationship between strain and structure in hypothetical stanene monolayers. (a) In-plane compressive strain increases the buckling height as shown by the cross-section of the strained layer (blue) superimposed on an unstrained layer (green/cyan). (b) A top view of stanene structure looking from the z-direction towards the origin, a green colour indicates the Sn atom is closer to the viewer, a cyan colour shows the Sn atom further away. The rhombus shape shows the primitive cell of the stanene lattice. (c) Pristine stanene at its equilibrium lattice constant has a well-defined buckling height $d = 0.888$ Å separating the Sn two sub-lattices. (d) An isometric view of the stanene structure which shows the bond-angle $\theta$ in degrees. (e) Tensile strain decreases the buckling height shown by superimposing the strained layer (red) on the unstrained layer (green/cyan). The median structure band structure of strained regions of (1), (2) and (3) are shown in (f), (g), (h). (i) The strain phase-diagram indicates a strong interplay between the cohesive energy, buckling, bond angle and the band-structures.
<table>
<thead>
<tr>
<th>Structure</th>
<th>BE per area (meV/Å²)</th>
<th>BE per Sn (meV/Sn)</th>
<th>Lattice (Å)</th>
<th>Interlayer separation (Å)</th>
<th>Stanene buckling height (Å)</th>
<th>Average Sn-Sn bond length (Å)</th>
<th>Average C-C bond-length (Å)</th>
<th>C-C (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>-19.16</td>
<td>-152.69</td>
<td>a=4.290, b=4.290</td>
<td>3.328</td>
<td>1.250</td>
<td>2.711</td>
<td>1.430</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>-24.72</td>
<td>-191.58</td>
<td>a=4.294, b=4.294</td>
<td>3.129</td>
<td>1.210</td>
<td>2.760</td>
<td>1.431</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>-11.12</td>
<td>-170.55</td>
<td>a=4.906, b=4.901</td>
<td>4.041</td>
<td>0.799</td>
<td>2.946</td>
<td>1.416</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>-17.105</td>
<td>-178.42</td>
<td>a=4.908, b=4.908</td>
<td>3.292</td>
<td>0.790</td>
<td>2.942</td>
<td>1.417</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>-12.00</td>
<td>-125.27</td>
<td>a=4.92, b=4.92</td>
<td>3.359</td>
<td>0.683</td>
<td>2.921</td>
<td>1.421</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-1 Summary of the binding energy, lattice constants, interlayer distances, buckling heights and bond-lengths for graphene/stanene bilayers in five different epitaxial
The resulting binding-energies, lattice constants, bond-angles and buckling parameters are summarized in Table 4-1. To summarise, the structures with the two sub-lattices rotated by 30 degrees give the lowest energy configuration, and overall S2 is the most stable. Of the collinear structures, the binding energy is relatively similar to past work[120], the difference being this study used the structurally-optimized lattice constant for the relaxed rotated and un-rotated configurations, as opposed to an average or idealised lattice constant used in Ref. [126]. Interestingly, the relaxed lattice constants for the collinear and non-collinear graphene and stanene lattices are very different. For the rotated lattices, the lattice is contracted (~4.28 Å) compared to pristine stanene (4.609 Å), whereas the lattice is expanded (~4.92 Å) for co-aligned bilayers. In general, the interlayer spacing is between 3.2-3.3 Å as typical for layered structures, however S3 has a larger separation. It appears S3 should be regarded as a metastable state trapped in a local minimum at the transition between S4 and S5, depending on the fine details of the optimization procedure.

From the optimized lattice parameters and bond length changes reported in Table 4-1, it is possible to conclude that the rotated structures (S1-S2) generates a compressive strain on the stanene layer and a tensile strain on the graphene layer of the bilayer. For the co-aligned structures S3-S5, it is possible to discern that the opposite is happening. Although both lattices were relaxed in the calculation, in general the effect on graphene is rather small yielding lattice constants that deviate less than 1% from ideal graphene (a=2.46 Å, 4.92 Å in the 2x2 collinear configuration or 4.26 Å in rotated configuration). In contrast, stanene experiences 5-6% strain.
Figure 4-2 The epitaxial stanene/graphene structure (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5 structures where grey atoms indicate carbon and green and cyan atoms indicate the two planes of Sn atoms with bond angle $\theta$ (°). (f), (g), (h), (i) and (j) are the corresponding band structures for the fully relaxed bilayer structures S1-S5. (k) A cross-section showing the interlayer separation (D) and the stanene buckling parameter (d). (l) Isometric representation of the bilayer structure.
Figure 4-3 The co-aligned structure (S4) can exhibit a gap around K point with either a) metallic bands at Γ or b) a gap at Γ, depending on the level and type of strain applied. The gap around the K point is only apparent for moderate degrees of compressive strain compared to the optimal bilayer lattice for the S4 structure c) and d) shows the band structures of the individual non-interacting layers of stanene and graphene respectively under the same level of compressive strain, and with same atomic structure constrained to the bilayer positions. This demonstrates gap formation at the K point is not a result of the strain on the individual layers but is instead a unique feature of the C-Sn interactions in the strained bilayer.
The resulting band structures for the optimized structures are also shown in Figure 4-2. For the rotated lattices S1 and S2, the band structure is drawn using the stanene frame-of-reference, and consequently one can identify the stanene Dirac cone at the K-point while the graphene Dirac cone, is rotated and appears near the Γ point. Importantly, the rotated structures (S1-S2) show no indication of a gap near the K-point, and Fermi level instead is shifted upwards into the conduction band. In contrast, for S3-S5 both Dirac cones occur at the K-point owing to the co-aligned lattices. Furthermore a gap does open in the K-point bands for the co-aligned structures (S3-S5), in qualitative agreement with past work[126]. However, overall, the system remains metallic owing to the lowering of bands that cross the point at the Γ. The latter detail differs from past work where somewhat idealized lattice constants were used[126], however it is perfectly in line with the behaviour identified in the tensile case Figure 4-1 (i) Region (3) of the single layer stanene, caused by the expanded lattice constant used in the optimized solutions.

To identify the specific conditions for forming a complete gap in the system both at K and Γ, calculations was performed for the system under moderate degrees of compressive strain. This approach is based on the insight from Figure 4-1 that strain should modify the band-crossing at the Γ point of the Sn while preserving the K point features. Figure 4-3 shows the band structure for S4 at lattice constants of 4.609 (Figure 4-3, a) and 4.908 (Figure 4-3, b) Å respectively. Clearly, the smaller lattice constants produce a gap with a magnitude of 103 meV at the K point. This gap is not just a result of the strain applied to either layer individually which can be shown through the electronic structure for when the lattice parameter is set to 4.908 Å on individual layers of stanene (Figure 4-3, c) or graphene (Figure 4-3, d), or the lattice parameter 4.609 Å on stanene (Figure 4-1, g). This shows that the gap is a result of the strain applied when the two layers are combined indicating graphene-stanene interactions play a role. It is well-known that DFT GGA and
PBE underestimate band-gaps, so it is likely that the experimental gap may be significantly larger.

It is intriguing that such small shifts in the lattice constant affect the electronic structure of the composite system so strongly because this behaviour indicates the possibility of tuning the conductivity in the bilayer system using a moderate degree of applied strain. Such behaviour could potentially offer a method to switch between conductive and semiconducting states, enabling a type “pressure-field-effect transistor”. It can be noted, however, that this feature only appears for the collinear structures, and not in the rotated structures. According to the binding energy (Table 4-1), the former is less energetically favourable, although they may appear as metastable structures experimentally. It is clear that gap formation at the K point is from interaction between the two layers, rather than the effect of strain on the individual layers, given that effect of strain in graphene is well-known from past studies[37, 211], and the calculation for stanene (Figure 4-1) also shows no gap. Clearly, the underlying interactions also depend closely on whether the lattices are co-aligned or rotated.

For the co-aligned bilayers when graphene, which has a gapless Dirac band-structure, is combined with stanene, which also has a gapless Dirac band-structure, the resulting band-structure possesses a clear gap at the K point (S3-5). For the rotated configurations, there is no gap at the Fermi level. It is clear in all cases that the Sn-C lattice is not only bonded through the vdW interaction since charge transfer also plays a role to give some ionic character to the system. However, the criteria for gap formation are determined by which orbitals are involved in the Sn-C interaction.
Figure 4-4. The orbital projected band structure and density of state for a) the S4 the co-aligned structure at the gap condition b) the lowest-energy S2 rotated structure and. The red show the s orbital contributions, green shows the total orbital contributions of the px, py and d orbitals, and blue represents the pz orbital contributions.

By mapping the contribution of orbitals in Figure 4-4 b of the rotated bilayer structure it can be observed that there is a mixing between pz and other contributions (px, py) at the Γ points as shown in Figure 4-4 a. Analysis for the separate elements indicates that the px, py and pz contributions arise from strain in stanene forcing the system away from sp2 bonding, causing a shift in the Fermi level as for the isolated layer in Figure 4-1. In contrast, for the co-aligned Sn-C structure, the states near the Fermi level are nearly of pure pz character (Figure 4-4 b) and the graphene and carbon Dirac cones overlap such
that gaps can be formed by relatively small charge transfers between the sublattices[123, 125, 214].

To better understand how the interacting stanene and graphene leads to the gap formation at the K-points for the collinear structures (S3-5), a comparison of the charge-transfer in the equilibrium state is made. Inspection of the Mulliken charges indicates that electrons move in the S1, S2, S3, S4, S5 structures from stanene to graphene by 0.19e, 0.3e, 0.2e 0.42e and 0.35e and dopes the graphene with electrons in every 2x2 graphene unit cell due to the buckling of the stanene. The result of the charge transfer between the Sn and Graphene layers results in the formation of a gapped graphene[215, 216] as a uneven doping of electrons causes the breaking of symmetry between the two sublattices[123, 125, 214], enforced by the staggering of the stanene. Charge transfer also occurs between the upper and lower layers of these Sn sublayer resulting in an average charge difference of 0.42e, 0.45e, 0.58e, 0.65e and 0.61e for all tin atoms between Sn atoms closest to the graphene and the second Sn layer. As a result of this charge difference, there is also a disparity within the sublattices of the stanene which results in the formation of a gap within the stanene layer[217]. By comparing the charge transfer and interlayer distance it is possible to see that there is also a correlation in that as interlayer distance increases, charge transfer decreases. From the electronic structure at the K point, it is clear that there is still a significant overlap between the two Dirac cones derived from the p\textsubscript{z} orbitals that implies interaction. For both the gapped and ungapped states, the difference in the Fermi level of the two combined layers is much larger for the stanene which has high energy 5p-orbitals compared to that of graphene 2p-orbitals. Consequently, the final Fermi level for stanene is effectively shifted down, while the final Fermi level for graphene is effectively shifted up resulting in p-type stanene and an n-type graphene.
Even if a gap is formed at the Dirac K-point in S3-S5, it is equally important to determine the band structure at the Γ point, as this may remain metallic if the stanene has an electronic structure similar to Region (3) in Figure 4-1. For a gap to form, the main contribution of p orbitals around the Fermi level must be from the p\textsubscript{z} orbital. If tensile strain is applied to stanene, this shifts electrons towards a sp-hybridization with a decrease of hybridization from electrons forming π-π bonds due to the increase in distance. The change in the hybridization results in the band becoming metallic at the Γ point. Based on this combined understanding of the K point gap and the Γ point gap, it can be predicted that there is a complete metal-to-insulator transitions in the bilayer system through the application of pressure.
Figure 4-5 a) & b). Side and top view of the adsorption position of H₂O molecule on the graphene with an electron density map of the H₂O molecule which adsorbs with the hydrogen closest to the graphene layer. c) and d) Shows the side and top view of the H₂O when adsorbed on the stanene layer. e) Representative band structure of S2 in which shows band structure before and after adsorption on either C or Sn Side of the structure
4.3.3. **Anisotropic H$_2$O adsorption in the stanene-graphene bilayer**

Water adsorption on 2D materials is of great interest, both because it provides an indication of their gas-selective gas-sensing ability, and because it will ultimately be an environmental factor for ambient devices. To test this aspect in the stanene-bilayer structure, adsorption energies calculations were performed on the bilayer for H$_2$O single molecules in lowest energy rotated bilayer structure (S2). Figure 4-5 a-b) shows the relaxed position of the water molecule on the graphene side of the bilayer surface respectively for S2 bilayer configuration. The calculation shows that the preferred orientation is a rotated orientation with one of the hydrogens facing down.

The binding energy for the H$_2$O adsorption on graphene side of the S2 bilayer was shown to be stable at -0.710 eV per unit cell. The final distance between the hydrogen of the H$_2$O and the graphene surface was found to be 2.44Å. H$_2$O adsorption on the graphene side with a charge transfer of 0.01e which is opposite to the charge transfer shown for monolayer graphene (-0.025e)[218] This shows that the graphene in the bilayer is an electron acceptor and hence quite different from monolayer graphene which is a donor[39]. For comparison, the H$_2$O adsorption on the stanene side of the S2 bilayer is shown in Figure 4-5 c) and d). The binding energy for H$_2$O adsorption on stanene is stable at -0.877 eV per unit cell, and lower than that of the graphene side, indicating it is energetically favourable for the H$_2$O to be preferentially adsorbed on the stanene layer. Furthermore, in the latter case, the hydrogen prefers a rotated configuration with one hydrogen facing the stanene and the other facing parallel to the plane of the stanene. The final vertical distance between the bottom most hydrogen and the topmost tin atom was 1.80 Å. The corresponding charge transfer is -0.01e, which smaller than the predicted value for pristine stanene (0.048e) [212].
To clarify how charge-transfer and structural modification from the H₂O affect the electronic properties, calculation was performed to obtain the band structures in Figure 4-6 b. Changes in the dispersion of the bands near the K-point appear before and after water adsorption compared to the water-free equivalent (S2). The latter features are fundamentally different from the pure electron-doping that causes gas sensing functionality in monolayer graphene. Similar analysis was performed of other structures (S1, S3-5), indicating that the molecular species does not initiate a complete metal-insulator transition, although the adsorbed species will modulate the intrinsic conductivity of the bilayer.
The work function values of the various adsorbed structures are shown in Figure 4-6, which shows dependence on the bilayer structure and the side in which H\textsubscript{2}O is adsorbed. A general trend can be seen in which the S1, S3, S4, S5 graphene adsorbed side shows a higher work function than the Sn side as the gas molecules hybridize with the lower energy orbitals of the graphene.

4.4. Conclusions

In summary, by looking at the interplay between of the stanene lattice and the electronic band structure it is possible to rationalise the complex behaviour of metallic states which exist in stanene/graphene heterostructures. Overall the rotated structures (S1-S2) are more stable than the co-aligned structures. The corresponding electronic structures in this family are rich and diverse. Depending on the level of strain and rotation, the Fermi level can host either Dirac or parabolic bands or a mixture of both. By closely examining the strain the system, it is possible to pinpoint the structures where a gap can be opened and suggest that it should be possible to drive this reach with external stimuli (pressure or strain). The mechanism for the metal-insulator transition is via adjusting the relative population of p\textsubscript{z} orbitals which exist in the structure, and thus affecting the buckling as well the electronic structure. Finally, results show that in a vacuum, water vapour will be adsorbed on the bilayer structure and will modulate the conductivity but will not greatly distort the band structure. While it remains to establish the effect of other adsorbed gases, these results are promising because they indicate the possibility of well-behaved electronic components that preserve their properties tuned by the level of strain.
4.5. Computational Methodology

In this work, first principle calculations were performed using density functional theory[156, 157] (DFT) implemented by the CASTEP package[194]. The exchange correlation function used to describe the exchange-correlation interaction was the General Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[162] formulation. The Ultrasoft Pseudo Potential was used along with a van der Waals (vdW) correction (DFT-D) implemented by Grimme[219]. Structures are optimized using the Broyden–Fletcher–Goldfarb–Shanno algorithm BFGS[203]. The atomic positions and cell vectors are relaxed until the energy, maximum force and maximum displacement are less than $5.0 \times 10^{-6}$ eV/atom, 0.01 eV/Å, and $5.0 \times 10^{-4}$. Furthermore, a vacuum space larger than 20 Å was utilized to prevent interactions between neighbouring layers in the direction normal to the graphene and stanene surface. The reciprocal space Brillouin zone paths selected for band structure calculations are the $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$ points.

In order to validate the calculation method, calculations had been performed on both graphene and stanene independently and the optimized band structures in both structures are comparable to experimental results[105] and in both structures, it was possible to obtain Dirac dispersions, comparable to that of other theoretical works[126, 212, 220]. Geometry optimization was performed for both trilayer and bilayer graphene where a 7x7x1 K-point set was used and a cutoff energy of 640 eV was selected and a binding energy ($E_b$) of -11.954 meV, which corresponds well with the experimental results ($E_b = -12$ meV)[120, 221, 222] Calculation was also performed on a monolayer stanene under strain with lattice changes, to observe the electronic states changes that occurs, in the stanene structure throughout the changing buckling that occurs in the stanene structure. Using the same parameters. Table 4-1 shows the final parameters for the calculations. For
each system, the average lattice between the stanene and graphene lattices was used as
the starting point this also resulted in a varied number of atoms per unit cell, for the rotated
structures S1 and S2 this results in a lattice parameter of 4.435 Å with 6 carbon atoms
and 2 tin atoms per unit cell. For the co-aligned structures, S3-S5, this resulted in a lattice
parameter of 4.764 Å with 8 carbon atoms and 2 tin atoms.

Adsorption calculations of a single molecule of H₂O were performed, to explore the
possibility of using adsorption to modify the buckling effect in the structure such effect
would mean it will be possible to detection and obtained the single molecule adsorption
energy, band structure, charge transfer, work function change and electron density
distributions for use as a gas sensor. The molecule H₂O is picked for its medium strength
dipole properties. For the adsorption systems, calculations were performed using GGA-
PBE using Grimme van der Waals dispersion correction. Gas adsorption on the five
configurations of the stanene/graphene bilayer structures these are S1, S2, S3, S4 and S5.
For each case single gas molecule adsorptions were performed on each side of the bilayer
individually. The All molecules were place with a starting position with about 1 Å from
the surface of the bilayer, in total 10 adsorption calculation were performed for each gas
molecule. The surface involved a 2x2 supercell of each of the S1-S5 bilayer structures.

Complementary calculations were carried out using VASP 5.3.4 to reproduce the main
features in the electronic structure, using the lattice configurations as described in Table
4-1 using the same formulations to calculate the orbital-dependent partial density of states
shown in Figure 4-4.
Chapter 5

5. The effect of symmetrical and asymmetrical stacking in trilayer heterostructures of stanene with hexagonal boron nitride and graphene

5.1. Overview

A group of three-layered heterostructures consisting of boron nitride, graphene and stanene are investigated using density functional theory through analysing the properties of the asymmetrically-stacked hBN/Stanene/Graphene and the symmetrically-stacked hBN/Stanene/hBN and Graphene/Stanene/Graphene. The analysed properties from the calculations include optimised lattice parameters, binding energies and electronic band structures. The calculation indicates that stacking of the layers results in two types of buckling, which occur under two main types of configurations: co-aligned or rotated. The rotated configurations generally have a more stable configuration. The electronic structure of hBN/Stanene/hBN showed that the stanene in heterostructure has an electronic structure that is not perturbed by interlayer-interactions and therefore resembles the ideal stanene monolayer. For the other heterostructures, however, strong bonding interactions across the interface generally modify the electronic structure. The primary results are presented in Section 5.3, using the methodology described in Section 5.5.
5.2. Introduction

2D materials provide an exceptional platform for materials design. The current family of 2D materials includes a variety of metals (e.g. NbSe$_2$)[223], semimetals (e.g. graphene)[12], semiconductors (e.g., MoS$_2$)[224], and insulators (e.g., hexagonal boron nitride (hBN))[225]. Many of these are stable under ambient conditions. While new materials are beginning to synthesized at an increasing rate (Silicene[226], Stanene[105], Germanene[227]), such materials often have limited stability at ambient conditions which are a crucial criterion for use in practical applications. One such strategy to increase the stability of these new 2D materials is the use of a capping layer and a substrate to greatly reduce interactions with ambient air conditions(e.g. oxidation). Hexagonal boron nitride(hBN) currently has been shown to be a suitable candidate for the insulation of interactions between ambient conditions and a suitable substrate for various materials[92, 228-230]. Such methods, however, are limited for electronic applications as often the substrate affects the structural configurations and is detrimental to the desired electronic properties of the material[125]. One family of materials that is extremely susceptible to these changes are the 2D Dirac gapless semimetals, as the band structures show a linear dispersion relationship around the Fermi energy. Because of their unique band structure, they are easily affected by adjacent layers due to electron-electron interactions.

One of the prominent influencers of electronic properties in most 2D Dirac materials, par atomically flat materials (e.g. graphene), is the degree of buckling. In these materials, the buckling determines the orbital configurations. This buckling results in the electron properties as seen in silicene[231]. Hence, one of the main challenges in the protection of a 2D Dirac materials is not only the selection of a material that provides chemical protection properties. This material all needs to have minimal effect on the electronic
properties, while only applying a minor maintaining the electronic properties of the material.

A well-known technique for minimising the strain between the protection layer and protected layer is through the epitaxial matching of the lattices. In systems with strong local bonds, controlling the epitaxial matching is critical to tuning the electronic properties. It is tempting to believe that the situation is different for layers of weakly interacting van der Waals force because these limit electronic interactions and charge transfer between the layers, potentially permitting a broader combination of the materials. If this is true, in general, a weakly-interacting van-der-Waals (vdW) composite should be merely the sum of its parts. On the other hand, the exact role of the competing effects has yet to be established, particularly for the more complicated 2D materials such as stanene. Owing to the tendency for the structure to buckle, the lattice parameter of stanene can vary by a significant degree, and a change of the lattice parameter through a mismatch of either the substrate or capping layer can cause a strain. This strain deforms the material which will result in a change of the buckling, bond length, bond angle and lattice parameters of mostly the stanene. In general, this may be detrimental in electronic applications, as it will change the electronic band structure. This chapter examines three materials because of their closely matched lattice structures, which are used to build up the heterostructures. These are stanene, graphene, and hBN. The lattice parameters of graphene(2.46 Å) and hBN(2.52 Å) in a 2x2 supercell configuration closely match the optimised lattice parameters of stanene 4.669Å, with a relatively low mismatch or around 5%-8%.

Three types of trilayer heterostructures: hBN/Stanene/hBN, hBN/Stanene/Graphene, and C/Sn/C are studied using density functional theory (DFT) modelling and analysis.
Investigations are performed into the mechanisms in how these layers interact and buckle within configurations of heterostructure materials, under different competing stacking configurations (symmetrical vs asymmetrical and rotated vs co-aligned configurations).

A key question is whether an hBN layer has hybridisations with or protects or the electronic properties of stanene.

Figure 5-1 Shows the structures of the various heterostructure systems for the a) BN/Sn/BN(aS(1-5)), b) C/Sn/BN(bS(1-5)) and c) C/Sn/C(cS(1-5)) systems. Blue indicates the nitrogen atom, white indicates the boron atom, green indicates the topmost tin atom, light blue indicates the bottom-most tin atom, and grey indicates the carbon atom.
Table 5-1 Summary of the binding energy, lattice constants, interlayer distances between topmost and stanene (D1) and bottom most and stanene (D2) layers as illustrated in Figure 5-1, buckling heights and bond-lengths for trilayer heterostructures in five different epitaxial configurations.

<table>
<thead>
<tr>
<th></th>
<th>Å</th>
<th>Atoms/layer</th>
<th>BE(meV)/Å²</th>
<th>D1</th>
<th>D2</th>
<th>d</th>
<th>Sn-Sn(Å)</th>
<th>C-C(Å)</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>aS1</strong></td>
<td>4.29</td>
<td>3B &amp; 3N</td>
<td>-21.98</td>
<td>3.32</td>
<td>3.32</td>
<td>1.22</td>
<td>2.77</td>
<td>1.43</td>
<td>101.59</td>
</tr>
<tr>
<td><strong>aS2</strong></td>
<td>4.29</td>
<td>3B &amp; 3N</td>
<td>-22.17</td>
<td>3.31</td>
<td>3.31</td>
<td>1.22</td>
<td>2.76</td>
<td>1.43</td>
<td>102.14</td>
</tr>
<tr>
<td><strong>aS3</strong></td>
<td>4.91</td>
<td>4B &amp; 4N</td>
<td>-19.33</td>
<td>3.38</td>
<td>3.35</td>
<td>0.58</td>
<td>2.89</td>
<td>1.42</td>
<td>116.61</td>
</tr>
<tr>
<td><strong>aS4</strong></td>
<td>4.93</td>
<td>4B &amp; 4N</td>
<td>-20.16</td>
<td>3.28</td>
<td>3.30</td>
<td>0.56</td>
<td>2.90</td>
<td>1.42</td>
<td>116.35</td>
</tr>
<tr>
<td><strong>aS5</strong></td>
<td>4.94</td>
<td>4B &amp; 4N</td>
<td>-20.11</td>
<td>3.29</td>
<td>3.28</td>
<td>0.55</td>
<td>2.91</td>
<td>1.43</td>
<td>116.23</td>
</tr>
<tr>
<td><strong>cS1</strong></td>
<td>4.29</td>
<td>6C</td>
<td>-6.19</td>
<td>5.39</td>
<td>5.06</td>
<td>1.26</td>
<td>2.71</td>
<td>1.43</td>
<td>101.39</td>
</tr>
<tr>
<td><strong>cS2</strong></td>
<td>4.29</td>
<td>6C</td>
<td>-6.10</td>
<td>5.25</td>
<td>5.25</td>
<td>1.26</td>
<td>2.71</td>
<td>1.43</td>
<td>101.44</td>
</tr>
<tr>
<td><strong>cS3</strong></td>
<td>4.91</td>
<td>8C</td>
<td>-12.67</td>
<td>3.87</td>
<td>3.87</td>
<td>0.83</td>
<td>3.00</td>
<td>1.42</td>
<td>116.29</td>
</tr>
<tr>
<td><strong>cS4</strong></td>
<td>4.93</td>
<td>8C</td>
<td>-15.46</td>
<td>3.73</td>
<td>3.49</td>
<td>0.81</td>
<td>3.00</td>
<td>1.42</td>
<td>116.35</td>
</tr>
<tr>
<td><strong>cS5</strong></td>
<td>4.94</td>
<td>8C</td>
<td>-4.79</td>
<td>5.38</td>
<td>5.36</td>
<td>0.79</td>
<td>3.00</td>
<td>1.43</td>
<td>116.30</td>
</tr>
<tr>
<td><strong>bS1</strong></td>
<td>4.29</td>
<td>6C, 3B &amp; 3N</td>
<td>-21.98</td>
<td>3.41</td>
<td>3.36</td>
<td>1.25</td>
<td>2.77</td>
<td>1.43</td>
<td>101.59</td>
</tr>
<tr>
<td><strong>bS2</strong></td>
<td>4.35</td>
<td>6C, 3B &amp; 3N</td>
<td>-22.17</td>
<td>3.34</td>
<td>3.28</td>
<td>1.24</td>
<td>2.73</td>
<td>1.45</td>
<td>103.09</td>
</tr>
<tr>
<td><strong>bS3</strong></td>
<td>4.94</td>
<td>8C, 4B &amp; 4N</td>
<td>-20.11</td>
<td>3.06</td>
<td>3.28</td>
<td>0.51</td>
<td>2.91</td>
<td>1.43</td>
<td>116.23</td>
</tr>
<tr>
<td><strong>bS4</strong></td>
<td>5.01</td>
<td>8C, 4B &amp; 4N</td>
<td>-19.33</td>
<td>3.07</td>
<td>3.28</td>
<td>0.52</td>
<td>2.94</td>
<td>1.45</td>
<td>116.29</td>
</tr>
<tr>
<td><strong>bS5</strong></td>
<td>5.01</td>
<td>8C, 4B &amp; 4N</td>
<td>-20.16</td>
<td>3.20</td>
<td>3.26</td>
<td>0.57</td>
<td>2.95</td>
<td>1.45</td>
<td>116.45</td>
</tr>
</tbody>
</table>

5.3. Results and Discussion

5.3.1. Chemical Structure

Figure 5-1 shows resultant heterostructures after optimisation with density functional theory (DFT). It illustrates the five possible configurations with closely matched lattices and arranges the heterostructures in increasing order of their lattice parameters.

The results in Table 5-1 clearly outlines the existence of two categories of structures. The (a-c)S3, (a-c)S4, and (a-c)S5 structures are non-rotated (co-aligned) and belonging to the first type of structures (type I). The (a-c)S1 and (a-c)S2 structures are rotations of the (a-c)S4 structure and belonging to the second type of structures (type II). The trends in the lattice constant for these two categories are also similar.

The emergence of two types of electronic structures corresponding to the two categories is dependent on the buckling parameters for stanene. One for co-aligned structures $d = 1.21-1.26$ Å (Figure 5-1 (a-c)S3, (a-c)S4, (a-c)S5) and one for rotated structures $d = 0.51-0.83$ Å (Figure 5-1 (a-c)S1, (a-c)S2). In the (a-c)S(1-5) systems $D_1$ shows the interlayer
distance between the topmost Sn in the stanene layer and the top hBN layer, $D_2$ shows
the bottom-most Sn in the stanene layer and the bottom hBN layer, $d$ shows the buckling
distance of the stanene layer (between the top and bottom Sn) and $T$ shows the total
distance between the hBN layers. Table 5-1 reports the lattice parameters, $d$, $D_1$, $D_2$, bond
lengths, and bond angle and that the structure forms into two distinct groups. The sections
below discuss the specific details of each structure.

Figure 5-2 Shows the relationship between the interlayer distances of the various heterostructures
hBN/Sn/hBN, hBN/Sn/C, and C/Sn/C trilayer structures. For the x-axis, the number represents an integer
between 1-5 for (a,b,c)S(X) structures where X correlates to the lattice parameters.
5.3.1.1. hBN/Sn/hBN trilayer

Figure 5-1 aS(1-5) shows the five configurations with closely matched lattices of the heterostructures arranged with increasing order based on their lattice parameters (i.e. \(a=b\) is aS1 < aS2 < aS3 < aS4 < aS5). The hBN/Sn/hBN trilayer structures are built starting from the aS4 structure with AA stacking between the hBN layers. Rotation of the stanene layer by 30°(clockwise) in the aS4 structure results in the aS2 structure. Through the translation of the aS2 stanene layer in the –(negative)y-direction, it is possible to obtain the aS1 structure. Through further rotation of the stanene layer by -30°(anti-clockwise) in the aS1 structures results in the aS5 structure. Finally, a slight translation of stanene in the aS5 structure in the (x,y) directions results in the aS3 structure.

For Table 5-1 the type I non-rotated (co-aligned, i.e. aS3, aS4, and aS5), and type II rotated (i.e. aS1 and aS2) hBN/Sn/hBN trilayer structures differ mostly regarding their structural lattice parameters. However, there is also a difference in the number of atoms per unit cell in the lattice of Type I vs Type II structures. The number of atoms reduces from the ten atoms(Type I structure) to eight atoms(Type II structure). This reduction in the number of atoms comes entirely from the hBN layers within the lattice, while leaving the same amount of Sn atoms. To accommodate for the decrease in the number of total atoms the lattice parameters decrease in size from ~4.9Å to ~4.3Å with a difference of ~0.6Å. The Sn-Sn bonds also decrease in length, but only by about ~0.15Å. Compensating for this difference in length between the Sn-Sn bond length and the lattice parameter (\(\Delta\sim0.45\AA\)) increases the buckling (d from ~0.6Å to 1.2Å) and bond angles (from ~102˚ to 116˚). This decrease in the lattice parameter also means that there is an in-plane compressive strain on the Sn atoms (which have a lattice parameter of ~4.6Å at the relaxed state)[232] by the B and N atoms which also will receive a tensile strain from the

Page 106 of 184
Sn atoms (as the stanene wants to return to the relaxed state). There are minor shifts in D₁ and D₂ with a max-min interlayer distance on the scale of 0.07 Å, illustrating the fact that hBN is fairly inert in its interaction with Sn. In the hBN/Sn/hBN trilayer structures D₁ is equal to D₂ in all cases and hence the trend for the hBN/Sn/hBN trilayer structures is symmetrical as seen in Figure 5-2. The binding energies for the structures show that the aS₂ rotated structure is the most stable out of the all hBN/Sn/hBN trilayer heterostructures at -22.1685 meV/Å². Both rotated structure showed lower energies while co-aligned this is due to the subtle shift from sp² to sp³ bonding states which causes the smaller or larger p₂ that reflect lower and higher energies in the order aS₂>aS₁>aS₄>aS₅>aS₃.

5.3.1.2. hBN/Sn/C trilayer

Five heterostructure configurations, with closely matched lattices found in Figure 5-1 bS(1-5) are arranged with increasing order based on their lattice parameters (i.e. \(a=b\) is bS₁ < bS₂ < bS₃ < bS₄ < bS₅). The hBN/Sn/C trilayer structures are built starting from the bS₄ structure with AA stacking between the hBN and graphene layers. Rotating the stanene layer by 30°(clockwise) in the bS₄ structure is results in the bS₂ structure. Through the translation of the bS₂ stanene layer in the –(negative)y-direction, it is possible to obtain the bS₁ structure. Through further rotation of the stanene layer by -30°(anti-clockwise) of the bS₁ structures results in the bS₅ structure. Finally, a slight translation of stanene in the bS₅ structure in the (X, Y) directions results in the bS₃ structure.

The type I co-aligned (i.e. bS₃, bS₄, and bS₅), and type II rotated (i.e. bS₁ and bS₂) hBN/Sn/C trilayer structures in Table 5-1 differ mostly regards their lattice parameters. There is also a reduction in the number of atoms per unit cell for the Type I structures (ten atoms) to Type II structures (eight atoms). For the lattice to compensate for this
reduction in atoms, there is a reduction in the lattice parameter from the Type I structure (~4.9Å) to the Type II structure (~4.3Å) to accommodate for the lesser space usage. The reduction in the number of atoms comes entirely from within the lattice of the hBN/graphene layers, while the amount of Sn atoms remain the same. Minor reduction of the lattice parameter usually results in the Sn-Sn bond to be compressed. However, because of the significant amount of energy, it would take for the Sn-Sn bond to be compressed any more than 2.75 Å. This reduction instead is converted to greater buckling, i.e. increase in buckling distance (d from ~0.5Å to 1.3Å) and an increase in bond angles (from ~102˚ to 116˚). There is also an additional compressive strain on the Sn atoms within the plane of stanene caused by the hBN/graphene layers which will also receive a tensile strain from the Sn atoms.

The binding energies for the structures show that the bS2 rotated structure is the most stable out of the hBN/Sn/C trilayer heterostructures at -22.168 meV/Å². Both rotated structure showed lower energies while co-aligned showed higher energies, with the order aS2>aS1>aS5>aS3>aS4. The result bS2 structure with lowest binding energy with the is reasonably understandable as the Sn atoms when places at the hexagonal centres of graphene or hBN are the most stable. In complimentary, the rotated structures are of higher binding energy as a result of the larger p_z orbitals in stanene caused by the strain from smaller lattice parameters.

There are significant differences in the D_1 and D_2 interlayer distances for all structures. The trend for D_1 as shown in Figure 5-2 closely correlates with the C/Sn/C trend. While the trend for D_2 closely follows the that of the hBN/Sn/hBN. The parallel in both interlayer distance is quite simply because D_1 is the distance between graphene and stanene, while D_2 is the distance between hBN and stanene. Although these correlations
have similarities, they differ significantly regarding their magnitude. For the same structure C/Sn/C \( D_1 > C/Sn/hBN \ D_1 \), but hBN/Sn/hBN \( D_2 \approx C/Sn/hBN \ D_2 \) indicating that the interactions are relatively weak for hBN/Sn and has minor effects on the interlayer distances, whereas the C/Sn interaction is quite strong and can decrease the interlayer distance significantly. In these C/Sn/hBN trilayer structures, \( D_1 \) does not equal to \( D_2 \) for all cases although it is relatively close for bS1 and bS2 cases. Hence, the trend for the hBN/Sn/C trilayer structures is asymmetrical as seen in Figure 5-2. The asymmetry in the composition of C/Sn/hBN resulted in a more significant interaction than C/Sn/C due to the higher binding energy -22.17 meV/Å².

5.3.1.3. C/Sn/C trilayer

The figures cS(1-5) in Figure 5-1 shows five configurations with closely matched lattices of the heterostructures arranged increasingly based on their lattice parameters. The C/Sn/C trilayer structures are built starting from the cS4 structure with AA stacking between the graphene layers. Then by rotating the stanene layer by 30°(clockwise) in the cS4 structure results in the cS2 structure. Through the translation of the cS2 structure’s stanene layer in the \(-\)y-direction, it is possible to obtain the cS1 structure. Further rotation of the stanene layer by -30°(anti-clockwise) in the cS1 structures results in the cS5 structure. Finally, a slight translation of stanene in the cS5 structure in the (x,y) directions results in the cS3 structure.

The results of the type I co-aligned (i.e. cS3, cS4, and cS5), and type II rotated (i.e. cS1 and cS2) C/Sn/C trilayer heterostructures in Table 5-1 carry different lattice parameters. There is also a difference in the number of atoms per unit cell as seen in Table 5-1, between the type I and II structures. There is a reduction in the lattice parameter from the type I structure (~4.9Å) to the type II structure (~ 4.3Å) and to accommodate for this
reduction. There is a decrease in the number of total atoms. The reduction in the number of atoms comes from the graphene lattice while leaving the same amount of Sn atoms. This reduction of lattice results shorter Sn-Sn bond lengths (from ~3.0 Å to ~2.7 Å), increased buckling (d from 0.8 Å to 1.3 Å) and higher bond angles (from ~101˚ to 116˚). The subtle difference between sp² to sp³ bonding states causes sizable D₁ and D₂ interlayer distances although cS5 is relatively small. In the C/Sn/C trilayer structures, D₁ is equal to D₂ for all cases.

The binding energies for the structures show that the cS4 co-aligned structure is the most stable out of the C/Sn/C trilayer heterostructures at -15.46 meV/Å². The binding energies are significantly lower than the results of C/Sn/hBN or hBN/Sn/hBN. For the most stable C/Sn/C trilayer heterostructure, which is already much lower (Δ 7 meV/Å²) than the lowest binding energy for C/Sn/hBN or hBN/Sn/hBN heterostructures. The weak binding is due to instabilities caused by competition of graphene layers that already have relatively large delocalized pᶻ orbitals depleting the pᶻ electrons in the stanene and as a result, decrease the interaction. Causing frustration within the system by increased interaction distance as seen in the D₁ vs D₂ in Figure 5-2 and Table 5-1 and weaker binding energy. The unusually weak binding energies of the cS1, cS2, and cS5 compared to the stronger cS4 and cS3 interactions is due to the asymmetry in the Sn sublattice for cS4 and cS3 in which one Sn atoms is within the hexagonal centre allowing for less overlap of the pᶻ orbitals and hence less depletion of electrons resulting in a more stable structure. Compared where there is a fully symmetrical interaction that causes full depletion of the pᶻ orbitals.
5.3.2. **Electronic Structures**

Figure 5-3 a), c), e) Shows the projected band structure and dos for the orbital contributions $s$, $(p_x, p_y, d)$, total, and $p_z$ orbitals of the structures aS5, bS5, and cS5 respectively b), d), f) shows the projected band structure and dos for atomic contributions of carbon, Sn, B, N atoms in the structures aS5, bS5, and cS5 respectively. g), i), k) Shows the projected band structure and dos for the orbital contributions $s$, $(p_x, p_y, d)$, total, and $p_z$ orbitals of the structures aS2, bS2, cS2 respectively h), j), l) shows the projected band structure and dos for atomic contributions of carbon, Sn, B, N atoms in the structures aS2, bS2, and cS2 respectively.

Figure 5-3 gives the electronic structure and partial density of states for (a-c)S(1-5). In order to identify the differences in the electronic properties for all the structures and to understand the general features in the band-structure, it is first necessary to understand the schematics of the Brillouin zone for overlapped structures with different cell sizes (2×2/1×1). Figure 5-4 shows the band-folding and rotation effects that occur in the position
of Dirac point in reciprocal space. It is interesting to note that there is an effect of a folded band structure in superposition with non-folded band structure.

Figure 5-4 Brillioun Zones of type I co-aligned (left) and II rotated (right) band structures and their corresponding K points. The dashed hexagon represents the 1×1 graphene BZ with the corresponding K-point path represented by the red dashed line, while the solid hexagons represent the new BZ with the corresponding K-point path represented by the solid blue line.

Figure 5-4 gives an idea of the differences in BZ between the rotation and co-aligned structures. The figure visualises the shift in the k-point position of the Dirac points that occur between co-aligned and rotated structures. The matching of the 2×2 supercell of graphene/hBN with the BZ of 1×1 stanene results in the new (Figure 5-4 dashed hexagons) BZ for 1×1 stanene and the bigger BZ for 1×1 graphene (Figure 5-4 solid hexagons).

In the new BZ of the type I structure in Figure 5-4 (solid hexagons), the Gamma point of the solid hexagon overlaps with the M point for the dashed hexagons. Hence, in the new BZ, the new Gamma point is equivalent to the 1×1 graphene M point, while the new K
point of remains in the same as 1×1 graphene K point. So, for (b,c)S5 structures in Figure 5-3 in which the structure is co-aligned, there are overlapping Dirac points at the K-point.

In the new BZ of the type II structure in Figure 5-4 (solid hexagons), the Gamma point of the solid hexagon overlaps with the K point for the dashed hexagons. Hence, in the new BZ, the new Gamma point is equivalent to the 1×1 graphene K point, while the new M point of remains in the same as 1×1 graphene M point. So, for (b,c)S2 rotated structures in Figure 5-3, the new Dirac point for graphene can be found at the Gamma point.

5.3.2.1. hBN/Sn/hBN trilayer

The partial density of states and electronic band structure for the type I hBN/Sn/hBN trilayer structures is shown in Figure 5-3 a), b). Only the aS5 configuration band structures are presented in the figure, as the results for the other structures are relatively similar. By using Figure 5-3, it is possible to identify the Sn atoms as the main contributors towards the Fermi level.

Further by looking into the projected orbital of the Sn in Figure 5-3, it is possible to identify that pz orbitals of the Sn atoms at the K-point and some hybrid sp orbitals at the Γ-point are the main contributors towards the metallicity of the systems. For the hBN/Sn/hBN trilayer system does not induce a gap. The behaviour of the metallic bands is consistent with an unstrained stanene as in Chapter 4.

The partial density of states and electronic band structure for the type II hBN/Sn/hBN trilayer structures is shown in Figure 5-3 g), h). For brevity, only the aS2 configuration band structures are presented in the figure, as the results for the other structures are
relatively similar. By using Figure 5-3, it is possible to identify the Sn atoms as the main contributors towards the Fermi level.

Further by looking into the projected orbital of the Sn in Figure 5-3, it is possible to identify that $p_z$ orbitals of the Sn atoms at the K-point and some hybrid $sp$ orbitals at the $\Gamma$-point are the main contributors towards the metallicity of the systems. For the hBN/Sn/hBN trilayer system does not induce a gap. The behaviour of the metallic bands is consistent with a strained stanene as in Chapter 4.

As such, in hBN/Sn/hBN the sandwiching of the stanene layer serves as preserving the ideal electronic structure of the stanene.

**5.3.2.2. C/Sn/hBN trilayer**

The partial density of states and electronic band structure for the type I C/Sn/hBN trilayer structures are shown in Figure 5-3 c), d). Only the bS5 configuration band structures are presented in the figure, as the results for the other structures are fairly similar. By using Figure 5-3, it is possible to identify the Sn/C atoms as the main contributors towards the Fermi level.

Further by looking into the projected orbital of the Sn and C in Figure 5-3, it is possible to identify the hybrid $sp$ orbital from Sn atoms at the $\Gamma$-point are the main contributors towards the metallicity of the systems and no contribution at the K-point due to a gap forming. The main contribution contributors to the gapped bands at the K-point are $p_z$ orbitals of majority C and partially some Sn atoms. In this instance, the ideal electronic structure of the stanene is not preserved. The behaviour is constant with unstrained stanene as shown in the previous chapter.
The partial density of states and electronic band structure for the type II C/Sn/hBN trilayer structures are shown in Figure 5-3 i), j). Only the bS2 configuration band structures are presented in the figure, as the results for the other structures are relatively similar. By using Figure 5-3, it is possible to identify the Fermi level as being dominated by electronic bands derived from Sn/C atoms.

Further by looking into the projected orbital of the Sn and C in Figure 5-3, it is possible to identify that \( p_z \) orbitals of Sn atoms at the K-point and \( p_z \) orbitals of C atoms at the \( \Gamma \)-point are the main contributors towards the metallicity of the systems. For the C/Sn/hBN trilayer system does not induce a gap. The behaviour of the metallic bands is consistent with a strained stanene as in Chapter 4.

As such, interestingly in C/Sn/hBN the sandwiching of the stanene layer with graphene and hBN can serve as preserving electronic structure of the strained stanene when rotated but does not preserve the ideal electronic structure when co-aligned.

5.3.2.3. C/Sn/C trilayer

The partial density of states and electronic band structure for the type I C/Sn/C trilayer structures are shown in Figure 5-3 e), f). Only the cS5 configuration band structures are presented in the figure, as the results for the other structures are relatively similar. By using Figure 5-3, it is possible to identify the Sn/C atoms as the main contributors towards the Fermi level.

Further by looking into the projected orbital of the Sn and C in Figure 5-3, it is possible to identify the sp hybrid orbitals from Sn atoms at the \( \Gamma \)-point, and \( p_z \) orbitals from Sn and C are the main contributors towards the metallicity of the system. In this instance, the
ideal electronic structure of the stanene can be preserved, due to the weak interaction as seen in the weak binding energies between graphene and stanene isolating both layers. The behaviour is constant with unstrained stanene as shown in the previous chapter.

The partial density of states and electronic band structure for the type II C/Sn/Ctrilayer structures are shown in Figure 5-3 k), l). Only the cS2 configuration band structures are presented in the figure, as the results for the other structures are relatively similar. By using Figure 5-3, it is possible to identify Sn/C atoms as the main contributors towards the Fermi level.

Further by looking into the projected orbital of the Sn and C in Figure 5-3, it is possible to identify that p_z orbitals of Sn atoms at the K-point and p_z orbitals of C atoms at the Γ-point are the main contributors towards the metallicity of the systems. For the C/Sn/C trilayer system does not induce a gap. The behaviour of the metallic bands is consistent with a strained stanene as in Chapter 4. The Dirac point of the graphene is consistent with the rotated graphene band structure with majority contribution from the P_z-orbitals moving to the Γ point due to band folding as described in Figure 5-4.

Interestingly in C/Sn/C, the sandwiching of the stanene layer with graphene can serve as preserving the electronic structure of the strained stanene, but because of the low binding energy of the system is likely not experimentally useable.
5.3.3. Layer Interactions

Figure 5-5 Shows the HOMO orbitals at the Fermi level for the type I structures of a)hBN/Sn/hBN(aS5), c)C/Sn/C(cS5), and e) hBN/Sn/C(bS5) aswell the type II structures of b)hBN/Sn/hBN(aS2), d)C/Sn/C(cS2), and f) hBN/Sn/C(bS2). Positive and negative phase wavefunctions are given in yellow and blue respectively.

Figure 5-5 shows the HOMO of the (a-c)S5 and (a-c)S2 structures. For the (a-c)S5 structure, there is a constant trend of overlapping $p_z$ orbitals between the positive wavefunction phases. While there is no overlapping in the $p_z$ orbitals in the negatives phases, there is also consistent antibonding between the phases. The overlapping $p_z$ is characteristic of sp$^2$ orbitals with delocalised $p_z$ orbitals.
The lack of overlapping HOMO between the same phases on the stanene in the type II structures, is reasonably attributed to the high buckling of stanene. The result of larger buckling causes a shift towards in the $sp^3$ configuration. So in these orbitals of the Stanene as seen in Figure 5-5 d), e), f). The orbitals will appear to follow regions where there are interactions between the layers, and consequently, the larger orbitals of the stanene slightly follow the shapes of the above and below layers.

Bader charge transfer for hBN/Stanene/hBN trilayer structures shows that there is zero interference between the layers of hBN and Stanene for the co-aligned structures. Although some charge transfer exists for the rotated structures, this is due to the compressive strain in the XY plane which forces an increase in the $sp^3$ px orbital hence increasing the orbital overlap between the hBN and Stanene.

As for the bilayer system discussed in the previous chapter, a repeating feature of the C/Sn heterostructures is that when graphene, which has a gapless Dirac band-structure, is combined with stanene, which also has a gapless Dirac band-structure, the resulting band-structure possesses a clear gap at the K point if the lattice is a type II structure.[232] By comparing the charge transfer, binding energy, buckling, Sn-Sn bond length, buckling distance and interlayer distance, it can be seen that there is also a correlation with the interlayer distance that increases as binding energy decreases, and charge transfer decreases. Consequently, it is clear the Sn-C lattices are not merely bonded by the vdW interaction.

Charge transfer is minimal in the trilayer in the C/Sn/C configuration due to the symmetrical balancing of charges that exist on both side, wherein the bilayer configuration electrons of stanene are pulled towards the graphene side, but if the pulling
effect is applied to both sides of stanene electrons, there is instead a repulsive force against the graphene. This result can be seen, as the interlayer distance between the graphene and stanene is much larger than that of the interlayer distance for hBN and Stanene or hBN/Stanene/Graphene configurations.

The work functions for each trilayer in Figure 5-6 show that there is a clear distinction between the rotated structure and co-aligned structures. For the aS(1-5) trilayer structures there is a much lower work function for the co-aligned structures. In contrast, the rotated structures have a much higher work function, this is attributed to the fact that the changes between sp$^3$ and sp$^2$ orbitals which causes a lower Fermi energy and as a result a higher work function. Whereas sp$^2$ has higher Fermi energy and as a result it has a lower work function, the reverse is happening for the C/Sn/C cS(1-5) and C/Sn/hBN bS(1-5). This can be attributed to the relatively high energy of the stanene layer and the higher energy of the graphene layer due to the compressive strain on the graphene which as a result increases the overall fermi energy. When this strain has decreased the Fermi, energy drops and hence increases the work function.

Figure 5-6 (Left), the binding energies of the (a-c)S(1-5) structures with the x-axis as the lattice parameter, (Right) the work functions of the (a-c)S(1-5) structures with the x-axis as the structure number.
By analysing the change in energy with the change in the lattice parameter show in Figure 5-6, it is possible to find the preferred lattice parameter of the type I hBN/Sn/hBN trilayer heterostructure these maxima are located at around a=b=4.35Å.

<table>
<thead>
<tr>
<th></th>
<th>Bilayer BE meV</th>
<th>Trilayer BE meV</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>hBN/Sn/hBN</td>
<td>-343.323</td>
<td>-700.576</td>
<td>357.253</td>
</tr>
<tr>
<td>C/Sn/C</td>
<td>-332.695</td>
<td>-890.286</td>
<td>557.591</td>
</tr>
<tr>
<td>C/Sn/hBN</td>
<td>-332.695</td>
<td>-686.819</td>
<td>354.124</td>
</tr>
<tr>
<td>C/Sn/hBN</td>
<td>-343.323</td>
<td>-686.819</td>
<td>343.496</td>
</tr>
</tbody>
</table>

Table 5-2 Shows the binding of bi- and tri- layers and their binding energy difference.

By looking at the energies of both the bilayer and trilayer in Table 5-2, it is possible to determine the order in which it is energetically favourable to place the trilayer. In calculations using DFT-D2(Grimme), it is found that the difference in binding energy between the Type I trilayer hBN/Sn/hBN systems at 700.576meV and bilayer hBN/Sn at 343.323 meV which resulted in difference of 357.253 meV. The Type I trilayer C/Sn/C systems at 676.301meV and bilayer C/Sn at 332.695meV which yielded a difference of 343.606 meV, Type I trilayer hBN/Sn/C systems at 686.819meV and bilayer hBN/Sn at 343.323 meV which resulted in difference of 343.469 meV, and the Type I trilayer hBN/Sn/C systems at 686.819meV and bilayer C/Sn at 332.695meV which resulted in difference of 354.124 meV. From these results, it is possible to see that starting with the Bilayer hBN/Sn systems it is more energetically more favourable for the addition of another hBN layer as hBN/Sn/hBN - hBN/Sn = 357.253 meV is higher than that of hBN/Sn/C - hBN/Sn= 343.469 meV. Starting with the C/Sn system it is more energetically favourable also for the addition of another hBN layer compared to graphene, but the energy difference is as C/Sn/C- C/Sn = 343.606 meV is less than that of hBN/Sn/C- hBN/Sn= 354.124 meV.
5.4. Conclusion and Outlook

Using density functional theory, the calculations results showed that, by encapsulating stanene layers in symmetrically AA stacked hBN It is possible to preserve the Dirac dispersion within stanene. This preservation of the stanene Dirac dispersion is independent of either rotation or translation of the Sn layer(aS(1-5)). Symmetrically AA stacked graphene is also capable of preserving the stanene dispersion while at the same time co-existing with the Dirac dispersion of graphene. This preservation of the Sn layer sandwiched between the graphene layers is independent of the rotation or translation of the Sn layer(cS(1-5)) with the two Dirac dispersion staying at the same k-point unless rotated due to band folding this rotation moves the Dirac point of the graphene from K to the Γ-point. The preservation of Sn is destroyed if sandwiching of the Sn layer using graphene and hBN performed asymmetrically due to the higher tendency of stanene to hybridise with graphene. In the asymmetrical case of graphene and hBN sandwiching the Sn layer, the resultant structure shows similar results to that of bilayer graphene stacked on top of stanene. An exciting conclusion is that although graphene is likely to hybridise with stanene, two graphene will not, this is due to the symmetry introduced in the stacking in that when stacked symmetrically and asymmetrically there is a difference in the physical and electronic structure, although both independently will not have large hybridisations.
5.5. Computational Methodology

In this work, first principle calculations were performed using density functional theory (DFT)[156, 157] implemented by the VASP package. The exchange-correlation function used to describe the exchange-correlation interaction was the General Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[162] formulation, a van der Waals (vdW) correction (DFT-D2) implemented by Grimme[219].

The atomic positions and cell vectors are relaxed until the energy, maximum force, and maximum displacement is less than $5.0 \times 10^{-6}$ eV/atom, 0.01 ev/Å, and $5.0 \times 10^{-4}$. Furthermore, a vacuum space larger than 25 Å was utilised to prevent interactions between neighbouring layers in the direction normal to the graphene and stanene surface. The reciprocal space Brillouin zone paths selected for band structure calculations are the $\Gamma \to K \to M \to \Gamma$ points.

To investigate the trilayer heterostructures, the five symmetry combinations of the matching honeycomb lattices were constructed as shown in Figure 5-1, in the order of increasing lattice constant. The structures shown corresponds to the final states after ionic relaxation, and lattice optimization was performed to minimise energy and the internal atomic coordinates, the structures although different in rotation and translation of the Sn layer fall into two distinct families these are Type I (S1-S2) which have a lattice parameter of $\sim 4.2$ Å and Type II (S3-S5) which has a lattice parameter of $\sim 4.9$ Å. To evaluate the interaction between the layers of in the trilayer heterostructure, the binding energies were calculated for the trilayers, regarding the binding energy per area $E_{b/\text{area}}$ using the formulas:

\[ E_{b/\text{area}} = \text{binding energy} / \text{area} \]
Where $E_{L/Sn/L}$ is the enthalpy energy of the bilayer, $E_L$ is the enthalpy energy of monolayer graphene or hBN, $E_{Sn}$ is the enthalpy energy of monolayer stanene, $A$ is 2D area of the (001) plane across the unit cell. The resulting $D_1$, $D_2$, $d$, and $T$ distances for the structure as well as the lattice parameters, bond lengths, bond angles and binding energies summarized in Table 5-1. The structures overall (a, b)S2 is the most stable. The relaxed lattice constants for the various configurations of the heterostructures of hBN, graphene and stanene lattices are very different. For the Type I structures, the lattice parameter has contracted (~ 4.28 Å) compared to pristine stanene (4.6 Å), whereas for Type II structures the lattice has expanded to (~ 4.92 Å). The resulting band structures for the optimized structures are also shown in Figure 5-3. For the Type I lattices, the band structure is drawn using the appropriate stanene frame-of-references, and consequently one can identify the stanene Dirac cone at the K-point while the graphene.
Chapter 6

6. Defect introduced paramagnetism and weak localization in two-dimensional metal VSe$_2$

6.1. Overview

The \textit{ab initio} calculations presented in this chapter were performed in order to complement a detailed experiment investigation of the magnetism, valence state, and magnetotransport in VSe$_2$ bulk single crystals, as well as in laminates obtained by mechanical exfoliation. In sharp contrast to the ferromagnetic behaviour reported previously, here, no ferromagnetism could be detected for VSe$_2$ single crystal and laminate from room temperature down to 2 K. The curie paramagnetism expected due to the $3d^1$ odd-electronic configuration of covalent V$^{4+}$ ions were not found. Rather, intrinsic VSe$_2$ is a non-magnetic alloy without local moment. Only a weak paramagnetic contribution introduced by defects is noticeable below 50 K. A weak localization effect due to defects was also observed in VSe$_2$ single crystals for the first time.

6.2. Introduction

Since many unconventional properties have been observed in graphene\cite{233, 234}, other two-dimensional (2D) inorganic nanomaterials, particularly ultrathin layered nanosheets of layered transition metal dichalcogenides (TMDs) \cite{235, 236}, have been receiving extensive research attention in recent years. Owing to the wide range of physical and chemical properties not available in graphene, 2D TMDs provide fertile ground for harvesting new fundamental science and emergent applications. Remarkably,
explorations of 2D TMDs have revealed numerous intriguing features, such as layer-dependent tunable band gaps and direct-to-indirect band-gap crossovers [224], charge density waves (CDW) [237], gate tunable superconductivity [238], photo-switching, and valley-selective optical excitation [239], to name a few. In contrast to the relatively well explored properties, such as electronic [240], optical [241], and mechanical properties [242], magnetism in 2D TMDs remains an elusive but increasingly popular topic. If ferromagnetic ordering can be achieved in 2D materials, it would be extremely exciting, as it opens the door to future-generation spintronics devices in which charge, and spin manipulation could be combined in 2D atomic crystals. For instance, one can imagine that graphene with ferromagnetism could lead to novel transport phenomena such as the quantized anomalous Hall effect [243], which is very promising for dissipationless transport [244]. Therefore, studying the magnetism in 2D TMDs not only advances the understanding of low-dimensional magnetism, but also provides great potential for application in spintronic nanodevices.

Recently, theoretical calculations predicted that ferromagnetic ordering could be achieved in VSe$_2$ bulk [245], nanosheet [246], and monolayer [247]. Experimentally, Xie et al [248] reported that there was coexistence of room temperature (RT) ferromagnetism and a CDW transition in liquid-exfoliated VSe$_2$ nanosheets. In contrast to the non-magnetic ground state for most primitive TMDs, the emergence of ferromagnetic order in VSe$_2$ attracted considerable attention. Nevertheless, many relevant questions about the ferromagnetic order of VSe$_2$ are still pending: (1) the mechanism that could lead to the strong interaction required for RT ferromagnetism is unclear, particularly whether the ferromagnetism is inherited from the parent three-dimensional (3D) system. (2) Both the ferromagnetism and the CDW behaviour in VSe$_2$ were tentatively attributed to the presence of V $3d^6$ odd electrons and the interaction between them [247, 248].
Surprisingly, there is no evidence to confirm the $V^{4+}$ and $Se^{2-}$ state assignments so far. (3) The magneto-transport properties of VSe$_2$ still remain poorly understood. It is an intriguing topic to investigate the magnetotransport in such a 2D correlated metallic system.

With these questions in mind, investigations of the valence states, magnetic, and transport properties were performed for VSe$_2$ single crystal and laminate, respectively. The experimental results demonstrated that intrinsic VSe$_2$ is a non-magnetic alloy without a local moment. Only at temperatures below 50 K, there was notable paramagnetic contribution, despite the fact that the maximum response that could be achieve was limited to one moment per 440 VSe$_2$ molecules for single crystal and one moment per 180 VSe$_2$ molecules for laminate. Therefore, the paramagnetism is explained by the defects present in VSe$_2$ lattice. Meanwhile, a weak localization effect induced by defects was observed in VSe$_2$ for the first time.

6.3. Computational details

In this work, first principle calculations were performed using density functional theory[156, 157] (DFT) implemented using the CASTEP package[194]. The exchange correlation function used to describe the exchange-correlation interaction was the General Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[162] formulation, a van der Waals (vdW) correction (DFT-D) implemented by Grimme[219] was added. Structures are optimized using the Broyden–Fletcher–Goldfarb–Shanno algorithm BGFS[203].
In order to validate the XRD results, an optimization was performed on the lattice parameter used and resulted in lattice parameter of 3.39 Å this lattice consistent with the experimental lattice parameter of 3.36 Å with an error of 1%.

To evaluate the ferromagnetic vs non-magnetic stabilities, calculations on the binding energy per atom ($E_b$) was performed using the following definition:

$$E_b = \frac{(nE_V + mE_{Se} - E_{VSe_2})(n + m)}{n + m},$$

where $E_V$, $E_{Se}$, and $E_{VSe_2}$ represent the total energies of free V atom, Se atom, and VSe$_2$ per unit cell, respectively, $n$ ($m$) denotes the number of V (Se) atoms in a unit cell. According to this definition, systems with larger $E_b$ values (positive) are energetically more favourable. The results showed a binding energy ($E_b$) of 8.039 eV for the Nonmagnetic state and 6.589 eV for the magnetic state. This outcome shows that the more favourable state is the nonmagnetic state. This was done by optimising the magnetic structure by setting the total spin to either zero for the nonmagnetic state or 2 for V as the starting point the ferromagnetic state for a single unit cell.
For the calculations regarding the electronic energies of the ferromagnetic vs non-magnetic energies. Convergence of the energy cut off for the VSe$_2$ system was first performed then using the optimised system shown in Figure 6-5 a) and b).

The validation of individual layers, optimizations were performed with an energy cutoff of 700eV with a 17x17x8 points set. The reciprocal space K Point paths selected for band structure calculations are the $\Gamma\rightarrow K\rightarrow M\rightarrow \Gamma$ points for the 2D structures, while $\Gamma\rightarrow A\rightarrow H\rightarrow K\rightarrow M\rightarrow L\rightarrow H$ high symmetry points for the 3D BZ.

The K points of 17x17x8 was set for the geometry optimization and Density grid of 30x30x54 for accurate electronic characteristics calculations, and the smearing value was 0.001 eV occupancy with the spin optimised after every 2 optimization steps. The energy cut off was set at 700eV in conjunction with the convergence findings for the energy cut off as shown in Figure 6-1. The calculations with an on the fly all electron pseudopotential.
6.4. DFT Results

Using the optimized structures of VSe$_2$ produced band structures which are comparable with other theory calculations$^{[110]}$ and have comparable electronic properties to the experimental results in chapter, in which both showed metallic conductivity. Possible band structures of VSe$_2$ were also calculated in the antiferromagnetic(Figure 6-4) and ferromagnetic(Figure 6-3) phases determine if any changes in conductivity would occur if any changes in the magnetic phases would occur.

Figure 6-2. a) Band structure of the Bulk phase VSe$_2$ for a non-magnetic arrangement b) Band structure of the Monolayer VSe$_2$ for a non-magnetic arrangement
The DFT band structures results Figure 6-2 for monolayer and bulk shows that in either case the materials has metallic conductivity. Looking more closely at the partial densities, this rise in conductivity can be attributed to the d-orbital of the vanadium atom.

Energy calculations were able to determine that the binding energy of the non-magnetic phase is lower than that of the FM phase shown in Table 6-1 and that this was true even accounting for various charge and spin states Table 6-2, which is in agreement with the experimental measurement results. The optimised spin state showed a spin of a 0.6041 Bohr Magnetons.

<table>
<thead>
<tr>
<th></th>
<th>NM</th>
<th>FM ∆eV</th>
<th>AFM ∆eV</th>
</tr>
</thead>
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<td><strong>TS</strong></td>
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<td>0.225970263</td>
<td>0.22597</td>
</tr>
<tr>
<td><strong>Grimme</strong></td>
<td>0</td>
<td>0.232967152</td>
<td>0.23297</td>
</tr>
</tbody>
</table>

Table 6-1 Shows the for the system with two types of van der Waal corrections the Grimme and TS corrections the energy difference in respect to NM state.

<table>
<thead>
<tr>
<th></th>
<th>Energies Fixed Occupancy ∆eV</th>
<th>Energies No Fixed Occupancy ∆eV</th>
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<tbody>
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<td><strong>VSe2 4+</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-Magnetic (S</td>
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<td>0.294</td>
</tr>
<tr>
<td>of V =0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferromagnetic (S</td>
<td>0.216</td>
<td>0.216</td>
</tr>
<tr>
<td>of V =1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anti Ferromagnetic (S of V =1, -1)</td>
<td>0.216</td>
<td>0.089</td>
</tr>
<tr>
<td>Non-Magnetic (S</td>
<td>0.216</td>
<td>0.216</td>
</tr>
<tr>
<td>of V =0)</td>
<td></td>
<td></td>
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<tr>
<td>Ferromagnetic (S</td>
<td>0.216</td>
<td>0.216</td>
</tr>
<tr>
<td>of V =2)</td>
<td></td>
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</tr>
<tr>
<td>Anti Ferromagnetic (S of V =2, -2)</td>
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<td>0.089</td>
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<tr>
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<td>0.216</td>
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<tr>
<td>of V =0)</td>
<td></td>
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</tr>
<tr>
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<td>0.216</td>
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<tr>
<td>of V =3)</td>
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<td>of V =0)</td>
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<tr>
<td>of V =4)</td>
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<td>of V =0)</td>
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<td>of V =3)</td>
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<td></td>
</tr>
<tr>
<td>Anti Ferromagnetic (S of V =3, -3)</td>
<td>0.216</td>
<td>0.089</td>
</tr>
</tbody>
</table>

Table 6-2 Bulk Phase 4U U of V=3eV, Se=-2 Ecut=800 Shows the energy values for various energy calculations a.
Figure 6-3. Shows the alpha (left) and beta (right) spin band structures for VSe$_2$ with a ferromagnetic spin arrangement.

Figure 6-4. Shows the band structure for VSe$_2$ for an antiferromagnetic spin arrangement.
6.5. Fabrication and experimental setup

In this work, well defined VSe$_2$ single crystals were synthesized by a conventional solid-state method. A 5% excess was given to Se to achieve the proper stoichiometric ratio, as VSe$_2$ is known to form metal-rich alloys. The elements V and Se in the form of powder were heated in an evacuated quartz tube to 900 °C with a heating rate of 10 °C min$^{-1}$ and then kept at 900 °C for 40 h. After that, the samples were slowly cooled to 600 °C in 10 h and then shut down the furnace. The thickness of single crystal VSe$_2$ flakes is between 5–10 μm checked by scanning electron microscope. The VSe$_2$ laminate was prepared by mechanical exfoliation in order to avoid any contamination from chemical solvents. First, a piece of bulk VSe$_2$ flake was adhered onto a piece of Scotch tape. Subsequently, the tape with the VSe$_2$ flake was folded and separated repeatedly for so many times to get few-layer sheets. The unexfoliated VSe$_2$ flake remaining in tap was removed before measurements. The laminate weighed several mg and was encapsulated for superconducting quantum interference device (SQUID) magnetometry.

The crystal structure of the samples was characterized by x-ray diffraction (XRD) (Cu Ka radiation). The thickness of the nanosheets was preliminary checked by optical microscopy based on its different optical contrast and further determined by atomic force microscopy (AFM). Energy dispersive x-ray was used to check the elemental compositions of the VSe$_2$, which confirms the existence of V and Se with V/Se ratio of very close to 1:2. The chemical composition and especially the valence states of V and Se in single crystal and laminate were characterized by x-ray photoelectron spectroscopy (XPS). The magnetism was measured by SQUID from RT down to 2 K. Transport measurements were performed on single crystal VSe$_2$ flake by standard four-probe
transport measurements using a Quantum Design physical properties measurement system.

6.6. Results and discussion

Vanadium diselenide (VSe$_2$) is a typical TMD material [249, 250]. As shown in Figure 6-5(a) and (b), the VSe$_2$ monolayer is composed of metal V atoms that are each sandwiched between two Se atoms, and the Se–V–Se layers are stacked in the (001) direction without lateral displacement, forming a trigonal (T) phase crystal in the bulk. As shown in Figure 6-5(c), only (001) peaks related to hexagonal VSe$_2$ phase can be observed, indicating the single-crystal character of the samples. For VSe$_2$ laminate, as shown in Figure 6-5 (d), the relative intensity of the peaks in their XRD pattern is quite different from those of the corresponding ones for the bulk VSe$_2$ polycrystalline powder [248, 251], in which the (001) peaks present distinctly enhanced intensity values and other peaks are suppressed. The XRD pattern exhibits a highly crystalline orientation along the $c$-axis, as expected for high quality laminate. The thickness of the exfoliated nanosheets in the laminate was evaluated by AFM. The representative AFM image shown in Figure 6-5(e) reveals that the height of the exfoliated nanosheets ranged from 6 to 11 nm, which means that the nanosheets are composed of about 10–18 Se–V–Se atomic layers (since the thickness of a single-layer VSe$_2$ slab along the [001] direction is 0.61 nm). These characterization results indicate that bulk 1T-phase VSe$_2$ was successfully exfoliated into 2D ultrathin nanosheets with high crystallinity and high $c$-axis orientation.
Figure 6-5. (a) Side and (b) top views of the atomic structure of VSe$_2$. XRD patterns of VSe$_2$ single crystal (c) and laminate (d). (e) AFM image of the VSe$_2$ nanosheets with height profiles along the indicated paths.

For magnetization measurements, the results showed no hysteresis caused by ferromagnetism in the field dependence of the magnetization, as shown in Figure 6-5(a) and (b). Both the single crystal and the laminate exhibit weak paramagnetism from RT down to 2 K. Figure 6-5(c) and (d) plots the measured mass magnetization ($M$) as a
function of temperature ($T$) under parallel fields for the single crystal and laminate, respectively. Both cases show a cusp at around 110 K, corresponding to the onset temperature of the CDW transition, which is consistent with previous data reported in the literature[248, 252]. For bulk single crystal, the mass magnetization $M$ (Figure 6-6(c)) is temperature-independent from RT down to the CDW transition temperature, showing Pauli paramagnetic behaviour. In the case of VSe$_2$ laminate, the temperature dependence of $M$ (Figure 6-6 (d)) also exhibits a small and flat susceptibility above the CDW transition temperature. Despite the absence of ferromagnetism, both the VSe$_2$ single crystal and the laminate exhibit noticeable low $T$ paramagnetism, which is revealed by the S-shape in the $M$–$H$ curves as well as an upturn in the $M$–$T$ curves below 50 K. In addition, curves showed the similar paramagnetic contribution as in perpendicular field: i.e., the paramagnetism is isotropic.
Characterization of the magnetic species contributing to the observed behaviour at low temperature was performed by plotting $M$ as a function of the reduced field $H/T$. The observed behaviour for both single crystals and laminates is well described by the standard Brillouin function:

$$M = N g \mu_B \left\{ \frac{2J + 1}{2J} \coth \left[ \frac{(2J + 1)x}{2J} \right] - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \right\},$$

where $x = \frac{gJ \mu_B H}{k_B T}$, $\mu_B$ the Bohr magneton and $k_B$ as the Boltzmann constant. The $g$ factor and the angular momentum number $J$ define the initial slope of $M(H/T)$, whereas the
saturation level depends on the number of spins that are present, $N$. Assuming that $g = 2$ [253, 254], the Brillouin function provides excellent fits only for $J = 1$ in both cases. The trivial free electron $J = \frac{1}{2}$ expected for vacancies and adatoms cannot fit the data. If for some reasons the g factor is enhanced [255-259], the experimental data can be described by a smaller $J$, but the fit becomes progressively poor. So far, there are no reports that g-factor in VSe$_2$ may be changed. Figure 6-7 allows the conclusion that the observed low temperature paramagnetism is a result of the same species, with the magnetic moment $\mu = g|\mu_B| = 2\mu_B$. The concentration of paramagnetic centres is 0.2% (one moment per 440 VSe$_2$ molecules) for single crystal, and 0.5% (one moment per 180 VSe$_2$ molecules) for laminate. Consequently, the low temperature paramagnetic centres cannot attribute to V atoms. Intrinsic VSe$_2$ is non-magnetic without local moment. Defects could play an important role in observed paramagnetism. Based on the magnetic data, however, no unambiguous identification of the nature of the defect is possible. Since the low temperature paramagnetism with $J = \frac{1}{2}$ disagrees with existing theories for point defects with $J = \frac{1}{2}$ such as magnetic vacancies and adatoms, edge-related defects could be responsible to the paramagnetism. In particular, the origin of the paramagnetism could be attributed to localized states with 2 unpaired electrons present at layer edges [260]. Furthermore, the magnetization of laminate is nearly double that of bulk single crystal, which also points in the direction of edge-related magnetism [261, 262]. However, it cannot be excluded that the observed signal comes from trace interstitial atoms or dislocations with broken bond [263, 264].
Figure 6-7. Determination of the angular momentum quantum number $J$ from $\Delta M$ versus $H/T$ curves. Magnetic moment $\Delta M$ (after subtracting the linear Pauli paramagnetic background) as a function of reduced field $H/T$ for VSe$_2$ single crystal (a) and laminate (b). Fits of the data were drawn using the Brillouin function with different values of $J$.

Since most of the research thus far has been focused on semiconducting TMDs, it is the currently accepted view that bulk crystalline TMDs are stacked structures with strong
covalent bonding between the metal and the chalcogen atoms, and weak van der Waals interactions between adjacent layers [250]. If so, there seems to be no explanation for the absence of any local magnetic moment for covalent V$^{4+}$ ions ($3d^1$ odd-electronic configuration). Therefore, investigation was performed on the valence states of V and Se by using an x-ray photoelectron spectrometer (XPS) with an Al Ka (1486.6 eV) source. In all cases, the peak position indicated on the XPS spectra was charge referenced to the C 1s line (taken to be 284.6 eV). Typical XPS V 2p spectra together with the nearby O 1s lines are shown in Figure 6-8(a). The XPS spectra of the VSe$_2$ samples are quite different from those of VO$_2$, which indicates that the V is not in V$^{4+}$ form. In contrast to VO$_2$, the V 2p$_{3/2}$ peak position of VSe$_2$ is shifted to the low energy value of 514 eV, which is closer to that of V metal (512.4 eV) [265]. The O 1s peak is located at 532.7 eV for VSe$_2$, corresponding to adsorbed oxygen [266] or hydroxide contamination [267, 268] at the surface. Instead, the binding energy of O 1s is around 529.4 eV for VO$_2$, which is typical of O$^{2-}$ in metal oxides [269, 270]. Figure 6-8(b) shows the XPS spectra of the Se 3d peak in pure Se and in the VSe$_2$ single crystal and laminate, respectively. No noticeable difference could be detected between VSe$_2$ and pure Se within the resolution of the spectrometer. The binding energy value (55.2 eV) of the Se 3d peak is far from the results for SeO$_2$ (59.9 eV) [271], which indicates that Se is not in the oxide form. It is worth mentioning that no disparity in V 2p and Se 3d could be detected between the bulk single crystal and the laminate, which indicates that the valence states of V and Se remain the same for both cases. In all, the results of XPS reveal that VSe$_2$ bulk single crystal and laminate both show an alloy, rather than a covalent character. Thus, the absence of local moment is well explained. Similar to Vanadium metal, 3d electrons are delocalized and free.
Figure 6-8. XPS spectra of (a) V 2p and (b) Se 3d regions for the VSe₂ single crystal and laminate, respectively. For comparison, the VO₂ and elementary Se spectra are also included.

The temperature dependence of the resistance is shown in Figure 6-9(a). The in-plane resistance decreases with temperature, and then an upturned kink emerges around 110 K. This anomaly in the resistance corresponds to the onset temperature of the CDW transition, which is consistent with the results of susceptibility measurements. In the high temperature range, VSe₂ presents metallic behaviour, and its resistivity shows a linear
relationship with temperature, i.e. $\rho \propto T$, showing that the electron-phonon scattering is
dominant at high temperatures. On the other hand, a resistance minimum with an upturn
is observed at low temperature. As shown in Figure 6-9(b), the sample exhibits a
logarithmic increase in the resistance below 6 K. This behaviour has been extensively
studied, and several mechanisms have been considered for its interpretation [272].
Specifically, the logarithmic corrections to the resistance in the low-temperature limit
could be due to weak localization [273], inter-electron interference [274, 275], or the
Kondo effect [276].

![Figure 6-9. CDW and weak localization in VSe$_2$ single crystal. (a) Temperature dependence of resistance from RT down to 2 K. The blue dashed line indicates the CDW transition. (b) Logarithmic temperature dependence of the resistance at low temperature. The solid red line is only a guide to the eyes. (c) and (d) Magnetoresistance normalized by $\rho$, the resistance at zero magnetic field, at various temperatures.](image-url)
In order to clarify the origin of logarithmic increase in the resistance below 6 K, magnetoresistance (MR) measurements were carried out at different temperatures with the magnetic field applied perpendicular to the sample surface.

As shown in Figure 6-9(c), a positive parabolic MR can be observed at high temperature. A small negative MR, however, emerges at low field at $T < 6$ K, as shown in Figure 6-9(d). In a disordered metallic system, the phase coherence of the two time-reversed electronic wave functions, which is responsible for weak localization, can be destroyed by a weak magnetic field, leading to a negative MR [277]. In contrast, the diffusion channel for inter-electron interference, in which the dominant effect comes from the splitting of the spin states by magnetic field (or the Zeeman contribution), manifests itself in positive MR. So inter-electron interference can be ruled out. Furthermore, the MR exhibited in Figure 6-9(d) is a superposition of negative MR at low field and positive MR at high field. This is a signature of the weak localization, since only weak localization can be reliably suppressed in finite magnetic fields [278]. This behaviour precludes a magnetic Kondo effect as the origin of the resistivity anomaly, since a high field would cause a substantial negative MR [279].

To further confirm this, MR anisotropy measurements can be used to distinguish between weak localization and Kondo scattering [280]. Because of the nature of spin, the Kondo effect is isotropic, whereas weak localization is anisotropic as a result of the anisotropic nature of the orbit. So, the angular ($\theta$) dependence of MR at 2 K was investigated, where $\theta = 0$ corresponds to magnetic field being perpendicular to the plane of the sample and $\theta = 90$ corresponds to magnetic field being parallel to the current. As shown in Figure 6-10, the negative MR is vanished by tilting magnetic field from $\theta = 0$ to 90. It is clear that the
MR is anisotropic, suggesting that the lnT dependences of resistivity and negative MR are due to weak-localization effect rather than Kondo effect.

Figure 6-10 Orientation-dependence of MR for VSe$_2$ at 2 K. The VSe$_2$ flake is in $x$-$y$ plane, the current is parallel to $x$-axis.

It is worthy to mention that the origin of the positive MR at low temperature is still not very clear. It could be due to a combination of several different mechanisms, such as classical MR or/and electron–electron interaction [281]. Deutscher and Fukuyama [282] pointed out that in the Pt films there was also an unexplained positive contribution in addition to a negative MR. And it is even more complicated by considering the effect of a magnetic field to CDW dynamics, which remains unsolved so far. For example, NbSe$_3$, which is known as an imperfect nesting CDW system, exhibited a large positive MR below CDW transition temperature [283]. More studies are needed for the unaccounted positive MR observed in the VSe$_2$ at low temperature. All in all, no sign of magnetism
can be found by transport measurements from RT down to 2 K. Similar to magnetism measurements, defect-induced weak localization was observed in VSe$_2$.

6.7. Conclusions

A detailed investigation of their magnetism, valence states, and magnetotransport was carried out for VSe$_2$ single crystal and laminate, respectively. The results reveal that intrinsic VSe$_2$ is a non-magnetic alloy with no local moment. Only a paramagnetic contribution is noticeable below 50 K, which is due to a single species of defect exhibiting approximately one moment per 440 VSe$_2$ molecules for single crystal and one moment per 180 VSe$_2$ molecules for laminate. In addition, a weak localization effect introduced by defects was observed in VSe$_2$ for the first time.
Chapter 7

7. Summary and conclusions

This thesis investigates some of the principles that apply when considering the construction of van der Waals heterostructures. *Ab initio* density functional theory with van der Waals corrections implemented by Grimme (DFT-D2) correctly models this class of heterostructures. This *ab initio* method lays the groundwork to understand some of the current landscape of 2D heterostructure materials. For the selected single layers and heterostructures explored in this thesis, the results of this *ab initio* process also provide some general insights needed to develop new heterostructures, because many of the principles should be universally applicable, as they are not material specific. Key findings in this thesis show that the stacking order, alignment, symmetry or asymmetry, and the rotation of the individual layers is essential for the control that is needed to give specific desired properties. The implication of this is that interlayer interactions in vdW heterostructures are more complex than those involved in just a weakly interacting system.

Investigations involving the stanene-graphene bilayer heterostructure system revealed evidence of a mixed interaction system. Although the majority of the interlayer interactions originate from the van der Waals components, this work has identified that a minor hybridisation does occur between the $p_z$ orbitals of graphene and stanene. This hybridisation, in certain circumstances, was able to induce a gapped state in the final electronic structure. The electronic structure could also be tuned due to the intrinsic competition between the $sp^2$ and $sp^3$ hybridisation, through the rotation of the stanene
layer on top of the graphene layer. This tuning changes the strain on stanene, in which compressive strain favoured the $sp^3$ hybridised stanene, while tensile strain favoured the $sp^2$ hybridised configuration of stanene.

The bilayer system demonstrated stability against single $H_2O$ molecules, which caused limited changes to the electron density at the Fermi level while maintaining essentially the same band structure. The limited change establishes the bilayer system as a suitable candidate for use in gas sensing applications with high selectivity due to layer anisotropy.

Studying the trilayer configurations of 2D van der Waals heterostructures using combinations of graphene, stanene, and hBN in various stacking orders and rotations revealed rules of asymmetric and symmetric stacking of the layers. Asymmetric stacking resulted in increased interlayer bonding interaction, as seen in the hBN/Sn/C, as the Sn/C interaction is stronger than the Sn/hBN interaction, as demonstrated by the shorter interaction distance and electronic structures. hBN/Sn/C has gapped states which closely match those of bilayer Sn/C structures, indicating that the stronger interaction is intrinsic to the Sn/C layers, which dominate the overall electronic properties of the hBN/Sn/C system. The longer interlayer spacing distance of the hBN/Sn layers indicates that the hBN layer is inert towards the bilayer Sn/C structure and that the binding which occurs is predominantly thorough vdW interactions that largely preserve the electronic structure of the bilayer Sn/C.

Surprisingly, bonding asymmetry also appears in the compositionally symmetrically stacked C/Sn/C structures. The binding energies and interlayer distances of two groups of structures revealed a difference in the symmetric and asymmetric interactions within the C/Sn/C. The asymmetric interactions between the two Sn sublattices in the cS3 and
cS4 stacking configurations revealed a mechanism in which the difference in the interacting atoms in the layer allows one atom to interact more strongly, resulting in higher binding energies and shorter interlayer distances. The symmetric interactions between the two Sn sublattices (cS1, cS2, and cS5 stacking configurations) show a mechanism in which the symmetry in the interacting atoms causes cancellation of forces and structural frustrations, resulting in lower binding energies and longer interlayer distances.

In contrast, symmetric interactions in hBN/Sn/hBN imply almost complete inertness towards the sandwiched Sn layer, and because of the relative inertness of the hBN on Sn, different stacking configurations caused minimal change in the binding energy. This minimal change makes hBN an enticing candidate for the isolation and preservation of the desired electronic properties. The differences between the combinations of C and hBN layers on stanene highlight how bonding can be purely vdW or a mixture of vdW and covalent bonding.

The 3D-2D crossover effect in transition metal dichalcogenides (MX2) from single crystal VSe2 crystals to few-layer VSe2, as modelled in ab initio DFT calculations, was used to complement experimental transport and magnetometry data. The compound did not show any metal-to-insulator or non-magnetic to magnetic transitions, and the resistivity-temperature dependence of the VSe2 single crystal showed an approximately linear relationship with a CDW transition. This linear relationship presents an overall metallic behaviour, in agreement with the ab initio results, which show that the metallic state in a VSe2 single crystal survives in its few-layer structure. Measurements of the magnetic properties in the magnetisation curves of both single crystal and laminate structures indicated paramagnetism with a minor difference in the magnetic moment. In agreement
with experiment, the \textit{ab initio} results found that the non-magnetic state of VSe$_2$ is energetically favourable by 0.225 eV/atom. Both the electronic and magnetic properties match the results calculated through DFT-D2, validating the methodology used.

In summary, the diverse range of interactions studied in this thesis shows that the stacking composition, stacking order, strain, rotation, sublattice equivalence, symmetry, and asymmetry all play an important role in vdw heterostructures. Future theoretical work on a larger range of materials and the effect of the interactions studied in this work on different properties such as magnetism could lead to more new and exciting materials and exotic quantum states. Furthermore, experimental methods need to be advanced to allow better control of the orientation and stacking order of heterostructures with greater precision to test the DFT predictions. In conclusion, controlling the emergence of new states in vDW heterostructures offers an enticing a way to achieve atomic-scale engineering of materials with unprecedented properties.
8. Publications

8.1. Works and collaborative works published:


8.2. Other works published during this thesis


• Sang, L., P. Maheswari, Z. Yu, F.F. Yun, Y. Zhang, S. Dou, C. Cai, V.P.S. Awana, and X. Wang, Point defect induced giant enhancement of flux pinning in Co-doped FeSe0. 5Te0. 5 superconducting single crystals, AIP Advances, vol.7. 115016. 2017


8.3. Future related works in preparation or under submission

- Yun, F.F., D.L. Cortie, and X.L. Wang, The effect of symmetrical and asymmetrical stacking in trilayer heterostructures of stanene with hexagonal boron nitride and graphene, 2018

- Yun, F.F., D.L. Cortie, and X.L. Wang, Electronic structure and stabilities of hBN, graphene, stanene, in multilayers (up to five) in combinations of asymmetric and symmetric composition and stacking, 2018
9. Bibliography


[38] Huang, M., H. Yan, C. Chen, D. Song, T.F. Heinz, and J. Hone, *Phonon softening and crystallographic orientation of strained graphene studied by*


nanosheets via chemical reduction of exfoliated graphite oxide, Carbon, vol.45. 1558. 2007


### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AE</td>
<td>All Electron</td>
</tr>
<tr>
<td>AFM</td>
<td>Antiferromagnet, Atomic Force Microscopy</td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-resolved photoemission spectroscopy</td>
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<tr>
<td>BFGS</td>
<td>Broyden–Fletcher–Goldfarb–Shanno algorithm</td>
</tr>
<tr>
<td>BLYP</td>
<td>Becke, Lee, Yang, Parr Exchange-Correlation Potential</td>
</tr>
<tr>
<td>BN</td>
<td>Hexagonal Boron Nitride</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>CASTEP</td>
<td>Cambridge Serial Total Energy Package</td>
</tr>
<tr>
<td>CDW</td>
<td>Charge Density Wave</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>FM</td>
<td>Ferromagnet</td>
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<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>hBN</td>
<td>Hexagonal Boron Nitride</td>
</tr>
<tr>
<td>HF</td>
<td>Hybrid Function DFT, Hartree Fock</td>
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<tr>
<td>HPC</td>
<td>High-performance cluster</td>
</tr>
<tr>
<td>HSE</td>
<td>Heyd, Scuseria, Ernzerhof Exchange-Correlation Potential</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LAPW</td>
<td>Linearized Augmented Plane Wave</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LSDA</td>
<td>Local Spin Density Approximation</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
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<tr>
<td>MX₂</td>
<td>Transition Metal Dicalcogenide</td>
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<tr>
<td>NCI</td>
<td>National Computing Infrastructure</td>
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<tr>
<td>NM</td>
<td>Non Magnetic</td>
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<tr>
<td>PAW</td>
<td>Projector-Augmented-Wave method</td>
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<td>PBE</td>
<td>Perdew–Burke–Ernzerhof</td>
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<tr>
<td>PBE</td>
<td>Perdew, Burke, Ernzerhof Exchange-Correlation Potential</td>
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<tr>
<td>PM</td>
<td>Paramagnet</td>
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<tr>
<td>PP</td>
<td>Pseudo-Potential Method</td>
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<tr>
<td>PPMS</td>
<td>Physical Property Measurement System for conductivity and magnetic susceptibility</td>
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<tr>
<td>PS</td>
<td>Pseudo</td>
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<tr>
<td>PW</td>
<td>Perdew, Wang Exchange-Correlation Potential, Plane Wave</td>
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<tr>
<td>QAH</td>
<td>Quantum Anomalous Hall</td>
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<tr>
<td>QSHE</td>
<td>Quantum Spin Hall Effect</td>
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<tr>
<td>SCF</td>
<td>Self Consistent Field calculation</td>
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<tr>
<td>SOC</td>
<td>Spin-Orbital Coupling</td>
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<tr>
<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-Dependent Density Functional Theory</td>
</tr>
<tr>
<td>TEM</td>
<td>Tunnelling Electron Microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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<tr>
<td>VASP</td>
<td>Vienna Ab initio simulation package</td>
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<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
</tbody>
</table>
List of Tables

Table 2-1 The possible combinations of in-plane and out-of-plane bonding interactions in all types of heterostructures. ........................................ 37

Table 4-1 Summary of the binding energy, lattice constants, interlayer distances, buckling heights and bond-lengths for graphene/stanene bilayers in five different epitaxial configurations .................................................. 85

Table 5-1 Summary of the binding energy, lattice constants, interlayer distances between topmost and stanene (D₁) and bottom most and stanene (D₂) layers as illustrated in Figure 5-1, buckling heights and bond-lengths for trilayer heterostructures in five different epitaxial configurations. ........................................ 104

Table 5-2 Shows the binding of bi- and tri- layers and their binding energy difference. ........................................ 120

Table 6-1 Shows the for the system with two types of van der Waal corrections the Grimme and TS corrections the energy difference in respect to NM state. ........................................ 130

Table 6-2 Bulk Phase 4U U of V=3eV, Se=-2 Ecut=800 Shows the energy values for various energy calculations a. ........................................ 130
List of Figures

Figure 2-1 a) The graphene lattice viewed along the c-axis; b) side view of the graphene lattice. c) The optimised band structure for graphene. The dashed lines in (a) and (b) indicate the edges of the primitive graphene unit cell. (Frank.F.Yun 2018) ................................................. 14

Figure 2-2 Shown the various 3D HOMO-LUMO E-k diagrams that describes various different types of particles and the various forms of
equation which model them, \( m^* \) refers to the effective mass, \( p \) is the
momentum operator, \( H \) is the Hamiltonian, \( \sigma \) is the Pauli matrix, \( v_f \) is
the fermi velocity and \( c \) is the speed of light. (A) Classical Schrödinger’s
particle (B) Dirac particle, (C) Dirac particle in graphene with 2D
pseudospin between the two sublattices (red and green). (D) Particles
in bilayer graphene with pseudospin and left, right chirality (blue and
yellow). Figure adapted from Ref. [23] ....................................................... 15

Figure 2-3 Realization and characterization a) shows a graphene crystal
exfoliated using the scotch tape method on top of oxidized silicon
substrate[23]. b) Shows atomically thin steps of mono-, bi- and tri-
layers (red 1, purple 2 and green 3) on top of a SiC substrate[23], c)
Atomic-resolution image of pristine graphene using high-angle annular
dark field–scanning tunneling microscopy (HAADF-STEM); the scale
bar is 1 nm[32]. .......................................................... 17

Figure 2-4 a) Phases of boron nitride: hexagonal phase (h-BN), b) cubic
phase (c-BN), c) wurtzite phase (w-BN). .................................................. 19

Figure 2-5 a) The BN lattice viewed along the c-axis; b) a side view of
the BN lattice. c) Optimized band structure of BN. The dashed lines in
(a) and (b) indicate the edges of the primitive BN unit cell. (Frank. F.
Yun 2018) .......................................................... 20

Figure 2-6 a) Optical microscope image of hBN sheets on a SiO\(_2\)
substrate[76]. b) STM image of hBN on an Rh(111) surface with steps;
the inset shows an enhanced image. c) High-resolution TEM (HRTEM)
image of monolayer hBN, with the inset showing an outline of the
structure[76]. .......................................................... 21

Figure 2-7 a) The stanene lattice viewed along the c-axis b) a side view
of the stanene lattice c) the optimized band structure for stanene. The
dashed lines in (a) and (b) indicate the edges of the primitive stanene
unit cell. .......................................................... 23

Figure 2-8 a) Atomically resolved STM image of stanene, b) height line
profile across the red line in a); c) Large-scale STM topography of
stanene film, and d) height line profile across the red line in c). Figure
from Ref. [105] .......................................................... 24

Figure 2-9 a) Shows overlaid STM images with yellow sphere
indicating Sn-A atoms in stanene on top of a grey Te in the Bi\(_2\)Te\(_3\)
substrate, b) Shows overlaid STM images with Sn-A(large) and Sn-
B(small) atoms in stanene on top of a grey Te in the Bi\(_2\)Te\(_3\) substrate.
c) Show a side view of the atomic structure [105]. .................................... 25
Figure 2-10 a) epitaxial stanene on top of Bi$_2$Te$_3$, as demonstrated in [105] from the top (left) and side (right) views, b) DFT band structure of stanene on five layers of Bi$_2$Te$_3$(111), with red dots showing the contribution from stanene, c) Comparison of experimental band structure with DFT.[105] ........................................................................ 27

Figure 2-11 (a) Top and (b) side views of the H (left) and T (right) phase atomic structures with lattice vectors $a$ and $b$; (c) contours show the total charge density. (d) Charge density illustration showing the charge density difference of charges (e) isosurfaces showing the charge density of $p$–$d$ hybridization a Mo–O bond. Figure adapted from Ref. [110] ........................................................................ 29

Figure 2-12 Predicted stable transition-metal combinations by Ataca [110]. Metallic atoms are divided into 3d, 4d, and 5d groups. Each box indicates either gray (unstable), white-red (H is stable), white-green (T is stable, red-green (T is more stable than H), or green-red (H is more stable than T). (+), (*), and (***) indicate half-metallic, metallic, and semiconducting systems, respectively. Figure from Ref. [110] ........................................................................ 30

Figure 2-13 The calculated electronic band structures of lower-energy stable MX$_2$ 2D materials, as predicted by Ataca et al. for all compounds except MoS$_2$. EF is the Fermi level as marked by the red dash-dotted lines. Nonmagnetic states only show blue lines. For magnetic structures, blue and orange represent spin-up and spin-down, respectively.[110] ........................................................................ 32

Figure 2-14 Parameters of charge, orbital spin, the lattice, charge transfer, strain, symmetry breaking, electrostatic coupling, and frustration as the fundamental strategies to tune the interactions and properties that occur within bulk layered heterostructures. [118] ........................................................................ 36

Figure 2-15 Graphene on hBN can form a Moiré pattern for graphene. A) Illustration of the exaggerated lattice mismatch of up to ~10%. B) Experimental data for the conductivity ($T = 150$ mK) near the charge neutrality of four heterostructure devices (A1, A2, B1 and B2), respectively. Left inset: schematic diagram of the measurement set-up and right inset: AFM image, respectively. Scale bar is three μm. C) Experimental resistance vs. gating voltage range. Figure adapted from Ref. [121] ........................................................................ 38

Figure 2-16 a), b), c), and d) Stanene/graphene bilayer structures calculated by Chen et al. and their corresponding band structures, e) shows the side view in which D is the interlayer distance, $\Delta d$ is the buckling height. The C, upper Sn, and lower Sn are represented by grey, blue, and yellow, respectively. The lattice is defined by the red dashed lines. Figure adapted from Ref. [126] ........................................................................ 40

Figure 2-17 Ab initio calculations performed by Wang et al.: a) Structure of the stanene/hBN heterostructure, $a = 4.35$ Å, b) the band structure for $a = 4.35$ Å; c) Phonon spectra of Sn; d) Phonon spectra of hBN; e)Electronic structure of hBN/stanene for $a = 4.72$ Å; f) Edge states for $a = 4.72$.[127] ........................................................................ 41

Figure 2-18 Band structures of the stanene/hBN system when lattice is fixed to $a = 4.72$ Å, while the interlayer distance $d_2$ varied from (a) 2.70 Å, (b) 3.00 Å, and (c) 3.60 Å (d)shows the interlayer distance $d_2$ between stanene and the h-BN vs the binding energy per Sn atom with the lattice set to $a = 4.72$ Å from ref [127] ........................................................................ 42
Figure 2-19 a) shows a top view of the crystal structure of the stanene/hBN system, (b) shows band structure of the system without strain and (c) band structure of the system with a compressive strain of 1%. [127]

Figure 2-20 Band structure of hBN/Stanene heterostructure: (left) with SOC, (right) without SOC from ref [120].

Figure 2-21 Band structures of trilayer heterostructures. Insets show the structures for the varying stacking configurations. a), b) and c) show (AB) stacking layers, d), e) ,f) show rhombohedral (ABC) stacking. [129]

Figure 2-22 (a) Shows the band structure of BN/graphene/BN stacked in the ABA configuration results in a gapped graphene (b) Shows the band structure of graphene/BN/graphene stacked in the ABA configuration with the overlapping Dirac points result in a gapped and a ungapped band. [129]

Figure 2-23 a) Shows tuning of the band gap using in a varied electric field for bilayer BN/graphene (AB stacked), trilayer BN/graphene/BN(ABA-stacked) and trilayer graphene/BN/graphene (ABA stacked), (b) Shows tuning of the band gap in a varied electric field for graphene/BN/graphene three configurations AAA-stacked, ABA-stacked and ABC stacked. [129]

Figure 2-24 Shows a thickness vs band gaps relationship of graphene(G)/BN/graphene(G), the black line indicate the BN/G/BN structure while the red line indicates the G/BN/G structures. As studied in ref[134].

Figure 2-25 (a) Shows the asymmetric bilayer structure all three monolayers (silicene or germanene or stanene)/hBN from the side and top views, (b) shows the symmetric trilayer structure of hBN/(silicene or germanene or stanene)/hBN from the top and side views, (c) shows the Brutouin zone for the resulting supercell. (d) shows the binding energy curves for silicene, germanene, and stanene on h-BN substrate, the labels $E_D$ and $E_d$ are the energy of the asymmetric heterostructures with the optimized interlayer distance $D$ and the stretched interlayer distance $d$. [120]

Figure 2-26 (a) B−C−C−B stacking, (b) B−C−C−N stacking, and (c) N−C−C−N stacking. [129]

Figure 2-27 Density of states of bilayer graphene (BLG) alone (a, b) and in BN/graphene/graphene/BN (c, d), arise from $p_z$ orbitals projected on individual carbon in external fields of (a, c) 0 and (b, d) 2 V/nm. [129]

Figure 2-28 Band structure for (a) BLG (b) B−C−C−B, (c) N−C−C−N, and (d) B−C−C−N. Insets shows the band gap ($E_g$) and the gap at K ($\Delta_k$). Figure adapted from Ref. [129]

Figure 3-1 Illustration of Jacobs ladder of chemical accuracy as described by Perdew[150].

Figure 3-2 Shows a model of the many-body system described by the full many-body Hamiltonian in Equation 3-4.

Figure 3-3 Overlap of DFT methods with semi-classical method with
respect to the electron correlation length from [178], highlighting the problematic medium-range correlation region.

Figure 3-4 A perspective given by Grimme[178] of the different DFT and empirical methods that account for dispersion. $E_{KS}$ is the Kohn–Sham energy of the system, $V_{KS}$ refers to the various potentials within the KS scheme, $E_{pairs}$ is the empirical energy, $V_{1e}$ is the one electron potential.

Figure 3-5 Diagrams of the SCF method used to converge the KS Hamiltonian, in which the closeness of the densities should be specified to allow convergence otherwise will convergence will not be achieved.

Figure 4-1 The relationship between strain and structure in hypothetical stanene monolayers. (a) In-plane compressive strain increases the buckling height as shown by the cross-section of the strained layer (blue) superimposed on an unstrained layer (green/cyan). (b) A top view of stanene structure looking from the z-direction towards the origin, a green colour indicates the Sn atom is closer to the viewer, a cyan colour shows the Sn atom further away. The rhombus shape shows the primitive cell of the stanene lattice. (c) Pristine stanene at its equilibrium lattice constant has a well-defined buckling height $d = 0.888 \, \text{Å}$ separating the Sn two sub-lattices. (d) An isometric view of the stanene structure which shows the bond-angle $\theta$ in degrees° (e) Tensile strain decreases the buckling height shown by superimposing the strained layer (red) on the unstrained layer (green/cyan). The median structure band structure of strained regions of (1), (2) and (3) are shown in (f), (g), (h). (i)The strain phase-diagram indicates a strong interplay between the cohesive energy, buckling, bond angle and the band-structures.

Figure 4-2 The epitaxial stanene/graphene structure (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5 structures where grey atoms indicate carbon and green and cyan atoms indicate the two planes of Sn atoms with bond angle $\theta$ °. (f), (g), (h), (i) and (j) are the corresponding band structures for the fully relaxed bilayer structures S1-S5. (k) A cross-section showing the interlayer separation (D) and the stanene buckling parameter (d). (l) Isometric representation of the bilayer structure.

Figure 4-3 The co-aligned structure (S4) can exhibit a gap around K point with either a) metallic bands at $\Gamma$ or b) a gap at $\Gamma$, depending on the level and type of strain applied. The gap around the K point is only apparent for moderate degrees of compressive strain compared to the optimal bilayer lattice for the S4 structure c) and d) shows the band structures of the individual non-interacting layers of stanene and graphene respectively under the same level of compressive strain, and with same atomic structure constrained to the bilayer positions. This demonstrates gap formation at the K point is not a result of the strain on the individual layers but is instead a unique feature of the C-Sn interactions in the strained bilayer.

Figure 4-4 The orbital projected band structure and density of state for a) the S4 the co-aligned structure at the gap condition b) the lowest-energy S2 rotated structure and. The red show the s orbital contributions, green shows the total orbital contributions of the p_x, p_y and d orbitals, and blue represents the p_z orbital contributions.
Figure 4-5 a) & b). Side and top view of the adsorption position of H₂O molecule on the graphene with an electron density map of the H₂O molecule which adsorbs with the hydrogen closest to the graphene layer. c) and d) Shows the side and top view of the H₂O when adsorbed on the stanene layer. e) Representative band structure of S₂ in which shows band structure before and after adsorption on either C or Sn Side of the structure ........................................... 94

Figure 4-6. The work function of the heterostructure layer before and after adsorption and the adsorption anisotropy that arises before and after the adsorption of a single H₂O molecule. ........................................... 96

Figure 5-1 Shows the structures of the various heterostructure systems for the a) BN/Sn/BN(aS(1-5)), b) C/Sn/BN(bS(1-5)) and c) C/Sn/C(cS(1-5)) systems. Blue indicates the nitrogen atom, white indicates the boron atom, green indicates the topmost tin atom, light blue indicates the bottom-most tin atom, and grey indicates the carbon atom. ........................................... 103

Figure 5-2 Shows the relationship between the interlayer distances of the various heterostructures hBN/Sn/hBN, hBN/Sn/C, and C/Sn/C trilayer structures. For the x-axis, the number represents an integer between 1-5 for (a,b,c)S(X) structures where X correlates to the lattice parameters. ........................................... 105

Figure 5-3 a), c), e) Shows the projected band structure and dos for the orbital contributions s, (pₓ, pᵧ, d), total, and pₓ orbital of the structures aS₅, bS₅, and cS₅ respectively b), d), f) shows the projected band structure and dos for atomic contributions of carbon, Sn, B, N atoms in the structures aS₅, bS₅, and cS₅ respectively. g), i), k) Shows the projected band structure and dos for the orbital contributions s, (pₓ, pᵧ, d), total, and pₓ orbital of the structures aS₂, bS₂, cS₂ respectively h), j), l) shows the projected band structure and dos for atomic contributions of carbon, Sn, B, N atoms in the structures aS₂, bS₂, and cS₂ respectively. ........................................... 111

Figure 5-4 Brillouin Zones of type I co-aligned (left) and II rotated (right) band structures and their corresponding K points. The dashed hexagon represents the 1×1 graphene BZ with the corresponding K-point path represented by the red dashed line, while the solid hexagons represent the new BZ with the corresponding K-point path represented by the solid blue line. ........................................... 112

Figure 5-5 Shows the HOMO orbitals at the Fermi level for the type I structures of a)hBN/Sn/hBN(aS₅), c)C/Sn/C(cS₅), and e) hBN/Sn/C(bS₅) as well the type II structures of b)hBN/Sn/hBN(aS₂), d)C/Sn/C(cS₂), and f) hBN/Sn/C(bS₂). Positive and negative phase wavefunctions are given in yellow and blue respectively. ........................................... 117

Figure 5-6 (Left), the binding energies of the (a-c)S(1-5) structures with the x-axis as the lattice parameter, (Right) the work functions of the (a-c)S(1-5) structures with the x-axis as the structure number. ........................................... 119

Figure 6-1 Shows the convergence of energy cut off for the VSe₂ with dispersion correction ........................................... 127

Figure 6-2. a) Band structure of the Bulk phase VSe₂ for a non-magnetic arrangement b) Band structure of the Monolayer VSe₂ for a non-magnetic arrangement ........................................... 129
Figure 6-3. Shows the alpha and beta spin band structures for VSe$_2$ with a ferromagnetic spin arrangement. ............................................. 131

Figure 6-4. Shows the band structure for VSe$_2$ for an antiferromagnetic spin arrangement. ............................................. 131

Figure 6-5. (a) Side and (b) top views of the atomic structure of VSe$_2$. XRD patterns of VSe$_2$ single crystal (c) and laminate (d). (e) AFM image of the VSe$_2$ nanosheets with height profiles along the indicated paths. ............................................. 134

Figure 6-6. $M$–$H$ curves at various temperatures for (a) VSe$_2$ single crystal and (b) VSe$_2$ laminate. $M$–$T$ curves under various fields for (c) VSe$_2$ single crystal and (d) VSe$_2$ laminate. The magnetic field was applied parallel to the flake plane. ............................................. 136

Figure 6-7. Determination of the angular momentum quantum number $J$ from $\Delta M$ versus $H/T$ curves. Magnetic moment $\Delta M$ (after subtracting the linear Pauli paramagnetic background) as a function of reduced field $H/T$ for VSe$_2$ single crystal (a) and laminate (b). Fits of the data were drawn using the Brillouin function with different values of $J$. ............................................. 138

Figure 6-8. XPS spectra of (a) V 2p and (b) Se 3d regions for the VSe$_2$ single crystal and laminate, respectively. For comparison, the VO$_2$ and elementary Se spectra are also included. ............................................. 140

Figure 6-9. CDW and weak localization in VSe$_2$ single crystal. (a) Temperature dependence of resistance from RT down to 2 K. The blue dashed line indicates the CDW transition. (b) Logarithmic temperature dependence of the resistance at low temperature. The solid red line is only a guide to the eyes. (c) and (d) Magnetoresistance normalized by $\rho$, the resistance at zero magnetic field, at various temperatures. ............................................. 141

Figure 6-10 Orientation-dependence of MR for VSe$_2$ at 2 K. The VSe$_2$ flake is in $x$–$y$ plane, the current is parallel to $x$-axis. ............................................. 143