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Interlayer effects revealed in two-dimensional heterostructures by angle-resolved photoemission spectroscopy

by

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Abbreviations

µARPES  spatially-resolved angle-resolved photoemission spectroscopy

µLEED  micrometre spot-sized low energy electron diffraction

2D  two-dimensional

3D  three-dimensional

AFM  atomic force microscopy

ARPES  angle-resolved photoemission spectroscopy

CBM  conduction band minimum

CDW  charge density wave

CVD  chemical vapour deposition

DFT  density functional theory

DOS  density of states

EDC  energy distribution curve

hBN  hexagonal boron nitride

LEEM  low energy electron microscopy

LS-DFT  linear-scaling density functional theory
PDMS  polydimethylsiloxane

PFM  piezoresponse force microscopy

PMMA  polymethyl-methacrylate

PTMC  post-transition metal chalcogenide

SPEM  scanning photoemission microscopy

SPIM  scanning photocurrent microscopy

STS  scanning tunneling spectroscopy

TBG  twisted bilayer graphene

TMD  transition metal dichalcogenide

UHV  ultra high vacuum

VBM  valence band maximum
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Declarations

I declare that this thesis contains an account of my research work carried out at the Department of Physics, University of Warwick between October 2018 and March 2022 under the supervision of Professor Neil R. Wilson. The research reported here has not been previously submitted, wholly or in part, at this or any other academic institution for admission to a higher degree.

Parts of this thesis that have been published by the author between October 2018 and March 2022:


Publications the author has contributed to between October 2018 and March 2022 that have contributed to this work but are not covered in detail in this thesis:


Other parts of this thesis to be published shortly:


All work presented here was completed by myself, except for the following:

- The µARPES data was acquired with the help of A. Barinov, V. Kandyba, A. Giampietri and M. Cattelan at the Elettra synchrotron.
- The majority of the exfoliated samples were fabricated by P.V. Nguyen and H. Park as part of D.H. Cobden’s and X. Xu’s groups at the University of Washington.
- The samples used in Chapter 3 were made by M.J. Hamer as part of R.V. Gorbachev’s group at the University of Manchester.
- J. Zultak, also part of R.V. Gorbachev’s group at the University of Manchester, created the 3D band structure schematics and contour plots presented in Chapter 3.
• The µLEED data was acquired by A. Barinov, A. Locatelli and F. Genuzio at the Elettra synchrotron.

• The DFT calculations in Chapter 3 were performed by T. Salazar, who is part of N.D.M. Hine’s group at the University of Warwick.

• The InSe DFT band structure calculation overlaid in Fig. 3.2 was performed by V. Zolyomi at the University of Manchester.

• The DFT band structure calculation overlaid in Fig. 5.4 was performed by N.D.M. Hine at the University of Warwick.

• The PFM measurements shown in Fig. 6.6 were performed by P.V. Nguyen and H. Park as part of D.H. Cobden’s and X. Xu’s groups at the University of Washington.

Additional publications the author has contributed to (not contained within this thesis) between October 2018 and March 2022:


Abstract

Since the isolation of the first monolayer material, graphene, in 2004, the field of two-dimensional (2D) materials has evolved significantly. Semiconductors, metals, insulators and superconductors have now all been fabricated in the monolayer form. The weak van der Waals forces between the layers allows any 2D material to be stacked upon any other 2D material, creating a wide range of systems that can be studied for new emergent quantum phenomena that depend upon the interlayer coupling and the twist angle between the layers. Twist-dependent interlayer interactions, such as moiré potentials, have been shown to give rise to novel physical properties such as moiré excitons and electronic bands with a flat dispersion and a high density of states. These twist-dependent properties can be exploited to create new 2D twistronic devices, adding to the variety of 2D electronic, spintronic, valleytronic and optoelectronic devices that have already been created.

In this thesis, angle-resolved photoemission spectroscopy with micrometre spatial resolution (µARPES) has been used to visualise interlayer interactions in 2D van der Waals heterostructures. We observe twist-dependent interlayer Umklapp scattering in heterostructures of graphene combined with monolayer and multi-layer post transition metal chalcogenides, such as InSe and GaSe.

Additionally, we combine µARPES measurements with in-situ electrostatic gating to study the conduction band in heterobilayers of transition metal dichalcogenides, a popular family of semiconducting 2D materials with chemical composition MX$_2$, where M is a transition metal atom and X is a chalcogen atom. We determine band gaps and band alignments for the heterobilayers; MoSe$_2$/WSe$_2$, WS$_2$/MoSe$_2$ and WS$_2$/WSe$_2$. At high carrier concentrations, intralayer band gap renormalisation is observed within the layer which charge is injected, leaving the heterobilayer interlayer band gap unaltered.

µARPES with in-situ electrostatic gating was used to study moiré effects within the conduction band of WS$_2$/WSe$_2$ heterobilayers. Furthermore, we observe moiré induced replica bands in graphene on WS$_2$/WSe$_2$, due to the moiré potential in the heterobilayer. In this work, it is important to distinguish between replica bands observed in µARPES spectra due to initial state effects and those due to final state photoelectron diffraction.

Overall, we show µARPES combined with in-situ electrostatic gating to be a powerful technique in characterising 2D materials and their interlayer interactions.
Chapter 1

Introduction

1.1 Introduction

As the demand for greater data storage, faster computation, and more complex technology grows, research into new materials has never been more important. As predicted by Moore’s law [1], the number of microprocessors on a silicon chip has increased rapidly through the development of smaller and smaller electronic components, and need for more compact devices continues to increase. A promising new method for building ultra-compact electronic devices is vertical stacks of two-dimensional (2D) materials.

The idea of being able to create a 2D material was first eluded to as far back as 1973 [2], but it wasn’t until 2004 that two Russian physicists at the University of Manchester, Andre Geim and Konstantin Novoselov, isolated the first monolayer material, graphene [3]. As well as isolating graphene, by exfoliating a bulk graphite crystal with scotch tape, they demonstrated control of its carrier concentration by electrostatic doping using a back gate. Six years later, their work won the Noble Prize in physics, as their break through opened up a new research field of 2D materials with great promise for future technological advancements.

Since the discovery of graphene and the excitement it generated, other layered materials bound by weak van der Waals forces have been isolated down to the monolayer [4, 5]. Today, there is a large variety of 2D materials, these can be divided into families based on their constituents and properties, as shown in Fig. 1.1. These families include 2D metals, semi-metals, semiconductors, insulators, and even superconductors and many of them have now been synthesized in the monolayer form.

Combining different 2D materials into heterostructures facilitates the de-
sign of different devices which can host unique properties for particular electronic applications. So far, 2D heterostructures have been used to make electronic and optoelectronic devices such as field effect transistors [6, 7], light-emitting diodes [8, 9], photodetectors [10, 11], photovoltaic devices [12, 13] and flexible electronics [14, 15]. 2D heterostructures are also being explored for a variety of other applications, such as the development of chemical sensors [16, 17], water purification [18], energy storage [19] and quantum computing [20, 21]. As well as their wide range of applications, 2D materials and their heterostructures hold the potential to revolutionise modern technology with new functionalities that are otherwise inaccessible in conventional three-dimensional (3D) devices [22].

In order for 2D devices to be relied upon for everyday use, not only do the properties of the individual layers need to be well understood, but also how the properties of the layers change with stacking and relative orientation. Within this thesis, the electronic properties of 2D heterostructures are studied. The 2D materials focused on are from the semiconducting transition metal dichalcogenide (TMD) family and the semiconducting III-VI family, combined with either graphene, hexagonal boron nitride (hBN) or other members of the same family. Throughout this thesis, I refer to the semiconducting III-VI family as the post-transition metal chalcogenides (PTMC).
1.2 Graphene

Graphene, a single layer of graphite, is made up of carbon atoms arranged in a hexagonal structure, as shown in Fig. 1.2 a). The hexagonal structure is formed from two interpenetrating triangular A and B sublattices, highlighted by the atoms coloured in blue and yellow. Each unit cell is comprised of two atoms, one from each sublattice, and the lattice vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, with magnitude 2.46 Å [23], can be written as:

$$
\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}) \quad \text{and} \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}),
$$

(1.1)

where $a = 1.42$ Å is the carbon-carbon bond length.

The carbon atoms bond to one another via $sp^2$ hybridised orbitals, one $s$ orbital and two $p$ orbitals hybridised to form three $sp^2$ orbitals, which form the covalent $\sigma$-bonds between each carbon atom. The remaining electron in the out-of-plane $p_z$ orbital of each carbon atom forms half-filled delocalised $\pi$-bonds, which are responsible for the unusual electronic properties of graphene.

Graphene has a hexagonal Brillouin zone, as shown in Fig. 1.2 b), with reciprocal lattice vectors, $\mathbf{b}_1$ and $\mathbf{b}_2$, given by:

$$
\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}) \quad \text{and} \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}),
$$

(1.2)

The interesting physics, due to the half-filled $\pi$-bonds, is at the Brillouin zone corners, $\mathbf{K}$ and $\mathbf{K}'$. The electronic dispersion of graphene’s $\pi$-band is shown in Fig. 1.3 a), described by a tight-binding model where electrons are allowed to hop between nearest- and next-nearest-neighbour atoms [23]. Only at $\mathbf{K}$ and $\mathbf{K}'$ does the filled
Figure 1.3: a) The dispersion of the graphene π-band. Taken from [23]. b) The resistivity of graphene as a function of gate voltage, $V_g$. Dirac cone schematics show the change in the position of the Fermi level, $E_F$. Taken from [24].

valence band meet the empty conduction band, termed the Dirac point, making graphene a gap-less semiconductor or semi-metal.

The electronic dispersion close to the Dirac points is linear and can be expressed as:

$$E = \hbar v_F |k|$$  \hspace{1cm} (1.3)

where $E$ is the energy, $k$ is the wave vector relative to the Dirac point and $v_F$ is the Fermi velocity which is approximately $c/300$, where $c$ is the speed of light [24]. Due to the linear dispersion of the band structure, the electrons behave as massless Dirac fermions [25, 26].

The linear dispersion of the π-band is responsible for the remarkably high electron mobility observed in graphene [24]. As demonstrated by Geim and Novoselov, the carrier concentration can be controlled in graphene using a back gate. Fig. 1.3 b) shows how the resistivity changes when doping graphene, where a significant increase in resistance can be seen at the Dirac point, due to the decrease in density of states (DOS).

### 1.3 Hexagonal boron nitride

Hexagonal boron nitride (hBN) is another sp$^2$-bonded hexagonal lattice in the graphene family of 2D materials and is sometimes referred to as white graphene. Fig. 1.4 a) shows the atomic structure of monolayer hBN, where the A and B sub-lattice atoms are replaced with boron and nitrogen atoms, respectively. The lattice parameter of hBN is slightly larger than graphene, with a value of $a_{hBN} = 2.504$ Å [27].
Many 2D electronic devices use hBN as it is a wide band gap semiconductor or insulator and has a dielectric constant of $\varepsilon_{hBN} = 4.5$ \cite{29, 30}. Therefore, hBN can be used as a dielectric or tunnel barrier \cite{31} in 2D devices. The band structure of monolayer hBN is shown in Fig. 1.4 b). For monolayer hBN, the band gap is suspected to be direct at the $\mathbf{K}$ point but for an increase in the number of layers a direct-to-indirect transition is predicted, as the $\mathbf{M}$ point becomes the CBM with increased thickness \cite{28}. For all thicknesses of hBN, the band gap is $\sim 6$ eV \cite{28}.

### 1.4 Semiconducting 2D materials

#### 1.4.1 Transition metal dichalcogenides

The 2D family of transition metal dichalcogenides (TMDs) contain metals, semiconductors and superconductors, but it is the semiconducting TMDs that hold great promise for future optoelectronic applications due to their direct band gap in the monolayer.

Their chemical composition is MX$_2$, where the most widely studied are the MoWSeS semiconducting TMDs, where M = W or Mo and X = S or Se. Each layer is three atoms thick (X-M-X) and covalently bonded in a hexagonal lattice, as shown in Fig. 1.5 a). Fig. 1.5 b) shows the stacking of two TMD layers in the 2H configuration, where each layer is rotated 180° to one another. Other configurations such as 3R, 1T and 1T' are also possible but 2H is the most commonly seen configuration for the MoWSeS semiconducting TMDs.

Similar to graphene and hBN, TMDs have a hexagonal Brillouin zone, as shown in Fig. 1.5 c). The valence band maximum (VBM) and conduction band maximum (CBM)
Figure 1.5: a) Top view of the atomic structure of a monolayer TMD, where M = W or Mo and X = S or Se. b) Side view of the atomic structure of a bilayer TMD stacked in the 2H configuration. The unit cell is marked by the black dashed boxes. c) A Brillouin zone schematic for the TMDs, with the high symmetry positions defined. Adapted from [34].

minimum (CBM) in the monolayer reside at the Brillouin zone corners $\mathbf{K}$ and $\mathbf{K}'$. A density functional theory (DFT) calculation of the band structure of monolayer MoS$_2$, with the orbital composition from the metal atoms depicted, is shown in Fig. 1.6 a) [32]. At $\mathbf{K}$ and $\mathbf{K}'$, the orbital composition of the valence band edge is comprised mainly of in-plane $d_{x^2-y^2}$ and $d_{xy}$ orbitals from the metal atom, whereas the conduction band edge at $\mathbf{K}$ and $\mathbf{K}'$ is formed predominately of out-of-plane $d_{z^2}$ orbitals from the metal atom. Therefore, the CBM is more sensitive to the hybridisation between layers than the VBM. At $\mathbf{\Gamma}$, the valence band edge is formed of out-of-plane $d_{z^2}$ orbitals from the metal atom and out-of-plane $p_z$ orbitals from the chalcogen atoms, so therefore, is also sensitive to interlayer hybridisation. The other notable band edge within the band structure of monolayer TMDs is the conduction band edge at the $\mathbf{Q}$ point, which has part in-plane and out-of-plane orbital character. It is formed of a combination of $d_{x^2-y^2}$ and $d_{xy}$ orbitals from the metal atoms and a small contribution from the $d_{z^2}$ orbital, as well as, contributions from all three $p$ orbitals of the chalcogen atoms.

The band edges at $\mathbf{K}$ in the monolayer are spin-split due to the strong spin-orbit coupling from the heavy transition metal atoms, as illustrated by the schematic in Fig. 1.6 b). The magnitude of the spin-splitting in the valence band is $\sim$100-400 meV, whereas the spin-splitting in the conduction band is only $\sim$3-40 meV, with values depending on the chemical composition [33].

The spin-splitting at the bands edges is present in both the monolayer form and the bulk crystal, but the symmetry of the electronic states change with the number of layers. The unit cell of the bulk crystal consists of two layers and has inversion symmetry, therefore, the spin-split bands at $\mathbf{K}$ and $\mathbf{K}'$ are spin degenerate.
The monolayer TMDs have broken inversion symmetry and as a result, the spin-split bands at $\mathbf{K}$ and $\mathbf{K}'$ become spin-polarised, combined with time-reversal symmetry, the valleys at $\mathbf{K}$ and $\mathbf{K}'$ then become inequivalent but still degenerate in energy, therefore, each $\mathbf{K}$ point can be referred to as having a different valley pseudo spin. The valley pseudo spin and spin-orbit coupling are locked in the monolayer, such that there can only be spin up at $\mathbf{K}$ and spin down at $\mathbf{K}'$ for a given band. This spin-valley locking and the direct band gap is what makes the monolayer TMDs ideal candidates for valley-dependent optoelectronic devices [36, 37], as $\mathbf{K}$ and $\mathbf{K}'$ will only couple to right-handed and left-handed circularly polarised light, respectively.

The band gap of TMDs covers a wide spectral range from the near-infrared to the visible region of the electromagnetic spectrum, ideal for optoelectronic applications and energy harvesting [38, 39]. Increasing the number of layers beyond the monolayer changes the band gap from direct to indirect. Hybridisation between the out-of-plane orbitals cause the band at $\mathbf{\Gamma}$ to become the VBM and the $\mathbf{Q}$ point to become the CBM. The bands at $\mathbf{K}$ remain largely unchanged for increased layer number, as their orbital composition is not sensitive to the hybridisation between layers. DFT calculated band structures for monolayer and bilayer WS$_2$ are shown.
1.4.2 Post-transition metal chalcogenides

The post-transition metal chalcogenides (PTMCs) have a very similar crystal structure to TMDs but with an additional layer of metal atoms in each monolayer. The monolayer is therefore four atoms thick (X-M-M-X), as shown in Fig. 1.7 a), and has the chemical composition MX, where M = In or Ga and X = S or Se. Within each monolayer, the atoms are covalently bonded in a hexagonal lattice, as shown in Fig. 1.7 b), and have a hexagonal Brillouin zone, as shown in Fig. 1.7 c).

The monolayer PTMCs are indirect band gap semiconductors, where the CBM is at $\Gamma$ and the VBM is close to $\Gamma$, as shown by the DFT calculated band structure for monolayer InSe in Fig. 1.7 d). The dispersion of the valence band
edge around $\Gamma$ takes the shape of an inverted ‘Mexican hat’, as shown by Fig. 1.7 e). Around $\Gamma$ the orbital composition of the valence band edge is predominately formed of out-of-plane $p_z$ orbitals from the metal and chalcogen atoms. A DFT calculation of the band structure of monolayer InSe separated by each of the orbital contributions is shown in Fig. 1.8 a).

Like the TMDs, the PTMCs have a layer-dependent band structure due to the out-of-plane orbital character of the valence band edge around the $\Gamma$ point. Fig. 1.8 b) shows DFT calculated band structures for 3, 4 and 5 layer InSe [41]. For each additional layer, an extra band is present at $\Gamma$ in the valence band and the conduction band, reducing the energy gap as demonstrated by the lower right graph in Fig. 1.8 b). Increasing the number of layers also results in an indirect-to-direct
transition of the band gap, opposite to that of TMDs. Fig. 1.8 c) shows how the shape of the valence band edge around Γ changes for increasing number of layers, moving the VBM from close to Γ to exactly Γ [42].

The PTMCs hold promise for future optoelectronic devices, such as high performance photodetectors [43, 44], due to their large spectral range in the infrared to violet region of the electromagnetic spectrum [45] and their high carrier mobility due to their low effective mass at the band edges [46, 47]. Combining PTMCs with other materials, such as the bilayer or thicker TMDs, has been explored as a robust way of building broad spectral range optoelectronic devices [48], as the VBM is at Γ in the multi-layer TMDs and the CBM is at Γ in the PTMCs.

1.5 Building 2D heterostructures

2D materials can be synthesized via various methods, such as chemical vapour deposition (CVD), molecular beam epitaxy, physical vapour deposition and chemical exfoliation. But the method that creates the highest quality 2D materials is mechanical exfoliation. Mechanical exfoliation produces 2D materials that are typically very small in size, ∼1-100 µm across and therefore are more commonly used for research purposes. 2D materials grown by other methods, such as CVD, are typically of poorer quality, but significantly larger lateral sizes are achievable. Therefore, great efforts are going towards improving the quality of epitaxially grown 2D materials for the manufacture of 2D devices in the future [49, 50]. In this thesis, all 2D materials were fabricated by mechanical exfoliation, as their higher quality is essential for studying their fundamental properties.

Layered crystals held together by weak van der Waals forces can be easily exfoliated down to a single layer by repeatedly dividing the crystal between two pieces of scotch tape. This process does not damage the individual layers due to their strong in-plane bonds and creates 2D flakes that are approximately ∼1-10 µm in size. The mechanically exfoliated 2D flakes can then be identified under an optical microscope and their thicknesses determined via their optical contrast or further analysis with atomic force microscopy (AFM).

Once identified, the 2D flakes can be stacked into heterostructures with other 2D materials. The most versatile techniques are the dry transfer techniques that use either the polymer polymethyl-methacrylate (PMMA) or polydimethylsiloxane (PDMS) to pick up the 2D flakes [51, 52]. The PMMA assembly technique requires the 2D flake to be exfoliated directly onto the PMMA polymer membrane. The 2D flake can then be aligned and placed on another flake or substrate, after which
the membrane is removed. The PDMS assembly technique is very similar but uses PDMS coated stamps to pick up, align and place the 2D flakes [53].

Both assembly techniques involve exposing the 2D materials to polymer residue, which can contaminate the surface and interfaces between layers. Annealing the heterostructures in an Ar/H\textsubscript{2} atmosphere removes these contaminants, along with AFM cleaning [54]. To further avoid contamination, the exfoliation and assembly process is often carried out in a clean room and/or glove box and heterostructures can be designed with an encapsulating layer of graphene or monolayer hBN, to protect the underlying layers.

Encapsulating 2D materials in hBN has also been shown to improve their properties, such as reducing the exciton line widths in semiconducting TMDs [56] and increasing the carrier mobility in graphene [57]. Bulk hBN is also commonly used as a substrate, as it provides a much flatter surface than silicon, which is required for stable, high quality heterostructures [57].

Alternatively, heterostructures can grown by epitaxial methods, such as CVD [58]. However, these methods often require the optimisation of many growth parameters such as temperature, pressure, substrate and precursor. Compared to mechanical assembly techniques, it is difficult to control the number of layers, their size, relative orientation and phase. Both mechanical assembly and CVD growth of
2D heterostructures are illustrated in Fig. 1.9.

1.6 Twistronics

Unlike 3D devices, 2D devices have an additional degree of freedom, the relative crystallographic orientation between adjacent layers, commonly referred to as the twist angle. Different twist angles result in different amounts of interlayer coupling between layers and hence change the properties of the heterostructure. Many interlayer effects have been shown to be dependent on twist angle, such as charge transfer [59] and interlayer tunneling [60]. This additional degree of freedom opens up a new method for engineering band structures in 2D heterostructures and has already been explored in various ways [61], some of which are discussed in more detail below.

Interlayer excitons

The twist angle can be used to control the photoluminescence intensity and lifetime of interlayer excitons. The semiconducting TMDs and their heterostructures are commonly used to study excitonic effects due to their strong light-matter interactions.

Stacking two different monolayer TMDs together to form a heterobilayer creates a type II band alignment, where the VBM resides in one layer and the CBM resides in the other layer. Excitons can form within their individual layers, known as intralayer excitons, and excitons can form across the two layers, known as interlayer...
excitons, where the hole is in one layer, the electron is in the other layer and they are bound by Coulomb’s force. Fig. 1.10 a) shows a schematic of an interlayer exciton across the band edges of a MoSe$_2$/WSe$_2$ heterobilayer.

The twist angle between the layers controls the intensity of the photoluminescence (PL) peak seen from interlayer excitons, as shown in Fig. 1.10 b) for a MoSe$_2$/WSe$_2$ heterobilayer. Due to the large momentum mismatch between the CBM and VBM at 30°, the photoluminescence of the interlayer exciton is completely suppressed and only increases for angles approaching 0 and 60°, where the VBM and CBM become aligned in momentum. Additionally, the twist angle has been shown to red-shift the photoluminescence of interlayer excitons in twisted WSe$_2$ bilayers [64].

Furthermore, the spatial separation between the electron-hole pair leads to long exciton lifetimes, due to reduced overlap of the electron and hole wave functions [65, 66] and their lifetimes can be increased further by increasing the twist angle between the layers [62, 64], as shown in Fig. 1.10 c).

Moiré potentials

When stacking 2D materials into heterostructures, it is possible to create an additional long range periodic potential, known as a moiré potential. Moiré potentials are formed by superimposing two 2D lattices that differ in lattice constant, or, by rotating two 2D lattices with respect to one another. Fig. 1.11 a) shows how the periodicity of the moiré pattern changes with twist angle between two identical 2D lattices. The moiré wavelength can be found using the equation:

$$\lambda = \frac{(1 + \delta)a}{\sqrt{2(1 + \delta)(1 - \cos \theta) + \delta^2}} \quad (1.4)$$

where $a$ is the lattice constant of one lattice, $\delta$ is the difference in lattice constant between the two lattices and $\theta$ is the twist angle [67]. These moiré patterns have been imaged for multiple combinations of 2D materials via scanning tunnelling microscopy [67, 68, 69, 70] and piezoresponse force microscopy (PFM) [71], a modified form of AFM.

The superimposing of the two periodic lattices creates a superlattice with a new larger unit cell, whose size depends on the twist angle and the lattice constants of the two interacting layers, making it possible to synthesize artificial lattices of any size. In reciprocal space, this leads to the formation of multiple mini-Brillouin zones, as illustrated in Fig. 1.11 b). The reciprocal lattice vector of the superlattice
is given by:

\[ \mathbf{G}_M = \mathbf{G}_1 - \mathbf{G}_2, \]

(1.5)

where \( \mathbf{G}_1 \) and \( \mathbf{G}_2 \) are the reciprocal lattice vectors of the two individual layers.

The primary band structure of the individual layers is folded by \( \mathbf{G}_M \) resulting in multiple replica bands present within the band structure. The intersection of the moiré-induced replica bands with the primary bands can open up energy gaps within the band structure, as first observed for misaligned graphene on hBN in scanning tunneling spectroscopy (STS) measurements [67] and transport measurements [72]. Via tuning the twist angle, it is possible to engineer hybridisation gaps in the superlattice’s band structure at chosen energies. For specific orientations, or ‘magic’ angles, these interactions have now been shown to give rise to new and exciting quantum phenomena, as discussed in the next section.

Moiré potentials also have promising applications in optoelectronic devices. The moiré potential between two semiconducting 2D materials can trap interlayer excitons, confining them to quantum-dot-like potentials [74], as illustrated by Fig. 1.12 a). Therefore, moiré excitons could be used to build single-photon emitter arrays for quantum communications [76].

Superlattices formed of monolayer semiconducting TMDs are of most interest for studying moiré excitons due to their spin-valley locking optical selection rules and their ability to form relatively strong moiré potentials of \( \sim 250 \) meV [75]. As in the case of interlayer excitons, moiré excitons are observed for superlattices with
Figure 1.12: a) Schematic of a moiré superlattice with a twist angle, $\theta$. Below, a schematic of an exciton trapped in a moiré potential well. Adapted from [74]. b) Reflection contrast spectra of a WSe$_2$/WS$_2$ heterobilayer at small and large twist angles. Peaks labelled I, II, III highlight the peaks due to the moiré excition states. c) Reflection contrast spectra of a WSe$_2$/WS$_2$ heterobilayer for different carrier concentrations. The number on the right of each spectrum defines the carrier concentration in e$^-$cm$^{-2}$. Adapted from [75].

twist angles close to alignment, as shown by the reflection contrast spectrum in Fig. 1.12 b) for a WSe$_2$/WS$_2$ heterobilayer. Additionally, the absorption energy of the moiré exciton can be controlled by doping the device [65, 75]. Fig. 1.12 c) shows how the energy of moiré exciton states change with increased carrier concentration for a WSe$_2$/WS$_2$ heterobilayer.

'Magic' angles

Twisted bilayer graphene (TBG) has been studied for more than 10 years, but in 2018 the field exploded with experiments by Pablo Jarillo-Herrero et al. showing superconductivity [77] and correlated insulator electronic states [78] at the 'magic' twist angle of 1.1° previously theoretically predicted by Rafi Bistritzer and Allan MacDonald in 2011 [79].

The lattice mismatch between two twisted graphene layers creates a moiré potential leading to hybridisation between the layers, which for small angles, results in flat bands close to the Fermi energy. These flat bands have a very high DOS,
Figure 1.13: a) A band structure schematic of the first mini Brillouin zone of the superlattice of TBG at a twist angle of 1.05°. To the right, a plot of the DOS for free-standing graphene (purple) and TBG (blue). b) Resistivity plots showing the superconducting and Mott insulating phases in TBG at two different twist angles close to the 'magic' angle. Taken from [77].

known as van Hove singularities (vHS) [80]. A band structure schematic of the mini Brillouin zone and a DOS plot for a TBG superlattice at a twist angle of 1.05° is shown in Fig. 1.13 a). At low temperature, different fractional fillings of the flat bands have shown phenomena such as Mott insulating states [78] and superconductivity [77], as shown by the two resistivity plots in Fig. 1.13 b) for two different twist angles close to the 'magic' angle.

Beyond TBG, systems such as twisted double-bilayer graphene [81, 82, 83], twisted monolayer-bilayer graphene [84, 85, 86], twisted trilayer graphene [87] and ABC-stacked trilayer graphene on hBN [88] are now being studied to further understand governing factors that are responsible for vHS and the quantum phenomena that appear as a result of engineered flat bands. As well as graphene systems, twisted TMD heterostructures, such as WSe$_2$/WS$_2$ [89, 90, 91] and twisted bilayer WSe$_2$ [92] are also being studied for their exotic quantum states that appear at specific twist angles. Compared to twisted graphene systems, twisted TMDs provide well isolated flat bands due to their gapped band structure, as well as, a reduced degeneracy of the moiré flat bands.
The advantage of some of these other systems, compared to TBG, is that they have ability to form flat bands over a wider range of angles [83, 86], making the fabrication of these devices easily repeatable.

Creating a moiré pattern between two 2D lattices does not always result in a moiré potential present between the layers. At large twist angles, the strength of the moiré potential decays due to weakened Coulomb interactions between the layers.

Other phenomena can also occur such as atomic reconstruction. The formation of different domains due to lattice reconstruction has been observed in scanning transmission electron microscopy measurements of twisted WS$_2$ and MoS$_2$ homobilayers [93] and commensurate-incommensurate transitions have been observed in graphene/hBN superlattices where, depending on the twist angle, the graphene stretches to adjust to the periodicity of the underlying hBN substrate [94].

1.7 Measuring the electronic structure of 2D heterostructures

To understand the origin of these quantum phenomena and to be able to exploit these twist-dependent quantum effects in future 2D devices, the electronic structure of 2D materials and their heterostructures needs to be well understood. Many techniques allow one to gain information of a material’s electronic band structure, such as transport measurements, optical spectroscopies, and STS. But only angle-resolved photoemission spectroscopy (ARPES) allows electronic states within a material to be directly visualised in both energy and momentum.

ARPES is a surface sensitive technique that can map the band structure of materials by collecting the photoemitted electrons from a sample surface. By measuring the kinetic energy and emission angle of the photoemitted electrons, a direct image of the filled electronic states in the material can be built up. The surface sensitivity of ARPES makes it ideal for the study of 2D materials and their heterostructures.

Graphene was the first 2D material to be extensively studied using ARPES. Fig. 1.14 a) and b) show high resolution ARPES spectra of graphene on SiC from a study by Bostwick et al. [95]. ARPES not only probes the single-particle dispersion but can also be a tool for studying correlated electron effects. In this study by Bostwick et al., ARPES was used to understand the quasi-particle dynamics in graphene with the aid of potassium doping. Doping the sample with an alkali
metal populates electronic states that would otherwise not be visible in ARPES spectra. Fig. 1.14 c) shows the ARPES spectra for increasing electron doping of graphene. Observed within the spectra, particularly Fig. 1.14 b), are replica graphene bands due to superlattice effects from the lattice mismatch of graphene and SiC. Superlattice effects in graphene were then further investigated using ARPES in other studies of graphene/SiC [96] and graphene/Ir [97].

Graphene is easily studied by many of the different ARPES techniques (see beginning of Chapter 2), as large domains can be grown via epitaxial techniques. ARPES typically has beam spot sizes of ~10-50 µm, too large for the study of mechanically exfoliated 2D materials. Therefore, ARPES is commonly used to study bulk crystals. The crystal is cleaved in vacuum prior to measurement to create a new clean surface. ARPES has been used to study black phosphorous [98], ferromagnetic
semiconductors such as CrGeTe$_3$ [99], and cuprate superconductors [100], allowing the study of many topological states in 3D crystals [101, 102].

The electronic topology of bulk semiconducting TMDs has also been studied using ARPES [103, 104, 105]. Alkali doping has been used to visualise the conduction band in ARPES measurements of bulk TMDs allowing the measurement of their band gaps [104] and carrier-induced renormalisation of their band structure [105]. Various other ARPES measurements of the wider TMD family have also been undertaken such as, the study of the orbital composition of the 1T phase of epitaxially grown ReSe$_2$ [106], the study of charge density waves (CDW) in cleaved NbSe$_3$ crystals [107] and epitaxially grown VSe$_2$ [108] and the observation of topological Fermi-arcs in cleaved WTe$_2$ crystals [109].

Advancements in the field of optics has now enabled the study of mechanically exfoliated 2D materials using ARPES with sub-micrometre spatial-resolution ($\mu$ARPES). Focusing optics are added to the path of the photon beam, which focuses the light down to spot sizes of a few micrometres or less (see Chapter 2). Over recent years, $\mu$ARPES has become a dominant technique in the study of the electronic properties of mechanically exfoliated 2D materials.

An example of one study that has been made possible by $\mu$ARPES is the observation of the layer-dependent band structure of PTMC InSe. The InSe heterostructure studied, built by mechanical exfoliation and the PMMA dry transfer technique, is shown schematically in Fig. 1.15 a). Fig. 1.15 b) shows the band structure of the monolayer InSe mapped by $\mu$ARPES, validating prior DFT predictions. Due to the high quality of the mechanically exfoliated 2D materials, the bands observed are sharp and the inverted ‘Mexican hat’ dispersion of the upper valence band around $\Gamma$ is clearly visible, Fig. 1.15 c). The InSe flake studied is shown in Fig. 1.15 d) and is formed of multiple micrometre scale regions with different numbers of layers. Using $\mu$ARPES, the band structure of each region can be measured individually, as shown by the $\mu$ARPES spectra of multiple regions in Fig. 1.15 e). Other layer dependent band structures have been visualised using $\mu$ARPES for MoS$_2$ [104] and WSe$_2$ [110].

Beyond the properties of the individual layers, interest is growing around the phenomena that can arise as a result of the interactions between different layers, as described in Section 1.6. $\mu$ARPES is capable of visualising these interactions within the electronic band structure of heterostructures. For example, interlayer hybridisation has been observed in $\mu$ARPES measurements of graphene/MoS$_2$ [111, 112], MoSe$_2$/WSe$_2$ [110] and MoS$_2$/WS$_2$ [113].

Replica bands due to a moiré potential have been reported in $\mu$ARPES mea-
Figure 1.15: a) Schematic of the InSe heterostructure studied by µARPES. b) µARPES energy-momentum slice of monolayer InSe in the high symmetry direction defined. Overlaid white and black dashed lines are the DFT calculated band structure of the valence and conduction band, respectively. The red dashed lines mark the graphene bands from the encapsulating graphene layer. c) Monolayer InSe upper valence band dispersion around Γ calculated by DFT. The experimental data from µARPES measurement is overlaid in the white dashed box. d) Optical image of the mechanically exfoliated InSe flake with the number of layers in each region defined by their optical contrast. The scale bar is 5 µm. e) µARPES energy-momentum slices around Γ for different regions of different thicknesses of the InSe flake. The overlaid white and black dashed lines are the DFT calculated band structure of the valence and conduction band, respectively. The scale bars are 0.2 Å⁻¹. Adapted from [40].

measurements of twisted graphene/WS₂ [114], twisted MoS₂/WS₂ [113] and twisted WS₂/WSe₂ heterobilayers [115]. Fig. 1.16 shows µARPES measurements acquired by Jones et al. for three twisted MoS₂/WS₂ heterobilayers, where replica bands are observed at the moiré vector of the superlattice. For an initial state effect, such as a moiré potential, the observation of hybridisation gaps between replica bands is required as evidence, as seen in the µARPES study of 30° misaligned TBG by Hamer et al. [116]. Replica bands can also be present within µARPES spectra due to final state effects, which can easily be misinterpreted as evidence of a moiré potential. This is further discussed in Chapter 4.

Alkali doping has been successful in studying carrier concentration dependent effects in 2D materials, such as observing the band gap renormalisation in WS₂
Figure 1.16: µARPES energy-momentum slices through twisted MoS$_2$/WS$_2$ heterobilayers with twist angles of a) 2°, b) 13° and c) 20°. The µARPES energy-momentum slices are taken in the direction of the black line in the Brillouin zone schematics. $G_m$ shows the moiré vector for each angle. The replica bands within the spectra are indicated by the orange and blue arrows. Taken from [113].

on hBN [117] and the tunable spin-splitting in WSe$_2$ [103], but it does have its disadvantages. The doping concentration and uniformity across the sample can be difficult to control and it can change the chemical nature of the material. To avoid these disadvantages, electrostatic gating via a back gate can be used to dope 2D materials instead [118, 119, 120]. This method of doping allows accurate control of the carrier concentration and does not distort the electronic spectrum of the material [118]. It has been used to determine the band gaps of the semiconducting monolayer, bilayer and trilayer TMDs and study carrier concentration renormalisation effects within WSe$_2$ [118].

Three-terminal 2D devices with a source, drain and back gate have now also been studied using µARPES allowing one to observe how the electronic bands behave when passing a current through the material, as in the case of an operating device [121, 122].

More recently, in-situ electrostatic gating during µARPES measurements has been used to study moiré systems, such as the electrical tunability of vHS formed in TBG [123]. The flat bands formed in 'magic' angle TBG have now also been directly visualised in µARPES studies by Lisi et al. [124] and Utama et al. [125].

1.8 Scope of Thesis

In this thesis, the electronic properties of 2D heterostructures and their interlayer interactions are studied using µARPES with the addition of in-situ electrostatic gating. Additionally, some of the challenges of interpreting features that resemble interlayer interactions in µARPES spectra are addressed. A brief overview of the
following chapters are as follows:

**Chapter 2** details photoemission theory including angular resolution and the ARPES spectral function. Following this, the experimental methods are described, which includes a description of synchrotron radiation and the µARPES beamline, SPECTROMICROSCOPY. Then follows details on how the experiments are performed, including in-situ electrostatic gating measurements and the sample preparation required.

**Chapter 3** describes a newly discovered twistronic effect observed in graphene/PTMC heterostructures, where strongly hybridised states outside the first Brillouin zone of the PTMC are scattered back into the first Brillouin zone via Umklapp scattering. The position of the strongly hybridised states in momentum and energy is shown to be controllable by tuning the twist angle between the layers.

**Chapter 4** identifies final state photoelectron diffraction in µARPES spectra of hBN/TMD heterostructures and discusses how final states effects can be distinguished from initial state effects such as a moiré potential.

**Chapter 5** studies band alignments in MoWSeS TMD heterobilayers with the addition of in-situ electrostatic gating. We determine band gaps and observe intralayer band gap renormalisation due to carrier concentration effects. Additionally, the determination of the Fermi energy, the position of the CBM and the Q-K band alignment in the conduction band for electron doped µARPES spectra are described.

**Chapter 6** studies partially graphene encapsulated WS₂/WSe₂ moiré superlattices using µARPES with in-situ electrostatic gating. We observe dispersion and moiré replica bands of the TMD heterobilayer CBM, as well as, moiré replica graphene Dirac cones displaced by the moiré vector of the underlying heterobilayer. Additionally, the challenges of resolving moiré replica bands in TMDs are described, along with final state photoelectron diffraction considerations.

**Chapter 7** concludes the findings of this thesis and discusses future projects that could be undertaken to resolve some of the open questions, moving forward the field of twist-dependent interlayer interactions in 2D devices.
Chapter 2

Methods

2.1 Angle-resolved photoemission spectroscopy

In this work, ARPES was used as the main measurement technique to study the electronic structure of 2D materials and their heterostructures. ARPES is a surface sensitive technique which uses the photoelectric effect, measuring the emission angle of the photoelectrons to probe the in-plane band structure of a material. ARPES is now widely used for studying electronic properties and has advanced many areas of research through the development of techniques such as spin-resolved ARPES, high-resolution ARPES, time-resolved ARPES and spatially-resolved ARPES (μARPES). For the study of 2D materials, μARPES is required due to the small lateral size of 2D flakes.

2.1.1 Photoemission spectroscopy

The photoelectric effect, the emission of electrons when light is incident on a material, was first discovered by Hertz in 1887 [126] and later explained by Einstein’s Noble Prize winning work in 1905. Since then, the photoelectric effect has been used to investigate the electronic structure of solids by applying the law of conservation of energy, as the kinetic energy of the photoemitted electron, $E_{\text{kin}}$, is characteristic of the binding energy of the electronic state within the material from which the photoelectron originated. The binding energy of the electronic state, $E_B$, can be determined using the photoemission equation,

$$E_{\text{kin}} = h\nu - \phi - |E_B| \ , \quad (2.1)$$
where $h$ is Planck’s constant, $\nu$ is the incident photon frequency and $\phi$ is the material’s work function. Fig. 2.1 shows how the measured photoemission spectrum is related to the energy of electronic states within a solid for an incident photon beam with energy $h\nu$.

2.1.2 Angular resolution

Combining the measured kinetic energy of the photoemitted electron with the angle the photoelectron is ejected from the sample surface allows the momentum dependent band structure of the material to be mapped. Fig. 2.2 shows the geometry of a typical ARPES experiment. When a photon beam of energy $h\nu$ is incident on a sample, electrons are emitted from the sample surface. The photoelectrons can be collected with an electron analyser at a particular emission angle $(\theta, \phi)$, where $\theta$ is the angle measured with respect to the surface normal and $\phi$ is the angle measured with respect to the $x$-direction. The in-plane momentum of the photoemitted electron is conserved in the photoemission process and therefore the crystal momentum
inside the solid can be determined using the equation,

$$\hbar k_\parallel = \sqrt{2mE_{\text{kin}}} \times \sin \theta,$$

(2.2)

where $k_\parallel = k_x + k_y$ is the in-plane momentum and $m$ is the mass of the electron. The momentum of the photoelectron perpendicular to the sample surface is not conserved in the photoemission process, therefore determining the momentum in the $z$-direction, $k_\perp = k_z$, is more complicated. Fortunately, for 2D materials $k_\perp$ is not required and the electronic dispersion, $E(k_\parallel)$, can easily be found.

2.1.3 Three-Step and One-Step model

Photoemission in ARPES experiments can be described in more detail by a Three-Step model or a One-Step model. The One-Step model combines the photon absorption, the photoelectron emission and the photoelectron detection in a single complex Hamiltonian. An illustration of the One-Step model is shown in the right diagram of Fig. 2.3. Due to the complexity of the Hamiltonian in the One-Step model, photoemission is generally described by the Three-step model and the sudden approximation which have been shown to be successful in describing the photoemission process, even though they are purely phenomenological.

The Three-Step model, as illustrated by the left diagram of Fig. 2.3, is made up of three stages:

1. The photoexcitation of an electron into an excited bulk state within the material
2. The excited electron travels to the surface of the material

3. The photoelectron escapes the sample surface into the vacuum

The product of the probabilities in all three stages gives the total ARPES intensity: the probability of photoexcitation, the probability of the electron scattering on the way to the surface and the probability the photoelectron will overcome the surface barrier potential.

Step 3 is simple and depends on whether the photoelectron has enough energy to overcome the material’s work function. Step 2, the probability of scattering, can be determined by the mean free path of the electron which depends strongly on the kinetic energy of the electron. Fig. 2.4 shows the universal curve for the inelastic mean free path of electrons in a solid. Step 1, the probability of photoexcitation, can be described by Fermi’s Golden rule:

$$\omega_{fi} = \frac{2\pi}{\hbar} |\langle \psi_f^N | H_{int} | \psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu),$$

(2.3)

where $\omega_{fi}$ is the transition probability of an optical excitation in a $N$-electron system from an initial ground state, $\psi_i^N$, to a final excited state, $\psi_f^N$, where $E_i^N = E_i^{N-1} - E_k$ and $E_f^N = E_f^{N-1} - E_{kin}$ are the initial and final state energies, respectively ($E_k$ is the binding energy of the photoelectron with momentum, $k$, and kinetic energy, $E_{kin}$). $H_{int}$ is the perturbation Hamiltonian describing the electron-photon interaction and
can be written as:

\[ H_{int} = \frac{e^2}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} , \]  

(2.4)

where \( \mathbf{p} = i \hbar \nabla \) is the electronic momentum operator and \( \mathbf{A} \) is the electromagnetic vector potential. Here, the commutator relation and the dipole approximation can be used [100, 129].

The initial and final electronic states can be written in terms of the wave function of the photoelectron with momentum \( k, \phi^k \), and the wavefunction of the (N-1) electron system after photoemission, \( \psi^{N-1} \):

\[ \psi^N_i = A\phi^k_i \psi^{N-1}_i \quad \text{and} \quad \psi^N_f = A\phi^k_f \psi^{N-1}_f , \]

(2.5)

respectively, where \( A \) is the antisymmetric operator satisfying the Pauli principle. In doing so, we use the sudden approximation. We assume the photoelectron is removed instantaneously from the system with no interactions. This approximation is valid for high energy photoelectrons, as in the case of ARPES experiments. Defining the initial and final electron states in this way, allows the matrix element in equation 2.3 to be expressed as:

\[ \langle \psi^N_f | H_{int} | \psi^N_i \rangle = \langle \phi^k_f | H_{int} | \phi^k_i \rangle \langle \psi^{N-1}_m | \psi^{N-1}_i \rangle , \]

(2.6)

where \( \langle \phi^k_f | H_{int} | \phi^k_i \rangle = M^k_{fi} \) is the one-electron matrix element. The matrix element depends on the electron’s momentum and the energy and polarisation of the incident photon beam used in the ARPES experiment. On the right-hand side of equation
2.6. $\psi_f^{N-1}$ has been replaced by $\psi_m^{N-1}$, where $m$ represents all possible excited states.

The total ARPES photoemission intensity can then be expressed as:

$$I(E_{kin}, k) = \sum_{f,i} |M_{f,i}^k|^2 \sum_{m} |c_{m,i}|^2 \delta(E_{kin} + E_m^{N-1} - E_i^{N-1} - h\nu) ,$$  \hspace{1cm} (2.7)

where $|c_{m,i}|^2 = \langle \psi_m^{N-1} | \psi_i^{N-1} \rangle$ is the probability an electron in state $\psi_i^{N}$ will be excited into the electronic state $\psi_m^{N-1}$. For a non-interacting electron system, there is only one $m$ for which $|c_{m,i}|^2 = 1$, which corresponds to the Koopman’s energy.

### 2.1.4 Single particle spectral function

For an interacting many-body system, $|c_{m,i}|^2$ can take on many values [100, 129].

The propagation of an electron in a many-body system can be described by a Green’s function [100, 129]. Using the Green’s function approach, the total ARPES photoemission intensity can be expressed as:

$$I(k,\omega) = I_0(k,\nu, A)f(\omega)A(k,\omega) ,$$  \hspace{1cm} (2.8)

where $I_0(k,\nu, A) \sim |M_{f,i}^k|^2$ and $f(\omega) = (e^{\hbar\omega/k_B T} + 1)^{-1}$ is the Fermi-Dirac distribution, as only populated electronics states contribute to the photoemission intensity. $A(k,\omega)$ is the single particle spectral function which now has a finite spread in energy and can be written as a function of momentum, $k$, and energy, $\omega$:

$$A(k,\omega) = -\frac{1}{\pi} \frac{\sum''(k,\omega)}{\omega - \epsilon_k - \sum'(k,\omega) + i \sum''(k,\omega)} ,$$  \hspace{1cm} (2.9)

where $\epsilon_k$ is the band energy and the self energy $\sum(k,\omega) = \sum'(k,\omega) + i \sum''(k,\omega)$ contains all the information on the interactions within the system including energy renormalisation and lifetime broadening, resulting in the ARPES spectra containing peaks of finite width that can be described by a Lorentzian function.

In practise, the peaks observed in ARPES spectra are additionally broadened by the convolution of a Gaussian function due to temperature vibrations, sample disorder, and instrumentation resolution.
2.2 Spatially-resolved angle-resolved photoemission spectroscopy

2.2.1 Synchrotron radiation

ARPES experiments require photon energies in the ultraviolet to soft x-ray range (5-200 eV). Light sources used for ARPES experiments can be gas-discharge lamps, lasers or synchrotron radiation. The use of synchrotron radiation has several advantages: a wide range of photon energies, coherent, high flux, and variable polarisation.

To produce synchrotron radiation, electrons are accelerated to relativistic speeds and forced to change direction, emitting electromagnetic waves perpendicular to their motion, known as synchrotron radiation. To generate this type of radiation, large circular accelerators are required, known as synchrotrons. As illustrated in Fig. 2.5 a) a synchrotron is built up of a linear accelerator (linac), booster ring, storage ring and many experimental beamlines. The electrons are accelerated from the linac into the booster ring where they gain energy from MeV to GeV, before being released into the storage ring. The electrons travel at the 99.9% the speed of light and their path is controlled by a series of magnets.

Once inside the storage ring, electrons are accelerated through bending magnets and insertion devices designed to create electromagnetic waves. Fig. 2.5 b) shows a simplified schematic of a typical storage ring. The electrons regain their energy lost via emitting radiation by passing through a radio frequency (RF) cavity. Insertion devices can be wigglers or undulators and have a significantly higher brilliance than bending magnets [130].

ARPES experiments are performed with light created by undulators. Undu-
Undulators consist of a series of many short magnets which cause the electrons passing through them to oscillate, producing coherent light due to the interference of the generated photons. Wigglers are very similar to undulators, however, have a much wider photon energy range and lower brilliance due to larger electron oscillations.

The photon beams generated from the bending magnets and insertion devices are passed down the beamlines to experimental end stations through a series of focusing optics and monochromators where the light is then used to perform many different spectroscopic experiments. Typical photon beam spot sizes range from $\sim 10-100 \, \mu m^2$. For the study of 2D heterostructures fabricated by mechanical exfoliation, beam spot sizes for ARPES beamlines are require to be $\leq 5 \, \mu m^2$, therefore additional focusing optics are required to improve the spatial resolution.

### 2.2.2 Spatial resolution

To perform $\mu$ARPES measurements, focusing optics such as a Schwarzschild objective, Fresnel zone plate or x-ray capillary mirror are inserted into the path of the photon beam just before illumination of the sample.

A Schwarzschild objective is built up of two concentric spherical mirrors, as shown in Fig. 2.6 a). The mirrors are separated by twice the system’s focal length and are capable of focusing the photon beam to spot sizes of $\sim 600 \, nm$ [132] while retaining $\sim 10\%$ of the initial photon flux [133]. The main limitation of using a Schwarzschild objective is that it has no beam energy tunability, as each objective is set-up for focusing a single beam energy. In order to change photon energy, one must change objectives which is a significantly time consuming process.

A Fresnel zone plate has beam energy tunability. A zone plate is a circular diffraction grating made up of alternating transparent and opaque rings, as shown...
Table 2.1: Spatial resolutions of µARPES beamlines at synchrotron facilities. For beamlines with multiple focusing optics/end stations each spatial resolution is listed. SO stands for Schwarzschild objective, ZP stands for zone plate and CM stands for capillary mirror. Spatial resolutions are found from beamline publications [132, 134, 135, 136].

<table>
<thead>
<tr>
<th>Synchrotron</th>
<th>µARPES beamline</th>
<th>Spatial resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLS (UK)</td>
<td>I05</td>
<td>400 nm (ZP) 5 µm (CM)</td>
</tr>
<tr>
<td>ALS (USA)</td>
<td>Maestro</td>
<td>120 nm (ZP) &lt;10 µm (CM)</td>
</tr>
<tr>
<td>Soleil (France)</td>
<td>ANTARES</td>
<td>30 nm (ZP)</td>
</tr>
<tr>
<td>Elettra (Italy)</td>
<td>SPECTROMICROSCOPY</td>
<td>600 nm (SO)</td>
</tr>
</tbody>
</table>

in Fig. 2.6 b). The spatial resolution is diffraction limited and depends on the photon energy. Typical spatial resolutions achieved vary between ~100-400 nm [134, 135], smaller than that achieved by a Schwarzschild objective, however, the final photon flux is also significantly reduced to ~1% of the initial photon flux [133, 136]. Therefore, µARPES measurements require longer measurement times and features within the band structure with very weak photoemission intensity are less likely to be observed.

More recently, µARPES beamlines are upgrading their focusing optics to x-ray capillary mirrors. Two of the leading µARPES beamlines, I05 at Diamond Light Source (DLS), UK, and Maestro at Advanced Light Source (ALS), Berkeley, have recently installed capillary mirrors on their µARPES beamlines. The advantage of using a capillary mirror is that you significantly increase the final photon flux to ~60% of the initial photon flux while still being able to tune photon energies and achieve the required beam spot sizes [133]. X-ray capillary mirrors are made of a reflective surface in the shape of an ellipsoid with a central stop to remove x-rays that will not be reflected and focused, as shown in Fig 2.6 c). Currently, beam spot sizes of 250 nm have been achieved [136], and with further manufacturing advancements the spatial resolution is expected to drop to around 50-100 nm in the future [133].

A table of µARPES beamlines and their current focusing optics with their corresponding spatial resolutions are listed in Table 2.1.

2.2.3 SPECTROMICROSCOPY, Elettra

All µARPES measurements presented in this thesis were performed at the SPECTROMICROSCOPY beamline, Elettra synchrotron, Italy [132]. A photograph of the beamline can be seen in Fig. 2.7 a). The beamline is comprised of multiple focusing mirrors and a monochromator, as shown by the schematic in Fig. 2.7 b). A Schwarzschild objective is used to focus the photon beam onto the sample. Two
Schwarzschild objectives are available, optimised for beam energies 27 and 74 eV. All µARPES measurements in this thesis were performed with a beam energy of 27 eV, as lower photon energies provide a higher cross-section for the TMDs and PTMCs. At 27 eV the photon flux incident on the sample was \( \sim 2 \times 10^{10} \) photons per second.

µARPES measurements are performed in ultra high vacuum (UHV) and the pressure inside the measurement chamber for all experiments was \( \sim 10^{-10} \) mbar. Fig. 2.7 c) shows a schematic of all the instruments inside the end measurement chamber, which include the Schwarzschild objective, a moveable sample stage, a cryostat and a hemispherical electron analyser. The electron analyser is mounted on a two-axis goniometer inside the measurement chamber and collects the photoemitted electrons from the sample. The electron analyser is significantly smaller than the typical analysers installed on other µARPES beamlines, which are commonly mounted outside the of the vacuum chamber.

A hemispherical electron analyser is formed of two-concentric hemispherical electrodes that bend the trajectory of the photoelectrons. The trajectory of the photoelectron through the hemisphere is different for different photoelectron kinetic energies and as a result they fall at different positions on the detector. Two parameters, the centre energy and the pass energy, are used to control the range of kinetic energies detected. The centre energy is equal to the original kinetic energy of the photoelectron from the sample that travels in a perfect circular path through
Figure 2.8: a) A schematic of the 2D detector image, where $\nu$ is the detector angle and $E_{\text{kin}}$ is electron kinetic energy. b) A diagram of the hemispherical analyser mounted on the two-axis goniometer. The analyser can be rotated in $P$ and $T$, where $(P, T) = (90^\circ, 0^\circ)$ measures the photoelectrons emitted normal to the sample surface.

The detector is two-dimensional, collecting photoelectrons as a function of kinetic energy and detector angle, $\nu$. A schematic of the 2D detector image is shown in Fig. 2.8 a). The angular resolution of the 2D detector is 0.3°, which is roughly equivalent to 0.03 Å⁻¹ at 27 eV, and it has an angular acceptance of ± 8°.

The hemispherical electron analyser can be rotated around the sample using the two-axis goniometer on which it is mounted. The angular geometry is not a standard coordinate system and is defined by angles $P$ and $T$. A diagram of the analyser and goniometer is shown in Fig. 2.8 b) where $P$ and $T$ are defined. At $(P, T) = (90^\circ, 0^\circ)$ photoelectrons emitted normal to a flat sample surface are collected by the electron analyser. $P$ and $T$ have angular ranges of 92 to 45° and -2 to 50°, respectively, which is equivalent to covering a momentum range of -0.1 to 1.3 Å⁻¹ in $k_x$ and -0.3 to 1.6 Å⁻¹ in $k_y$ at a photon energy of 27 eV.
Figure 2.9: a) and b) µARPES energy-momentum slice of a hBN/bilayer WSe$_2$ heterostructure, k-warped using equations 2.10 and 2.11 and equations 2.12 and 2.13, respectively. All photoemission intensities are displayed using a logarithmic intensity scale and all scale bars are 0.2 Å$^{-1}$.

Due to the unconventional coordinate system the equations required to convert kinetic energy and angle into in-plane momentum, a process commonly referred to as k-warping, are:

$$k_x = \frac{\sqrt{2mE_{kin}}}{\hbar} \left[ \cos(T) \left[ \cos(v) \sin(-t) + \cos(-p) \cos(-t) \sin(v) \right] + \sin(T) \left[ -\cos(-t) \sin(-p) \sin(P) + \cos(P) \left[ \cos(-p) \cos(-t) \cos(v) - \sin(-t) \sin(v) \right] \right] \right]$$ (2.10)

and

$$k_y = \frac{\sqrt{2mE_{kin}}}{\hbar} \left[ \cos(P) \cos(-t) \sin(-p) + \sin(P) \left[ \cos(-p) \cos(-t) \cos(v) - \sin(-t) \sin(v) \right] \right]$$ (2.11),

where $p$ and $t$ are the angle of $\Gamma$ for the sample with respect to $(P, T) = (90^\circ, 0^\circ)$. The angles $p$ and $t$ are required as the sample is usually mounted at a small angle relative to the expected normal causing the normal emission to be a few degrees away from the expected detector position $(P, T) = (90^\circ, 0^\circ)$. Note, for equations 2.10 and 2.11 $P$ has been redefined as $90 - P$. These equations are complex and, if required, can be approximated to:

$$k_x = \frac{\sqrt{2mE_{kin}}}{\hbar} \left[ \cos(P - p) \cos(v) \sin(T - t) + \cos(T - t) \sin v \right]$$ (2.12)
Figure 2.10: a) and b) Optical and SPEM image of a partially graphene and monolayer hBN encapsulated monolayer WSe$_2$ heterostructure. The scale bar is 5 µm. c) µARPES constant energy map at a binding energy of 1.1 eV taken at the position on the sample indicated by the black circle in b). d) µARPES energy-momentum slice in the direction of the black arrow in c). Photoemission intensities in c) and d) are displayed using a logarithmic intensity scale and scale bars are 0.2 Å$^{-1}$.

Using the approximated k-warping equations gives a good approximation when mapping the band structure over a small range of angles. When mapping a large angular range the full k-warping equations should be used, otherwise the processed spectra can contain artefacts of the processing procedure, as highlighted in the red circles in Fig. 2.9.

To begin each experiment, the sample is imaged using scanning photoemission spectroscopy (SPEM) to locate the region of interest. By scanning the moveable sample stage in the x- and y- directions, the photoemission intensity is recorded across multiple positions on the sample, at a given kinetic energy range and emission angle $(P, T)$. Each pixel of the image is given by the integrated photoemission intensity across the detector. The integrated photoemission intensity will be different for different materials due to their different electronic structures, giving contrast in the image. By comparing the SPEM image to optical images of the sample, the region of interest can be located. Fig. 2.10 a) and b) show an example of an optical image and a SPEM image, respectively, for a partially encapsulated graphene/monolayer hBN/monolayer WSe$_2$ heterostructure with the different 2D flakes outlined. The photon beam can then be focused onto the region of interest to perform µARPES experiments.

µARPES measurements are performed by collecting multiple detector images in a series of closely spaced angles of $P$ and $T$, which can be then be stitched together.
Figure 2.11: a) Schematic of 2D heterostructure device. b) Image of the silicon chip mounted in a chip carrier. c) Image of the chip carrier mounted on a beamline sample plate with electrical contacts. d) and e) Optical and SPEM images of the sample, respectively. The scale bar is 50 µm. f) µARPES energy-momentum slices at three different gate voltages, taken around the graphene $K$ point. The scale bars are 0.2 Å$^{-1}$. Adapted from [118].

to create a 3D dataset, $I(E_{kin},k_x,k_y)$, mapping the materials band structure. ARPES spectra are then usually presented in the form of constant energy maps, $I(k_x,k_y)$, and energy-momentum slices, $I(E,k_{||})$, with energy scales converted into binding energy. A µARPES constant energy map of the hBN/WSe$_2$ region of the heterostructure is shown in Fig 2.10 c) at a binding energy of 1.1 eV and a µARPES energy-momentum slice is extracted by interpolating between detector images and is shown in Fig. 2.10 d) for the direction of the black arrow in Fig. 2.10 c).

### 2.3 In-situ electrostatic gating

In-situ electrostatic gating during µARPES measurements of 2D heterostructures on the SPECTROMICROSCOPY beamline has only recently been realised [118, 120]. A schematic of a typical heterostructure for electrostatically doping graphene can be seen in Fig. 2.11 a). Graphene is stacked on a 5-20 nm thick hBN dielectric on graphite and encapsulated in monolayer hBN. The heterostructure is positioned between two, 30 nm thick, Pt/Ti electrodes on a SiO$_2$/Si substrate, deposited using laser lithography and sputter coating. The graphite acts as a back gate and is in contact with the small Pt/Ti electrode. The graphene is in contact with the large
Pt/Ti electrode which is grounded. As seen in Fig. 2.11 b), the large electrode covers most of the silicon chip to minimise electrostatic distortion of the ARPES spectrum when a gate voltage is applied. The silicon chip is then mounted into a chip carrier using silver epoxy. Each Pt/Ti electrode is gold-wire-bonded to a leg of the chip carrier.

The chip carrier is mounted onto beamline sample plates with electrical contacts, as shown in Fig. 2.11 c). The back of the chip carrier is insulating and glued with epoxy onto a riser. Copper wire is wrapped around the legs of the chip carrier that are in contact with the Pt/Ti electrodes and fixed with silver epoxy. The other end of the wires are connected to contact pins at the bottom of the sample plate and are positioned so that they are isolated from the rest of the plate. It is important that the Pt/Ti electrodes on the silicon chip are only in contact with the copper pins at the bottom of the sample plate. The contact pins make an electrical connection when inserted into the sample holder inside the measurement chamber. At SPECTROMICROSCOPY, a Keithley 487 Picoammeter is used to supply a gate voltage to the small Pt/Ti electrode and measure the current through the large Pt/Ti electrode.

The electrode design makes it easy to locate the heterostructure using SPEM, as shown by the optical and SPEM images in Fig. 2.11 d) and e), respectively. A gate voltage applied to the graphite back-gate uniformly shifts the electronic bands of the graphene with no distortions to the electronic spectrum, as shown in Fig. 2.11 f) by μARPES energy-momentum slices around the graphene Dirac cone at different gate voltages [118].

### 2.4 Sample preparation

The samples used in this thesis were fabricated using the mechanical exfoliation and dry transfer techniques outlined in Section 1.5. The graphene/PTMC samples studied in Chapter 3 were fabricated by Matthew Hamer from Roman Gorbachev’s group at the National Graphene Institute and the hBN/TMD and gated TMD heterobilayer samples studied in Chapters 4-6 were fabricated by Paul Nguyen and Heonjoon Park from David Cobden and Xiaodong Xu’s group at the University of Washington. Heterostructures that did not require gated measurements were often transferred onto silicon chips with patterned electrodes to aid the finding of the heterostructure in SPEM images.

μARPES measurements require extremely clean samples. As part of the fabrication process samples are annealed and AFM cleaned prior to arriving at
the synchrotron for μARPES measurements to remove any surface and interlayer contaminants. Samples are then annealed again in UHV on the beamline to higher temperatures to remove any surface contaminants that have been absorbed while being transported in air.

Ungated samples can either be mounted onto the beamline’s sample plates using conductive silver epoxy or spot welding, as shown in Fig. 2.12 a) and b), respectively. Samples mounted using the conductive silver epoxy require significantly longer annealing times, therefore, it is preferable to mount samples with spot welding if possible. When heated to high temperatures (300-400°C), the epoxy out-gasses, increasing the pressure inside the beamline’s preparation chamber. It is important during the annealing process that the pressure remains low, $10^{-9}$ mbar, to prevent particles reacting with the sample surface at high temperature.

To achieve the highest level of cleanliness, samples were heated slowly to their target temperature, keeping the pressure inside the preparation chamber $<9 \times 10^{-9}$ mbar. The graphene/PTMC samples were heated to $\sim350^\circ$C for $\sim6$ hours and the hBN/TMD samples were heated to $\sim400^\circ$C for $\sim4$ hours. Encapsulating semiconducting 2D materials in hBN or graphene allows samples to be heated to higher temperatures for longer as the encapsulating layer protects the lower layer from over-annealing. Graphene can also withstand much higher annealing temperatures. The gated TMD heterobilayer samples were heated to $\sim400^\circ$C and left overnight for $\sim12$ hours. Due to the large size of the sample and the use of epoxy glue, gated samples require a much longer annealing time.

The heating element in the preparation chamber is attached to the back of the sample plate and the temperature is measured by a thermocouple attached to the front of the plate close to, but not in direct contact with, the sample. Therefore, the temperature of the sample is not well known and is likely to be slightly different than the temperature recorded by the thermocouple.
We found allowing the preparation chamber to return to base pressure before beginning to slowly cool the samples back down gave the best results. Once samples had cooled to temperatures of <100 K they were transferred to the measurement chamber to perform µARPES experiments.

The annealing target temperature, duration, pressure, heating rate and cooling rate are all critical to achieve high quality, clean, samples required for µARPES measurements. Advances in sample preparation have led to new experiments being possible, such as the results presented in this thesis.
Chapter 3

Interlayer Umklapp scattering in 2D heterostructures

3.1 Introduction

The twist angle has become an exciting new degree of freedom unique to 2D heterostructures, capable of controlling the interlayer coupling. Due to the close proximity of out-of-plane orbitals in 2D heterostructures, electrons from one layer can undergo tunneling to adjacent layers and the twist angle can be used to enhance tunneling between the two consecutive layers [60, 137]. This enhancement, referred to as resonant interlayer tunneling, occurs when electronic bands from adjacent layers intersect in energy and momentum, often leading to phenomena such as avoided crossings and vHIS in the band structure. These phenomena can result in new emerging properties such as superconductivity [77, 78, 138] and other strong electron-electron correlations [77, 139, 140], which may then be exploited for future twistronic devices.

To study interlayer interactions, samples require atomically clean interfaces [29, 141, 142]. As μARPES measurements require extremely clean samples, hybridisation between layers can be observed within μARPES spectra of 2D heterostructures. TBG [124, 125], graphene on single-crystal metal substrates [97, 143] and graphene on the TMD’s MoS$_2$ [111, 112] and WSe$_2$ [110] have all exhibited evidence of resonant interlayer hybridisation in μARPES spectra of their band structures. However, it has only ever been observed at positions in energy and momentum where two electronic bands in the band structure intersect.

As described by Bloch’s theorem [144], all electronic states can be described within the first Brillouin zone. Any wave vector which falls outside the first Brillouin zone can also be described by a wave vector within the first Brillouin zone,
Figure 3.1: a) Illustration of the graphene/monolayer InSe heterostructure. b) Atomic structure schematic of the relative orientation of the graphene and InSe layers. The orientation of the lattices was confirmed by the µLEED pattern in c). d) Optical, e) SPEM and f) LEEM images of the sample respectively, with the monolayer InSe flake outlined in red. All scale bars are 5 µm. Red circles in e) and f) mark the position on the sample the µARPES and µLEED measurements were made, respectively.

satisfying the conversation of momentum for large momentum transfers in a crystal. This transformation, named Umklapp scattering by Peierls in 1935 [145], has been important for describing many fundamental properties of materials, such as the thermal conductivity of metals. More recently for 2D materials, Umklapp scattering has been essential for understanding optical transitions of moiré excitons in TMD heterobilayers [73] and electron kinetics in graphene/hBN superlattices [146].

This chapter will demonstrate how resonant interlayer hybridisation combined with interlayer Umklapp scattering can be used as a new band structure engineering tool to modify the electronic structure of highly incommensurate 2D heterostructures.
3.2 Results and Discussion

3.2.1 Sample structure

A mechanically exfoliated 2D heterostructure of graphene on monolayer InSe was fabricated by Matthew Hamer at the University of Manchester, using the PMMA dry transfer technique [51, 52]. A schematic of the heterostructure is shown in Fig. 3.1 a). The graphene and InSe layers were stacked onto graphite which was placed on a Ti/Pt-coated n-doped Si substrate in order to dissipate photocurrent during µARPES measurements [110].

Fig. 3.1 b) illustrates the crystallographic orientation of the graphene relative to the InSe, which was determined from the electron diffraction pattern shown in Fig. 3.1 c). Low energy electron diffraction measurements with micrometre spatial resolution (µLEED) were performed at the Nanospectroscopy beamline [147], Elettra synchrotron, by beamline scientists Alexei Barinov, Andrea Locatelli and Francesca Genuzio. An illuminating limiting aperture was inserted into the path of the electron beam to create a spot-size on the sample of 500 nm. Fig. 3.1 c) is an average of multiple electron diffraction patterns collected over the incident electron energy range of 30-60 eV in steps of 2 eV. First order diffraction spots are seen for only the graphene and InSe layers and the twist angle between the graphene and InSe was found to be 22.3° ± 0.6°. More details on how the twist angle is determined from the µLEED pattern can be found in Section 4.2.2.

Fig. 3.1 d), e) and f) show optical, SPEM and low energy electron microscopy (LEEM) images of the sample respectively, with the monolayer InSe flake outlined in red. The flake was approximately 25 µm in length and 5-10 µm in width. Acquiring the SPEM and LEEM images allowed the µARPES and µLEED measurements to be obtained at approximately the same position on the InSe flake. The hollow red circle in Fig. 3.1 e) and f) show the position the µARPES and µLEED measurements were taken respectively.

3.2.2 Formation of ‘ghost’ anti-crossings

A µARPES energy-momentum slice along the high symmetry direction Γ-K_Gr and 3D schematic of the graphene/monolayer InSe valence band structure are shown in Fig. 3.2. The µARPES measurements were performed with a photon energy of 27 eV and an acquisition temperature of 100 K. InSe has an in-plane lattice constant, a_{InSe}, of 4.00 Å [148], approximately 60% larger than the lattice constant of graphene, a_{Gr} = 2.46 Å. Due to the large difference in lattice constant, graphene’s Brillouin zone is approximately twice the size of InSe’s. Therefore the Dirac cones at
Figure 3.2: a) µARPES energy-momentum slice of graphene/monolayer InSe between high symmetry points $\Gamma$ and $K_{Gr}$. Right-hand side is the mirrored double-differential with respect to energy of the left-hand side. Overlaid on the left are the DFT calculated bands of isolated monolayer InSe (blue) and tight-binding model for the $\pi$ band of graphene (red) using the parameters $t$ and $t'$ equal to -3.2 and 0.0 eV [23]. The InSe Brillouin zone boundary is marked by the blue vertical line. Folding the graphene $\pi$ band into the first Brillouin zone of InSe gives the black dashed line, labeled ‘ghost’ graphene. The position of anti-crossings seen in the spectra are highlighted in the black and purple boxes. The scale bar is 0.5 Å$^{-1}$. b) 3D representation of the graphene and InSe valence band structure. The graphene and InSe Brillouin zones are shown by the black and blue hexagons respectively. The grey box shows the region measured in a). The red lines around each graphene Dirac cone show the shape of the intersection with the InSe upper valence band and the red arrow represents a folding of the anti-crossing at the band intersection into the InSe 1st Brillouin zone.
Figure 3.3: a) LS-DFT calculation of a graphene/monolayer InSe heterostructure, with a twist angle of 23°, in the \( \Gamma-K_{Gr} \) direction. The black and purple boxes highlight the anti-crossings observed in Fig. 3.2 a). b) and c) LS-DFT calculations of isolated graphene and monolayer InSe, respectively, in the same directions as a). The blue vertical line shows the InSe Brillouin zone boundary. All scale bars are 0.5 Å⁻¹.

the corners of graphene’s Brillouin zone fall around the centre of the second Brillouin zone of InSe. The graphene and InSe layers are weakly interacting, therefore, for the most part, the individual electronic structures for each layer are retained as expected for the isolated monolayers. Overlaid on the left of Fig 3.2 a) in blue is a DFT calculation of the isolated monolayer InSe band structure, performed by Viktor Zólyomi (University of Manchester) and in red a tight-binding model approximation of the graphene \( \pi \) band. The dispersion of the upper valence band of monolayer InSe is shaped as an inverted ‘Mexican hat’ around \( \Gamma \) [40], shown by the 3D band schematic in Fig. 3.2 b). At the Brillouin zone corners, the dispersion drops to higher binding energies, unlike the band structure of graphene [23]. See Sections 1.2 and 1.4.2.

Careful inspection of the band structure reveals anti-crossings where the graphene \( \pi \) band intersects the InSe upper valence band outside the first Brillouin zone of InSe, see purple box in Fig. 3.2 a). Within the first Brillouin zone of InSe, within a few electron volts below the Fermi energy, there are no band crossings between the graphene and InSe valence bands, independent of their relative orientation. However, a feature that resembles an anti-crossing is observed near the VBM of InSe, see black box in Fig. 3.2 a), despite there being no graphene bands at those
Figure 3.4: a) µARPES constant energy map of the InSe upper valence band in the first Brillouin zone. The binding energy is defined in top right corner. The black dashed box shows the region of momentum space probed by experiment. The colour scale shows the normalised photoemission intensity (arbitrary units). b) Energy contour plot of Fig 3.2 b). The graphene and InSe Brillouin zones are the black and blue hexagons respectively. The angle between lattices is defined in the top left corner. The shape of the intersection between the graphene Dirac cone and upper valence band of InSe is shown in the 3D band schematic in the bottom right corner. The position of the anti-crossings are marked by the red lines on the contour plot.

energy and momenta. This ‘ghost’ anti-crossing seen within the first Brillouin zone appears at a position which corresponds to the intersection of the InSe upper valence band and the graphene π band when graphene’s band structure is folded into the reduced zone scheme of InSe, as shown by the black dashed ‘ghost’ graphene band in Fig 3.2 a).

The same ‘ghost’ anti-crossing can be seen in linear-scaling DFT (LS-DFT) calculations [149, 150], performed by Nicholas Hine’s group (University of Warwick), Fig 3.3. These show that the anti-crossings are not an artefact of the photoelectron emission measurement and are, in fact, an intrinsic feature of the electronic structure of the stack. Fig. 3.3 a) shows the calculated band structure for graphene/monolayer InSe with a similar twist angle of 23°. The anti-crossings highlighted in the black and purple boxes correspond to the anti-crossings observed in the µARPES spectra in Fig. 3.2 a). Multiple other anti-crossings are also observed within the LS-DFT calculation which are not visible in the µARPES spectra, due to the weak photoe-
mission intensity of the higher binding energy InSe bands. Fig 3.3 b) and c) show the calculated band structure of isolated graphene and isolated monolayer InSe confirming these features are not present within the isolated layers.

The ‘ghost’ anti-crossing is a result of interlayer Umklapp scattering. The graphene $\pi$ band is Umklapp scattered by the InSe reciprocal lattice vector, $g_{\text{InSe}}$, and hybridises with the InSe upper valence band to create the ‘ghost’ anti-crossing. The anti-crossing state is not localised to an individual layer but hybridised across the two layers. The wave vector of a ‘ghost’ anti-crossing in the first Brillouin zone of InSe, $k_1$, is related to the wave vector of an anti-crossing outside the first Brillouin zone, $k_2$, by the Umklapp condition,

$$k_1 = k_2 - g_{\text{InSe}}.$$  \hfill (3.1)

This relationship is different to the scattering caused by a moiré potential. A moiré potential translates electronic states by the difference in the reciprocal lattice vectors.
of two interacting layers. Here, the hybridised electronic state is scattered only by the InSe reciprocal lattice vector. No moiré superlattice effects were observed within this heterostructure, as expected for the large difference in lattice constant and the large twist angle between the layers.

The nature of the interlayer Umklapp scattering is more apparent when looking across momentum space. A µARPES constant energy map of the InSe upper valence band in the first Brillouin zone is plotted in momentum space at a binding energy of 2.2 eV in Fig 3.4 a). The hybridisation gaps within the spectra form spiral patterns. The origin of this spiral pattern is described by the contour plot in Fig 3.4 b). All contour energy maps and 3D band schematics in this chapter were created by Johanna Zultak (University of Manchester). As illustrated by the 3D schematic in the bottom right-hand corner of Fig 3.4 b), the shape of the intersection between the InSe upper valence band and the graphene Dirac cone is shown by the red lines in the contour plot of Fig 3.4 b). The thickness of the red line represents the magnitude of the interlayer hybridisation factor and the darker the colour red indicates a lower binding energy of the anti-crossing within the band structure. The anti-crossings created at the intersections are then propagated back into the first InSe Brillouin zone by $g_{\text{InSe}}$. This happens around all six corners of the graphene Brillouin zone creating a 6-fold spiral pattern of hybridisation gaps within the first InSe Brillouin zone, as observed in the µARPES constant energy map.

The image processing of Fig 3.4 a) is detailed in Fig 3.5. The raw data

Figure 3.6: Top row, µARPES constant energy maps at the binding energies (eV) defined in bottom right corner. Black dashed box shows the region of momentum space data was collected over. Underneath, corresponding LS-DFT calculated spectra.
collected is shown in Fig 3.5 a). The data was averaged over 0.1 eV to reduce the noise in the spectra, Fig 3.5 b), and rotated by multiples of 60° to correspond with the 6-fold symmetry of the superlattice. Each image was stacked on top of one another in the order shown by Fig 3.5 c) and any overlapping data points were then averaged to smooth the final image, giving the result shown in Fig 3.5 d). This method of image processing was adopted because the full Brillouin zone could not be probed with the angular range available at the SPECTROMICROSCOPY beamline. Fig 3.4 a) is the same as Fig 3.5 d) in a different colour scheme but rotated so that \( k_x \) and \( k_y \) lie along the same plane within reciprocal space as the energy contour map.

Fig 3.6 shows how the shape of the anti-crossings within the first InSe Brillouin zone change with binding energy. The top row of images show the collected \( \mu \)ARPES spectra for increasing binding energy. The corresponding LS-DFT calculated spectra are shown below each image. There is good qualitative agreement between the experimental and calculated results.

Previously, Umklapp scattering of electronic states has been observed for TBG [151] and other materials such as NbSe\(_3\) and TaS\(_2\) which have shown avoided crossings appearing in ARPES spectra due to back folding of bands caused by the presence of CDWs [107] and spin density waves [152], respectively. The results we have presented here for interlayer Umklapp scattering of hybridisation gaps are unique, as no replica bands were observed for the highly incommensurate superlattice and they do not originate from an ordered phase within the material.

### 3.2.3 Twist angle, thickness, and material dependence

Interlayer umklapp scattering is not unique to the graphene/monolayer InSe heterostructure described in the section above. This phenomenon can be seen in other heterostructures with different twist angle, layer thickness and 2D material.

The twist angle between the two layers can be used to directly control the position of the strongly coupled states in energy and momentum. Fig. 3.7 shows the different patterns of anti-crossings that would be created for four different twist angles between graphene and monolayer InSe.

Two more graphene encapsulated PTMCs were studied with different layer thickness and 2D material. Different patterns of ‘ghost’ anti-crossings were observed for the two heterostructures. Fig 3.8 a) shows a constant energy map of the first Brillouin zone of a 4L (4 layer) InSe flake encapsulated in graphene. From the \( \mu \)LEED pattern shown in Fig 3.8 c), the relative twist angle between the graphene and InSe was found to be -11.8 ± 0.1°. The contour plot in Fig 3.8 d) shows the shape
Figure 3.7: Energy contour maps at four different relative twist angles between graphene and monolayer InSe. The graphene and InSe Brillouin zones are represented by the black and blue hexagons respectively. The angle between lattices is defined in the top left corner. The position of the anti-crossings are marked on by the red lines.
Figure 3.8: a) and e) µARPES constant energy maps, at a binding energy of 1.9 eV, for graphene/4L InSe and graphene/3L GaSe, respectively. The black dashed boxes show the region of momentum space data was collected over and the colour scales are normalised photoemission intensity (arbitrary units). b) and f) Atomic schematics of the relative orientation of the lattices, found from the µLEED measurements in c) and g), respectively. d) and h) Energy contour plots of the graphene π band with the upper valence band of 4L InSe and 3L GaSe, respectively. Red lines show the position of hybridisation gaps. The 3D band schematics in the bottom right-hand corners show the shape of the band intersections.

of the band intersections and their Umklapp scattered positions which reproduce the same pattern as seen in the µARPES measurement. ‘Ghost’ anti-crossings were also observed in a graphene/3L GaSe heterostructure with a twist angle of 28.9 ± 0.7°, determined from the µLEED pattern shown in Fig 3.8 g). Fig 3.8 e) shows a constant energy map of the first Brillouin of GaSe containing an almost circular gap in the spectra, which again agrees with the expected anti-crossing pattern seen in the contour plot, Fig 3.8 h).

An optical, SPEM and LEEM image of the graphene/4L InSe heterostructure is shown in Fig 3.9 a), b) and c) respectively. The different contrasts seen in the
optical image show the different regions of different thicknesses on the InSe flake. μARPES measurements were performed on the 4L region at the position indicated by the red hollow circle in Fig 3.9 a) and b). The red hollow circle shows the position of the μLEED measurement on the flake. The raw μARPES data used to construct Fig 3.8 a) is shown in Fig 3.9 d). ‘Ghost’ anti-crossings in this heterostructure are clearly visible in the energy-momentum slices in Fig 3.9 e) which are taken along the directions indicated by the dashed red and blue lines in Fig 3.9 d). The four valence sub-bands seen at \( \Gamma \) in the left spectra of Fig 3.9 e) confirm the 4L thickness of the InSe [40], see Section 1.4.2 and Section 1.7.

The interlayer hybridisation factor [153], \( \delta \epsilon \), can be determined from fitting the bands around the hybridisation gap. Fig 3.10 a) and b) show two energy-momentum slices. The two spectra are related by \( g_{\text{InSe}} \) as shown in Fig 3.10 c). The anti-crossing in Fig 3.10 a) shows the hybridisation gap between the graphene π band and the InSe upper valence band on a region of the InSe flake that has a thickness of 2L. The position of this measurement on the flake is indicated by the green hollow circle in Fig 3.9 a). An interlayer hybridisation factor of \( \delta \epsilon = 0.45 \pm 0.02 \) eV is found from the fitting of the bands within this spectra with Lorentzian profiles. Fig 3.10 b) is acquired on the same InSe flake with the same twist angle.
Figure 3.10: a) µARPES energy-momentum slice of the intersection of the graphene π band with the 2L InSe upper valence band. b) µARPES energy-momentum slice of the ‘ghost’ anti-crossing in the 4L InSe upper valence band. The right spectra in both a) and b) show the data after numerically differentiating twice with respect to energy. The scale bars are 0.2 Å⁻¹. c) Energy contour map showing the positions a) and b) were acquired in momentum space.

with respect to the graphene, at the position indicated by the red hollow circle in Fig 3.9 a), corresponding to 4L InSe. The interlayer hybridisation factor of the ‘ghost’ anti-crossing is found to be δε = 0.33 ± 0.02 eV. Both anti-crossings are similar in shape due to the same orientation with the graphene, however, their interlayer hybridisation factors differ because of the different thickness of InSe.

For the graphene/3L GaSe heterostructure, optical, SPEM and LEEM images are shown in Fig 3.11 a), b) and c) respectively. The µARPES and µLEED measurements were taken at the positions marked by the red spots in Fig 3.11 b) and c). This region on the flake was determined to be 3L thick from the presence of three valence sub-bands at Γ, as shown in Fig 3.11 d). The ‘ghost’ anti-crossing can be observed in the black box in the µARPES energy-momentum slice, Fig 3.11 e). Although the anti-crossing between the graphene Dirac cone and the GaSe upper valence band is not clearly resolved (purple box in Fig. 3.11 e)), due to the high photoemission intensity of the graphene band structure compared to GaSe, a clear deviation from the expected continuous dispersion of the GaSe valence band is ob-
Figure 3.11: a) Optical, b) SPEM and c) LEEM image of the graphene encapsulated 3L GaSe flake. Black box in b) shows the area of the LEEM image in c). d) µARPES energy-momentum slice around $\Gamma$. The scale bar is 0.2 Å$^{-1}$. e) µARPES energy momentum slice through the high symmetry direction $\Gamma-K_{Gr}$. Red dashed line is the tight-binding model $\pi$ band of graphene. The GaSe Brillouin zone boundary is marked by the blue vertical line. Folding the graphene $\pi$ band into the first Brillouin zone of GaSe gives the black dashed line. The position of anti-crossings in the spectra are highlighted in the black and purple boxes. The scale bars are 0.5 Å$^{-1}$.

served at a position that corresponds to the graphene $\pi$ band folded by $g_{GaSe}$, as shown by the black dashed line on the left hand side of the spectra, labeled ‘ghost’ graphene.

### 3.3 Conclusion

In this chapter, we have provided evidence for interlayer Umklapp scattering of anti-crossings in 2D heterostructures. µARPES spectra have been presented for three different heterostructures, differing in material, layer thickness and twist angle. We have demonstrated that these properties can be used to control the energy, momentum and strength of coupling between graphene and PTMCs close to the VBM of the 2D semiconductor.

Interlayer Umklapp scattering provides a new band structure engineering tool for very weakly interacting 2D lattices, who differ significantly in lattice constant.
Further control of the position of strong coupling in the band structure could be achieved by manipulating band alignments either via electrostatic or chemical doping. We expect interlayer Umklapp scattering to be generic to all 2D heterostructures with the possibility of engineering strong coupling at positions close to the Fermi energy, therefore capable of influencing properties such as optical transitions and electron mobility.

Twist-dependent interlayer charge transfer between 2D materials could also be influenced by interlayer Umklapp scattering. A report by Luo et al. shows combining the TMD MoS$_2$ with graphene provides faster photoresponses than the TMD monolayer alone [154]. Interlayer Umklapp scattering could play a role in developing fast electron transfer in future optoelectronics.
Chapter 4

Final state photoelectron diffraction observed in µARPES spectra of 2D heterostructures

4.1 Introduction

van der Waals heterostructures formed by stacking different 2D materials are not limited by lattice matching. Combining 2D materials with different lattice constants and/or controlling the twist angle between layers can modify the electronic properties of the heterostructure, resulting in a superlattice with phenomena such as unconventional superconductivity [77] and Mott insulating states [155]. The exact twist angle between the layers can be very important for properties such as superconductivity in TBG, where this phenomenon only occurs at the 'magic' angle of 1.1° [77]. Many, if not close to all, interlayer effects in 2D heterostructures, such as moiré potentials and interlayer hybridisation, strongly depend on the angle between the two (or more [87]) layers.

Direct evidence of modifications to the band structure of 2D heterostructures can be observed in µARPES experiments. µARPES measurements of superlattices often reveal replica bands within the band structure due to a moiré potential induced by the additional long-range periodicity between two misaligned layers [156, 157].

Moiré-induced replica bands appear within the band structure at positions where the primary bands are folded by a vector equal to the difference in the reciprocal lattice constants of the two interacting layers, creating multiple mini Brillouin zones (see Section 1.6). Evidence of moiré-induced replica bands have been reported for systems such as graphene/graphene [116, 156], graphene/hBN
Monolayer TMDs are direct band gap semiconductors with strong light-exciton interactions. Therefore, moiré potentials hold many promising applications for the family of TMDs due to the formation of moiré excitons, whose energy can be controlled by the relative twist angle between the layers.

Each of the systems mentioned above are comprised of 2D materials that share similar magnitude lattice constants. More recently replica bands have been observed in µARPES measurements of highly incommensurate heterostructures, such as graphene/WS\(_2\) and graphene/WSe\(_2\).

Replica bands can also appear in ARPES spectra, at the same position in momentum space as moiré-induced replica bands, due to measurement artefacts. The wavelength of the photoemitted electrons in ARPES experiments is comparable to the atomic spacing in 2D lattices. Therefore, the photoemitted electrons can undergo diffraction while travelling through encapsulating atomic layers to the surface. Final state photoelectron diffraction effects are a common artefact seen in high-energy ARPES spectra and are often seen in similar experiments where photoelectrons are scattered by a surface potential barrier. The question of whether replica bands seen in µARPES spectra of 2D heterostructures are a result of a final state photoelectron diffraction effect or a moiré potential has already been considered for studies of graphene/Ir(111), graphene/SiC(0001) and graphene/WS\(_2\); it has often proven difficult to separate the two different phenomena from one another.

In this chapter, we study monolayer hBN stacked on top of monolayer WSe\(_2\), at two different twist angles: 1.7° and 28°, where replica bands are present in their µARPES spectra. Additionally, we study three different regions on a partially hBN encapsulated MoSe\(_2\) heterostructure and accurately determine twist angles using µLEED.

### 4.2 Results and Discussion

#### 4.2.1 Sample structure

A hBN/WSe\(_2\) heterostructure was fabricated by Paul Nguyen at the University of Washington, using mechanical exfoliation and the PDMS dry transfer technique. Fig. 4.1 a) shows a schematic of the sample. Monolayer hBN is stacked on top of monolayer WSe\(_2\) which is placed on a thick hBN/graphite substrate on a SiO\(_2\)/Si wafer. The stacking of hBN on top of WSe\(_2\) creates a highly incommensurate heterostructure as WSe\(_2\) has a lattice constant of a\(_{WSe_2}\) = 3.28 Å.
is approximately 24% larger than that of hBN, $a_{\text{hBN}} = 2.50 \, \text{Å}$ [165]. Fig. 4.1 b) and c) show the relative size of the crystal lattices for hBN and the TMD WSe$_2$, respectively, with their lattice vectors defined. Due to the large difference in lattice constants a moiré potential is not expected to be present between these two materials. A Brillouin zone schematic defining the the high symmetry directions of the layers when misaligned is shown in Fig. 4.1 d), where their twist angle is defined as $\theta$.

### 4.2.2 Determining the twist angle

The twist angle can be controlled with some accuracy when assembling heterostructures by aligning flake edges that are assumed to be either zigzag or armchair. During the transfer process, it is common for 2D flakes to wrinkle or tear, changing their initial alignment. After transfer, relaxation causes flakes to align themselves in more energetically favourable positions. As a result, different regions on the same 2D flake will have different relative orientations to the underlying substrate. Therefore, the twist angle is largely unknown after fabrication and must be found using other experimental techniques after assembly. In order to determine the twist angle of specific regions of interest one needs to be able to probe only the desired location on the heterostructure, therefore techniques require high spatial resolution.

The twist angle of micrometre sized regions can be determined from $\mu$ARPES measurements. SPEM can be used to locate the region of interest on the heterostructure. Fig. 4.2 a) shows a SPEM image of the hBN/WSe$_2$ heterostructure. The black circle shows the position at which all $\mu$ARPES measurements on this sample were made, with a photon energy of 27 eV and a sample temperature of 100 K. Fig. 4.2
Figure 4.2: a) SPEM image of hBN/WSe$_2$ heterostructure. The monolayer WSe$_2$ flake is outlined in red and monolayer hBN fully covers the region imaged. The scale bar is 5 µm. b) and c) µARPES energy-momentum slices along the high symmetry directions defined, taken at the position of the black circle in a). d) and e) µARPES constant energy maps taken at the energy defined by the black dashed lines in b) and c), respectively. The first Brillouin zones of hBN and WSe$_2$ are shown by the overlaid blue and red hexagons, respectively. The dashed black lines show the direction of the µARPES energy-momentum slices in b) and c). The scale bars are 0.2 Å$^{-1}$.

b) and c) show µARPES energy-momentum slices in the $\Gamma$-K$_{WSe_2}$ and $\Gamma$-K$_{hBN}$ directions, respectively, from which the electronic bands leading to the Brillouin zone corners of each individual layer can be identified, as highlighted by the red and blue overlaid lines. Fig. 4.2 d) and e) show µARPES constant energy maps at the energies marked by the black dashed lines in Fig. 4.2 b) and c), respectively. From the µARPES constant energy maps, the twist angle can be determined by defining each layer’s Brillouin zone, as shown by the overlaid blue and red hexagons. The twist angle between the hBN and WSe$_2$ layers is found to be $\sim 2^\circ$.

The uncertainty of the twist angle determined in this way is $\sim \pm 2^\circ$, which can be significant for phenomena that only exist at precise twist angles, such as flat bands and correlated states. Additionally, determining the twist angle from ARPES measurements requires prior knowledge of the band structure of individual layers and a high cross section of the electronic states at the Brillouin zone corners or other high symmetry positions.
Figure 4.3: a) LEEM image of hBN/WSe₂ heterostructure. b) µLEED pattern acquired at an electron beam energy of 50 eV. The zeroth order diffraction spot is labelled 00. The first order WSe₂ and hBN diffraction spots are labeled 01 and circled in red and blue, respectively. c) Line profiles taken in the direction of the red and blue dashed lines in b).

Complementary to µARPES, µLEED, performed on the low energy electron microscope at the Nanospectroscopy beamline [147] at the Elettra Synchrotron, was used to determine the twist angle at well-defined locations on a 2D heterostructures with higher precision.

Fig 4.3 a) shows a LEEM image of the hBN/WSe₂ heterostructure. By comparison to the SPEM and optical micrograph, the location at which the µARPES spectra were acquired can be determined. This is indicated by the white circle. At this location on the sample, a µLEED pattern with an electron beam energy of 50 eV was acquired and is shown in Fig. 4.3 b). LEED is a surface sensitive technique therefore only diffraction spots from the top two layers are visible in the diffraction pattern. The first order diffraction spots from the hBN and WSe₂ layers are highlighted by the blue and red circles, respectively. As expected, the diffraction pattern of each layer has 6-fold symmetry.

The vector between the zeroth order diffraction spot, 00, and the first order WSe₂ and hBN diffraction spots correspond to the reciprocal lattice vectors of each layer, \(G_{WSe²}\) and \(G_{hBN}\) respectively. \(G_{hBN}\) is found to be \(22 \pm 2\%\) larger than \(G_{WSe²}\), as expected.

The position of the diffraction spots in the µLEED pattern are well defined,
by their sharp peak in intensity. Line profiles were taken over each diffraction spot, two of which are shown in Fig. 4.3 c), for the red and blue dashed lines in Fig. 4.3 b). The position of the diffraction peaks were found by fitting such line profiles, from which six pairs of reciprocal lattice vectors were determined. Averaging the twist angles found between all six pairs of reciprocal lattice vectors, a twist angle of \( \theta = 1.7 \pm 0.9^\circ \) was found for this hBN/WS\(_2\) heterostructure. Taking an average removes any stigmatism within the image of the diffraction pattern. (The twist angles in Chapter 3 were also determined using this method).

Additionally, other diffraction spots are observed around 00 at positions that correspond to the difference in reciprocal lattice vectors of the two layers, \( \bm{G}_M = \bm{G}_{\text{hBN}} - \bm{G}_{\text{WSe}_2} \). These arise as a result of the additional long-range periodicity of the hBN/WSe\(_2\) superlattice.

\( \mu \text{LEED} \) is a destructive technique, due to the sample mounting and grounding required, and therefore must be performed after all other measurements. All \( \mu \text{LEED} \) measurements were performed by beamline scientists Alexei Barinov, Andrea Locatelli and Francesca Genuzio, after all \( \mu \text{ARPES} \) measurements were acquired.

### 4.2.3 Replica bands in hBN/WSe\(_2\) heterostructures

The primary band structure of WSe\(_2\) appears as expected for an isolated non-interacting WSe\(_2\) monolayer, the upper valence band is comprised of a single band at \( \Gamma \) with the VBM at the \( \mathbf{K} \) point, as can be seen in Fig. 4.2 b). In addition to the non-interacting WSe\(_2\) band structure, replica bands of the WSe\(_2\) band structure are observed within the \( \mu \text{ARPES} \) spectra. A \( \mu \text{ARPES} \) constant energy map, at a binding energy equal to 1.2 eV, is shown in Fig 4.4 a). Three replica WSe\(_2\) valence bands around \( \Gamma, \Gamma_R \), are seen at positions indicated by the hollow black circles. An energy-momentum slice from \( \Gamma \) to \( \Gamma_R \) is shown in Fig 4.4 b). The replica bands appear at positions that correspond to shifts of the moiré vector between the hBN and WSe\(_2\) layers, \( \bm{G}_M = \bm{G}_{\text{hBN}} - \bm{G}_{\text{WSe}_2} \), relative to the primary bands, but a moiré potential is not expected for the size of the lattice mismatch in this heterostructure.

Symmetry dictates that a hybridisation gap should be present between the primary and replica bands at the mini Brillouin zone boundaries if formed by an initial state effect such as a moiré potential, as seen in other studies [96, 97, 156, 157, 166, 167]. No hybridisation gap is observed at the mini Brillouin zone boundary where the bands at \( \Gamma \) and \( \Gamma_R \) intersect, as shown by the white arrow in the middle spectrum of Fig. 4.4 b), where the photoemission intensity has been numerically differentiated twice with respect to energy. The bottom window of Fig. 4.4 b) shows an energy distribution curve (EDC), in blue, taken across the intersection of
Figure 4.4: a) µARPES constant energy map of the hBN/WSe\textsubscript{2} heterostructure with a twist angle of 1.7°, at a binding energy of 1.2 eV. The red lines mark the WSe\textsubscript{2} Brillouin zone boundaries. The solid grey circle and hollow black circles mark the primary WSe\textsubscript{2} valence band at $\Gamma$ and the replica WSe\textsubscript{2} valence bands around $\Gamma$, $\Gamma^R$, respectively. b) Top - µARPES energy-momentum slice along the direction of the white dashed line in a). Middle - same spectrum as above after numerically differentiating twice with respect to energy. Bottom - EDCs taken at the position marked by the corresponding red, blue and purple vertical lines overlaid in top spectrum. c) µARPES constant energy map at a binding energy of 1.0 eV. The solid and hollow red circles mark the primary WSe\textsubscript{2} valance bands at $K_{WSe2}$ and the replica WSe\textsubscript{2} valence bands around $K_{WSe2}$, $K_{WSe2}^R$ respectively. d) µARPES energy-momentum slice along the direction of the red dashed line in c). All photoemission intensities are displayed using a logarithmic scale and all scale bars are 0.2 Å\textsuperscript{-1}.

The primary and replica band. No measurable reduction in photoemission intensity is seen at the intersection. The band energy, effective mass and band width of $\Gamma^R$ is the same as the primary $\Gamma$ band showing they are exact replicas. The absence of the hybridisation gaps in our spectra could be attributed to the degree of hybridisation being far smaller than the energy resolution of the beamline as a result of very weak coupling between the layers.

Similarly, replica WSe\textsubscript{2} valence bands around $K_{WSe2}$, $K_{WSe2}^R$ can be seen shifted from the primary bands by vectors corresponding to the moiré vector, highlighted by the hollow red circles in the µARPES constant energy map in Fig 4.4 c). An energy-momentum slice from $K_{WSe2}$ to $K_{WSe2}^R$, taken along the red dashed line in Fig 4.4 c), is shown in Fig. 4.4 d). Again, no hybridisation gaps were observed
Figure 4.5: a) and b) µLEED patterns of the large twist angle hBN/WSe\textsubscript{2} heterostructure, taken with electron beam energies of 50 eV and 34 eV, respectively. First order WSe\textsubscript{2} and hBN diffraction spots are highlighted by red and blue circles, respectively. c) µARPES constant energy map at a binding energy of 1.1 eV. The red lines mark the WSe\textsubscript{2} Brillouin zone boundaries. The solid hollow circles mark the primary WSe\textsubscript{2} valence band at \( \Gamma \) and replica WSe\textsubscript{2} valence bands around \( \Gamma, \Gamma^R \), respectively. d) and e) µARPES energy-momentum slices along the direction of the white dashed line and the cyan dashed line in c), respectively. f) µARPES constant energy map at a binding energy of 0.6 eV. The solid and hollow red circles mark the primary WSe\textsubscript{2} valance bands at \( K_{\text{WSe}_2} \) and the replica WSe\textsubscript{2} valence bands around \( K^R_{\text{WSe}_2}, K^R_{\text{WSe}_2} \), respectively. g) µARPES energy-momentum slice along the direction of the red dashed line in f). All photoemission intensities are displayed using a logarithmic scale and all scale bars are 0.2 Å\textsuperscript{-1}.

between the primary and replica bands.

A second hBN/WSe\textsubscript{2} heterostructure was fabricated by Paul Nguyen at the University of Washington, with a larger twist angle between the monolayer hBN and monolayer WSe\textsubscript{2}. A twist angle of \( 28 \pm 1 \)° was determined from the µLEED pattern shown in Fig 4.5 a). The µLEED pattern again shows additional diffraction spots at positions corresponding to the difference in reciprocal lattice vectors, \( G_M \), which become more intense at lower incident electron energies of 34 eV, Fig. 4.5 b).

µARPES measurements of the band structure again show replica bands that appear displaced by the moiré vector of the hBN and WSe\textsubscript{2} layers. Within the
Figure 4.6: a) Brillouin zone schematic defining the hBN and WSe$_2$ reciprocal lattice vectors, $G_{hBN}$ and $G_{WSe_2}$, respectively, and moiré vector, $G_M$, for the 28° twist angle hBN/WSe$_2$ heterostructure. The blue and red hexagons represent the hBN and WSe$_2$ Brillouin zones, respectively. b) A schematic of the first WSe$_2$ Brillouin zone with the photoemission intensity of the WSe$_2$ valence bands around each $K$ point at a binding energy of 0.9 eV shown by the black lines. A WSe$_2$ valence band around $K^{(2)}$ is scattered by $G_M$ due to a moiré potential. c) Same schematic as shown in b), but with a WSe$_2$ valence band around $K^{(3)}$ scattered by $G_{hBN}$ due final state photoelectron diffraction. d) µARPES constant energy map at a binding energy of 0.9 eV. The photoemission intensity is displayed using a logarithmic scale and the scale bar is 0.2 Å$^{-1}$.

momentum space field of view, one replica WSe$_2$ valence band around $\Gamma$, $\Gamma^R$, is observed at the expected position for a 28° twist angle. Fig. 4.5 c) shows a µARPES constant energy map where $\Gamma^R$ is indicated by the hollow black circle. A µARPES energy-momentum slice along the white dashed line is shown in Fig. 4.5 d)). An additional, less intense, $\Gamma^R$ (hollow cyan circle in Fig. 4.5 c)) is also seen at a position corresponding to the alternative moiré vector where the angle between the vectors $G_{hBN}$ and $G_{WSe_2}$ is defined in the opposite direction, $\theta = 32 \pm 1°$. A
μARPES energy-momentum slice along the cyan dashed line can be seen in Fig. 4.5 e).

Multiple replica WSe$_2$ valence bands around $K_{WSe_2}$, $K^R_{WSe_2}$, are also observed. Fig. 4.5 f) shows a μARPES constant energy map at a binding energy equal to the VBM, where $K^R_{WSe_2}$ are highlighted by the red hollow circles. A μARPES energy-momentum slice along the red dashed line is shown in Fig. 4.5 f).

To summarize, we have observed replica WSe$_2$ valence bands that appear displaced by the moiré vector relative to the primary bands, for both small and large twist angle hBN/WSe$_2$ heterostructures. However, no hybridisation gaps were observed in the spectra.

In a previous study by Ulstrup et al. replica bands were observed in μARPES measurements of a similar magnitude lattice mismatch heterostructure, graphene/WS$_2$ [114]. In their work, replica bands were only observed at small twist angles between the layers and disappeared at larger angles, consistent with what is expected for a moiré potential, as the strength of a moiré potential between two 2D layers is expected to decrease with increasing twist angle. However, moiré superlattice potentials have recently been shown to persist down to moiré periodicity’s comparable with crystal lattice vectors [116].

Replica bands observed in μARPES spectra can also be described by final state photoelectron diffraction. Photoemitted electrons from the underlying layer, in this case the WSe$_2$, can be diffracted upon their exit from the heterostructure when travelling through the encapsulating hBN layer into the vacuum. This process creates replica bands in μARPES spectra at the same momentum as replica bands created by a moiré potential. By carefully inspecting the angular orientation of replica bands with anisotropic photoemission intensity, one can determine the primary band from which they originated.

Fig. 4.6 a) shows a Brillouin zone schematic of the large twist angle hBN/WSe$_2$ heterostructure, defining the hBN and WSe$_2$ reciprocal lattice vectors, $G_{hBN}$ and $G_{WSe_2}$, respectively, and the moiré vector, $G_M$. The photoemission intensity of the WSe$_2$ valence bands around each $K$ point of the first Brillouin zone are sketched in Fig. 4.6 b) for a binding energy of 0.9 eV. A moiré potential displaces electronic bands by $G_M$ as shown by the translation of $K^{(2)}$ in Fig. 4.6 b). The resulting replica band retains the symmetry of the primary band.

To create a replica band in the same position in momentum by photoelectron diffraction, $K^{(3)}$ must be scattered by $G_{hBN}$ as shown in Fig. 4.6 c). As the symmetry of the band is retained, the replica band’s angular orientation is different to that formed by a moiré potential.
4.2.4 Partially hBN encapsulated MoSe$_2$ heterostructure

Similarly, replica bands are observed in $\mu$ARPES measurements of a hBN/MoSe$_2$ heterostructure. MoSe$_2$ has a lattice constant equal to 3.29 Å [164], similar to that of WSe$_2$ and therefore is not expected to create a moiré potential when stacked with hBN. We study monolayer and bilayer MoSe$_2$ encapsulated by monolayer hBN, as well as, the opposite stacking order, MoSe$_2$/hBN.

A partially hBN encapsulated MoSe$_2$ heterostructure was fabricated by Paul Nguyen at the University of Washington. A sample schematic is shown in Fig. 4.7 a), where the three different regions studied using $\mu$LEED and $\mu$ARPES are defined. Fig. 4.7 b) shows an optical image of the heterostructure with the monolayer hBN flake outlined in pale blue and the MoSe$_2$ flake outlined in brown. The region within the yellow box was imaged using SPEM, Fig. 4.7 c), from which the three different regions on the heterostructure can be identified. To acquire $\mu$LEED measurements at the same locations as the $\mu$ARPES measurements, a LEEM image was acquired, Fig 4.7 d).

We first compare $\mu$ARPES measurements of monolayer MoSe$_2$/hBN (region 1) and monolayer hBN/moemonolayer MoSe$_2$ (region 2). $\mu$LEED was used to find the
Figure 4.8: a) and d) µLEED patterns acquired from region 1 (MoSe$_2$/hBN) and region 2 (hBN/MoSe$_2$), respectively. b) and e) µARPES constant energy maps at binding energies of 1.7 and 1.4 eV, for regions 1 and 2, respectively. The green lines mark the MoSe$_2$ Brillouin zone boundaries. The solid white circle and hollow black circles mark the primary MoSe$_2$ valence band at $\Gamma$ and the replica MoSe$_2$ valence bands around $\Gamma$, $\Gamma^R$, respectively. The solid and hollow green circles mark the primary MoSe$_2$ valence bands at $K$ and the replica MoSe$_2$ valence bands around $K$, $K^R$, respectively. c) µARPES energy-momentum slice taken in the direction of the green dashed line in b). f) and g) µARPES energy-momentum slices taken in the direction of the white and green dashed lines in e), respectively. All photoemission intensities are displayed using a logarithmic scale and all scale bars are 0.2 Å$^{-1}$.

twist angle between the top two layers of each region. In region 1, the twist angle between the exposed monolayer MoSe$_2$ and thick hBN substrate was determined to be 6.7 ± 0.1° from the diffraction pattern shown in Fig. 4.8 a). First order diffraction spots from the hBN substrate were not observed due to the three atom thickness of the above MoSe$_2$ monolayer, therefore the twist angle was determined from the relative position of the MoSe$_2$ first order diffraction spots and the additional diffraction spots seen at $G_M$, as $G_{hBN} = G_M + G_{MoSe_2}$.

Only one replica band was observed in µARPES measurements of region 1. Fig. 4.8 b) shows two constant energy maps, the left map at the binding energy of the MoSe$_2$ valence band edge at $\Gamma$, revealing no replica MoSe$_2$ valence bands.
around \( \Gamma \), and the right map at a binding energy just below the VBM of the MoSe\(_2\), showing one replica MoSe\(_2\) valence band around \( K_{\text{MoSe}_2}\). A \( \mu \text{ARPES} \) energy-momentum slice from \( K_{\text{MoSe}_2} \) to \( K^R_{\text{MoSe}_2} \) is shown in Fig. 4.8 c). As only one replica band is seen and no hybridisation gap is observed, this replica band is likely due to the MoSe\(_2\) photoemitted electrons scattering off the underlying hBN substrate, which has been shown to form replica bands in ARPES spectra [157].

Encapsulating MoSe\(_2\) in monolayer hBN (region 2) shifts the MoSe\(_2\) bands lower in binding energy by 0.04 eV. The same effect is seen, but an order of magnitude larger, when encapsulating WS\(_2\) in graphene [114]. A twist angle of 4.9 \( \pm \) 0.3° is found for the hBN/MoSe\(_2\) interface from the \( \mu \)LEED pattern shown in Fig. 4.8 d). Fig. 4.8 e) shows two constant energy maps, again, the left map at the binding energy of the MoSe\(_2\) \( \Gamma \) band and the right map just below the VBM of MoSe\(_2\). In the region of momentum space probed, three replica MoSe\(_2\) bands of \( \Gamma \) and four replica \( K_{\text{MoSe}_2} \) bands were observed, highlighted by the black and green hollow circles, respectively. No replica bands were observed from the MoSe\(_2\)/thick hBN interface. As in the case of the hBN/WSe\(_2\) heterostructure, no hybridisation gaps were observed between any of the primary and replica bands. \( \mu \text{ARPES} \) energy-momentum slices from primary to replica bands taken along the white and green dashed lines in Fig. 4.8 e), are shown in Fig. 4.8 f) and g), respectively.
The angular orientation of the replica bands are not easily resolvable due to their weak photoemission intensity. If these replica bands were formed by a moiré potential, one would naively expect a similar strength moiré potential to be present between the MoSe$_2$/hBN (region 1) and hBN/MoSe$_2$ interface (region 2), given only the small difference in twist angle of the two regions. However, significantly fewer replica bands were observed for the MoSe$_2$/hBN stacking order.

So far, all data presented has been for monolayer TMDs where the VBM is at $K$. The third region studied consists of monolayer hBN/bilayer MoSe$_2$ (region 3). The twist angle in this region between the monolayer hBN and bilayer MoSe$_2$ was found to be $4.1 \pm 0.3^\circ$ from the µLEED diffraction pattern shown in Fig. 4.9 a). The difference in twist angle between regions 2 and 3 highlights the twist angle disorder in the sample, showing the importance of performing the µLEED measurements at exactly the same position on the sample as the µARPES measurements, even though the bilayer and monolayer MoSe$_2$ regions are part of the same 2D flake.

Fig. 4.9 b) shows two µARPES constant energy maps, the left map at the binding energy of the VBM (now the $\Gamma$ point) and the right map just below the binding energy of the MoSe$_2$ band at $K$. The same number of replica bands are observed as for region 2. µARPES energy-momentum slices are shown in Fig. 4.9 c) and d) between primary and replica bands. In Fig. 4.9 c), the bilayer nature of the MoSe$_2$ can be confirmed by the presence of two bands at $\Gamma$, due to the hybridisation between the two TMD layers [110].

To summarise, replica MoSe$_2$ valence bands were observed in all three regions, but with significantly fewer seen for the MoSe$_2$/hBN stacking order. As in the case of hBN/WSe$_2$, no replica bands were observed for the hBN band structure and no hybridisation gaps were observed between any of the primary and replica bands. Therefore, we suspect all replica MoSe$_2$ valence bands observed to be a result of final state photoelectron diffraction.

4.3 Conclusion

In this chapter, we have observed replica bands created by final state photoelectron diffraction for two hBN/WSe$_2$ heterostructures, at small and large twist angles, and three different stacking regions on a partially encapsulated hBN/MoSe$_2$ heterostructure. Given that an initial state effect of a moiré potential and the final state effect of photoelectron diffraction can create replica bands in µARPES spectra at the same momenta, careful interpretation is required to determine their nature.

For bands with anisotropic photoemission intensity the angular orientation
can be used to determined which primary band they originate from and hence whether they are displaced by the moiré vector or the reciprocal lattice vector of an encapsulating atomic layer. The observation of hybridisation gaps between primary and replica bands is essential for definitively assigning an initial state effect. Unfortunately, we did not observe them in our µARPES spectra.

The presence of a moiré potential between hBN and TMDs cannot be ruled out. However, the observation of replica bands within µARPES spectra alone is not enough evidence to show a moiré potential is present between the two 2D materials.

Additionally, we have shown µLEED is a complementary technique to µARPES for determining the twist angle between surface layers at specific locations on 2D heterostructures. As the twist angle can significantly influence the properties of a heterostructure, techniques to accurately quantify relative orientations of 2D materials are important for the growing field of twistronics.
Chapter 5

Band alignments in gated transition metal dichalcogenide heterobilayers

5.1 Introduction

The semiconducting TMDs remain a large focus of interest for engineering new 2D devices. For two or more layers, TMDs are known to be indirect band gap semiconductors. However, the monolayer forms a direct band gap at the Brillouin zone corners [118], important for optoelectronic applications. The spin-polarised bands at the VBM and CBM of the monolayer TMDs [32], lead to spin-valley polarisation of electrons which can be exploited in valleytronic and spintronic applications [76].

Stacking together two different TMD monolayers, known as a heterobilayer, can create a type II band alignment where the VBM and CBM reside in opposite layers. This allows the formation of interlayer excitons, where the hole and electron are localised on separate layers resulting in long population and valley lifetimes [63, 65]. Although it is well established that the VBM is at K, the ground state interlayer exciton of the MoSe$_2$/WSe$_2$ heterobilayer has been reported in some studies to be the K-Q exciton [66] and in other studies to be the K-K exciton [110], showing that some confusion lies around whether Q or K is the CBM. High-quality fabrication of these samples also allows the formation of moiré trapped interlayer excitons, whose emission energy can be controlled by the relative twist angle between the two layers [73, 74, 158].

It has been shown that the emission energy of interlayer excitons can also be tuned with electrostatic gating [75, 168]. The change in emission energy is either
Figure 5.1: a) Sample schematic. b) Optical and c) SPEM images of the MoSe\textsubscript{2}/WSe\textsubscript{2} heterostructure: monolayer MoSe\textsubscript{2} and WSe\textsubscript{2} flakes are outlined in green and purple, respectively, and the heterobilayer region is marked by HS. The partially encapsulating graphene is outlined in black. The scale bar is 5 \( \mu \)m. d) and e) \( \mu \)ARPES energy-momentum slices in the \textGamma-\textK\ direction for the monolayer MoSe\textsubscript{2} and monolayer WSe\textsubscript{2} regions, respectively. The scale bars are 0.2 \( \text{\AA}^{-1} \). Overlaid lines are fits to the band dispersion.

due to the Stark effect, where an electric field across the layers changes their relative energy, or carrier concentration dependent renormalisation effects, where the increase in screening from the charge added to the layer modifies the band structure, or a combination of both.

In this chapter we determine band alignments and band gaps of TMD heterobilayers using \( \mu \)ARPES with in-situ electrostatic gating. We resolve the position of the CBM and determine gate-dependent electronic structure changes.

### 5.2 Results and Discussion

#### 5.2.1 Doping MoSe\textsubscript{2}/WSe\textsubscript{2} heterobilayers

Two MoSe\textsubscript{2} and WSe\textsubscript{2} heterobilayer devices, with opposite TMD stacking order, were fabricated by Paul Nguyen at the University of Washington using mechanical exfoliation and the PDMS dry transfer technique [51]. A schematic of the device is shown in Fig. 5.1 a). The device design is similar to that of a field-effect transistor with graphite as the back gate, hBN as the dielectric material, graphene as the drain, and the material of interest, in this case the TMD heterobilayer, sandwiched between the hBN and graphene layers. The graphite and graphene flakes are in contact with platinum electrodes on the SiO\textsubscript{2}/Si substrate, from which a gate voltage, \( V_G \), can be applied and a photocurrent current measured, respectively.
Figure 5.2: a) and b) Atomic and Brillouin zone schematics of each heterobilayer. Underneath, µARPES energy-momentum slices along the high symmetry directions defined at $V_G = 0$ V, for the MoSe$_2$/WSe$_2$ and WSe$_2$/MoSe$_2$ heterobilayers, respectively. Overlaid in green and purple are the fits of the bands from the MoSe$_2$ and WSe$_2$ layers, respectively. c) and d) µARPES energy-momentum slices along the high symmetry directions defined, at $V_G = +4$ V, for the MoSe$_2$/WSe$_2$ (hBN thickness = 9.4 ± 0.5 nm) and WSe$_2$/MoSe$_2$ (hBN thickness = 9 ± 1 nm) heterobilayers, respectively. Data presented in a black and white colour scheme shows the photoemission intensity in a logarithmic scale and all scale bars are 0.2 Å$^{-1}$.

For the MoSe$_2$/WSe$_2$ heterobilayer, an optical image of the heterostructure, before being transferred onto the hBN substrate, is shown in Fig. 5.1 b). The monolayer MoSe$_2$ and WSe$_2$ layers overlap in the region marked HS. The region enclosed by the white dashed box was imaged using SPEM, from which the individual monolayers, heterobilayer and graphene/heterobilayer regions can be identified, Fig. 5.1 c). A small gap is present in the partially encapsulating graphene, shown by the red arrows. Within the ~2 µm-wide gap, all µARPES measurements on the exposed heterobilayer were performed with a photon energy of 27 eV and a sample temperature of 80 K. µARPES energy-momentum slices for the MoSe$_2$ and WSe$_2$ monolayer regions are shown in Fig. 5.1 d) and e), respectively, in the $\Gamma$-$K$ direction. The band structure of the monolayers are as expected for the isolated materials, with a single band at $\Gamma$ and two spin-split bands at $K$.

A µARPES energy-momentum slice of the MoSe$_2$/WSe$_2$ heterobilayer region is shown in Fig. 5.2 a). From the position in momentum space of the MoSe$_2$ and WSe$_2$ bands at $K$, the heterobilayer is found to be perfectly aligned (see Section 4.2.2). An atomic schematic of the stacking order and the Brillouin zone orientation...
can be seen at the top of Fig. 5.2 a). Below a µARPES energy-momentum slice with no electrostatic doping \((V_G = 0 \text{ V})\) is shown. The electronic bands visible at \(\mathbf{K}\) which originate from the MoSe\(_2\) and WSe\(_2\) layers are highlighted by the overlaid green and purple fits on the right hand side of the spectra. Only one of the spin-split bands at \(\mathbf{K}\) for the WSe\(_2\) layer is visible, as the other is masked by the photoemission intensity of the MoSe\(_2\) bands, due to the surface sensitivity of ARPES. We find the VBM to reside in the WSe\(_2\) layer at the Brillouin zone corner, \(\mathbf{K}\), as expected, and a valence band offset of 0.31 \(\pm\) 0.04 eV relative to the MoSe\(_2\) valence band at \(\mathbf{K}\). Two bands are seen at \(\mathbf{\Gamma}\), separated in energy by 0.67 \(\pm\) 0.04 eV due to hybridisation between the MoSe\(_2\) and WSe\(_2\) layers.

For the opposite stacking order, on a second device, we now see both spin-split bands at \(\mathbf{K}\) for the WSe\(_2\) layer, as WSe\(_2\) is now the top layer of the heterobilayer. An atomic schematic of the stacking order and the relative Brillouin zone orientation is shown at the top of Fig. 5.2 b). Determined from the µARPES spectra, the heterobilayer is misaligned with a twist angle of 6 \(\pm\) 1 °. Fig. 5.2 b) also shows a µARPES energy-momentum slice along the \(\mathbf{\Gamma}-\mathbf{K}_{\text{WSe}_2}\) high symmetry direction at \(V_G = 0 \text{ V}\). We again find the VBM to reside in the WSe\(_2\) layer at \(\mathbf{K}\) and the same energy separation of the bands at \(\mathbf{\Gamma}\). All band alignments for the individual monolayers and both heterobilayers can be found in Table 5.1.

Electrostatically doping the heterobilayers populates the conduction band, making it visible in the µARPES spectra. Fig. 5.2 c) and d) show µARPES energy-momentum slices at \(V_G = +4 \text{ V}\) for the MoSe\(_2\)/WSe\(_2\) (hBN thickness = 9.4 \(\pm\) 0.5 nm) and WSe\(_2\)/MoSe\(_2\) (hBN thickness = 9 \(\pm\) 1 nm) heterobilayers, respectively. The ~2 \(\mu\)m gap in the encapsulating graphene provides a uniform electric field across the exposed heterobilayer. For both stacking orders, the CBM is observed in the MoSe\(_2\) layer at \(\mathbf{K}\), forming a type II band alignment, in agreement with optical measurements [65, 110]. For a similar carrier concentration of \(\sim 10^{13} \text{ cm}^{-2}\), the direct band gap of MoSe\(_2\)/WSe\(_2\) and WSe\(_2\)/MoSe\(_2\) are found to be 1.42 \(\pm\) 0.04 eV and 1.43 \(\pm\) 0.03 eV, respectively.

Weak photoemission intensity is also observed at the \(\mathbf{Q}\) point in the conduction band. The band alignment between \(\mathbf{Q}\) and \(\mathbf{K}\) must be on the order of tens of meV for both to be populated at carrier concentrations of \(\sim 10^{13} \text{ cm}^{-2}\). Due to the orbital composition of the band at \(\mathbf{Q}\), the energy of the electronic state is sensitive to hybridisation between the layers. For the TMD homobilayers the CBM is known to be at \(\mathbf{Q}\), and not \(\mathbf{K}\) [118]. This suggests the hybridisation between MoSe\(_2\) and WSe\(_2\) is weaker in the heterobilayer compared to their corresponding homobilayers.
Table 5.1: Band parameters for monolayer MoSe$_2$, monolayer WSe$_2$ and their heterobilayers. $E_K$ is the energy of the VBM, $E_\Gamma - E_K$ is the energy difference between the upper most band at $\Gamma$ and $E_K$, $\Delta SO$ is the spin-orbit coupling of the top layer of the heterobilayer, VBO is the valence band offset between the MoSe$_2$ and WSe$_2$ bands at $K$, $\Delta \Gamma$ is the energy separation of the bands at $\Gamma$ and $m_K^*$ is the effective mass of the bands at $K$, found from a parabolic fit in a symmetric window of 0.1 Å$^{-1}$. $E_G$ is the band gap. *Values from reference [118]. *Band gaps are for carrier concentrations of $(9.0 \pm 0.4) \times 10^{12}$ cm$^{-2}$ for MoSe$_2$/WSe$_2$ and $(10 \pm 1) \times 10^{12}$ cm$^{-2}$ for WSe$_2$/MoSe$_2$.

<table>
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<tr>
<th></th>
<th>$E_K$ (eV)</th>
<th>$E_\Gamma - E_K$ (eV)</th>
<th>$\Delta SO$ (eV)</th>
<th>VBO (eV)</th>
<th>$\Delta \Gamma$ (eV)</th>
<th>$m_K^*$ ($m_0$)</th>
<th>$E_G$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSe$_2$</td>
<td>1.18 ± 0.03</td>
<td>0.27 ± 0.04</td>
<td>0.18 ± 0.04</td>
<td>-</td>
<td>-</td>
<td>0.6 ± 0.1</td>
<td>1.64 ± 0.05$^*$</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>0.81 ± 0.03</td>
<td>0.64 ± 0.04</td>
<td>0.49 ± 0.04</td>
<td>-</td>
<td>-</td>
<td>0.4 ± 0.1</td>
<td>1.79 ± 0.03$^*$</td>
</tr>
<tr>
<td>MoSe$_2$/WSe$_2$ (0°)</td>
<td>0.74 ± 0.03</td>
<td>0.23 ± 0.04</td>
<td>0.21 ± 0.04</td>
<td>0.31 ± 0.04</td>
<td>0.67 ± 0.04</td>
<td>0.7 ± 0.1/0.4 ± 0.1</td>
<td>1.42 ± 0.04$^*$</td>
</tr>
<tr>
<td>WSe$_2$/MoSe$_2$ (6°)</td>
<td>0.78 ± 0.03</td>
<td>0.17 ± 0.04</td>
<td>0.52 ± 0.04</td>
<td>0.28 ± 0.04</td>
<td>0.65 ± 0.04</td>
<td>0.4 ± 0.1/1.0 ± 0.2</td>
<td>1.43 ± 0.03$^*$</td>
</tr>
</tbody>
</table>
5.2.2 Determining carrier concentration

The gate-induced carrier concentration can be calculated from the capacitance and sum of potentials acting on the sample. The sample geometry of gated 2D heterostructures allows them to be treated as parallel plate capacitors, where hBN is commonly used as a dielectric and has a dielectric constant of $\varepsilon_{\text{hBN}} = 4.5$ [29, 30]. The capacitance per unit area of the heterostructure can be calculated using,

$$C(Fcm^{-2}) = \frac{\varepsilon_{\text{hBN}} \varepsilon_0}{d_{\text{hBN}}},$$

(5.1)

where $d_{\text{hBN}}$ is the hBN thickness. The thickness of the dielectric in these devices is very important as 1 nm of hBN can maintain up to 0.7 V before breaking down [29].

The applied gate voltage, $V_G$, causes a shift in the semiconductor’s chemical potential. For small values of $V_G$, where the chemical potential falls within the band gap of the semiconductor, the electronic bands within the band structure shift linearly. Above a threshold value of $V_G$, the electrostatic shift of the bands is large enough so that the CBM of the semiconductor becomes aligned with the Fermi energy of the graphene (ground) contact and the semiconductor becomes conducting. At this point, due to the large DOS in the conduction band, any change in the chemical potential is significantly reduced for any further increase in $V_G$ [118]. Therefore, any change in chemical potential becomes negligible and the effective potential acting on the sample can be calculated from $V_G$ minus the shift of the bands, $V_G - \Delta E_T$, where $\Delta E_T$ can be directly measured from the µARPES spectra at $\Gamma$, Fig. 5.3 a) and b) show how $\Delta E_T$ and $V_G - \Delta E_T$ change with $V_G$, for the MoSe$_2$/WSe$_2$ device. The carrier concentration of electrons, $n_e$, can then be calculated using the equation,

$$n_e(cm^{-2}) = \frac{C}{e}\left|\left(V_G - \frac{\Delta E_T}{e}\right)\right|,$$

(5.2)

and is plotted in Fig. 5.3 c) against $V_G$ for the MoSe$_2$/WSe$_2$ heterobilayer. Similarly, for hole doping, any changes in the chemical potential are significantly reduced once the VBM of the semiconductor reaches the Fermi energy of the graphene (ground) contact and the same equation can be used to calculate the carrier concentration of holes, $p_v$.

The corresponding photocurrent is plotted in Fig. 5.3 d). Close to $V_G = 0$ V, the increase in photocurrent is due to charge carriers in the encapsulating graphene layer from hBN pair generation and an additional photoemission induced
Figure 5.3: a) Shift of the bands at $\Gamma$, $\Delta E_{\Gamma}$, b) effective potential, $V_G - \Delta E_{\Gamma}$, c) carrier concentration, $n_G$, and d) photocurrent plotted against $V_G$ for the MoSe$_2$/WSe$_2$ heterobilayer. Pale blue regions mark the gate voltage at which the heterobilayer becomes conducting.

We measure photocurrent from the graphene as we are required to measure close to the edge of the graphene flake for a stable conductivity of the semiconductor, therefore the beam spot partially illuminates the encapsulating graphene layer. At the threshold voltage (pale blue regions), the semiconducting layer becomes conducting and an increase in photocurrent is observed. For any further increase in gate voltage, the photocurrent is a combination of both the graphene and the semiconducting layer.

### 5.2.3 Determining the Q-K conduction band alignment

$\mu$ARPES measurements were acquired at five different gate voltages, above the threshold voltage, for the MoSe$_2$/WSe$_2$ heterobilayer. Fig. 5.4 a) shows the $\mu$ARPES energy-momentum slices for the five different gate voltages and Fig. 5.4 b) shows the corresponding $\mu$ARPES constant energy maps at the Fermi energy. The lowest gate voltage at which the CBM, $K$, is observed was $+1.2$ V, in agreement with the
Figure 5.4: a) μARPES energy-momentum slices along the high symmetry direction shown for the aligned MoSe$_2$/WSe$_2$ heterobilayer at multiple gate voltages defined below each spectra. The scale bars are 0.2 Å$^{-1}$. The red overlaid lines in the μARPES energy-momentum slice at +4 V, are a DFT calculation of the MoSe$_2$/WSe$_2$ band structure from reference [110], where the DFT calculated valence band is aligned with the MoSe$_2$ valence band at $\mathbf{K}$, and the DFT calculated conduction band is aligned with the CBM in the μARPES spectra. b) μARPES constant energy maps at the Fermi energy at the gate voltages defined in the bottom right-hand corner. The green lines mark the Brillouin zone boundaries of the MoSe$_2$ layer. c) DFT calculated conduction band for the MoSe$_2$/WSe$_2$ heterobilayer with the position of the chemical potential marked by the grey dashed lines at +1.2 and +3 V. The scale bar is 0.2 Å$^{-1}$.

measured photocurrent in Fig. 5.3 d). At $V_G = +3$ V, the conduction band at $\mathbf{Q}$ becomes visible in the μARPES spectra. Fig. 5.4 c) shows a DFT calculation of the conduction band for the MoSe$_2$/WSe$_2$ heterobilayer, performed by Nicholas Hine (University of Warwick) and published in reference [110]. The DFT calculated band structure is also overlaid on the $V_G = +4$ V μARPES spectra in Fig. 5.4 a). We make the assumption that the chemical potential in the heterobilayer is aligned with the CBM at +1.2 V and then aligned with the conduction band at $\mathbf{Q}$ at +3 V, as illustrated by the grey dashed lines in Fig. 5.4 c). Therefore, we make the hypothesis that the change in chemical potential between these two gate voltages is equal to the energy difference between $\mathbf{Q}$ and $\mathbf{K}$ in conduction band of the heterobilayer,
At +2 and +4 V, a single replica band of the CBM is observed in the µARPES spectra, highlighted by the orange circles in Fig. 5.4 a) and b). This band is thought to be due to final state photoelectron diffraction as we only see one of the six expected replicas for a moiré potential. It is only present at +2 and +4 V due to small changes in measurement position on the sample. Therefore, the filling of this replica band has been ignored in the following calculations.

Using the carrier concentration calculated from equation 5.2, the energy difference between the chemical potential ($E_F$) and the CBM (or VBM), $E_F - E_C$ (or $E_V - E_F$), can be calculated from the DOS of the conduction band (valence band) and the Fermi-Dirac distribution using the equations:

$$n_c = \int_{E_c}^{\infty} g_c(E) \frac{1}{1 + e^{(E-E_F)/k_BT}} dE$$

(5.3)

and

$$p_v = \int_{-\infty}^{E_v} g_v(E) \frac{1}{1 + e^{(E_V-E_F)/k_BT}} dE.$$ 

(5.4)

For a 2D parabolic band, equations 5.3 and 5.4 can be solved analytically, as the DOS, $g_{2D}$, does not depend on energy. The DOS for a 2D parabolic band is given by:

$$g_{2D} = \frac{g_s g_v m_e^{*}}{\pi \hbar^2},$$

(5.5)

where $g_s$ is the spin degeneracy, $g_v$ is the valley degeneracy and $m_e^{*}$ (hole) is the electron effective mass. Therefore, for a single parabolic band, equations 5.3 and 5.4 can be written as:

$$n_c = g_{2D} k_BT \ln[1 + e^{(E_F-E_C)/k_BT}]$$

(5.6)

and

$$p_v = g_{2D} k_BT \ln[1 + e^{(E_V-E_F)/k_BT}],$$

(5.7)

respectively. Due to the high DOS of the conduction band, $E_F - E_C$ and $E_V - E_F$ are typically only a few tens of meV.

For the MoSe$_2$/WSe$_2$ heterobilayer we populate three 2D parabolic bands in the MoSe$_2$ conduction band when applying a gate voltage of +4 V. Therefore, to
Tabulated in Table 5.2 are the values found for $E_F - E_c$ from equation 5.8 for each carrier concentration at the experimental temperature, $T$, of 80 K. The Fermi-Dirac distribution at a finite temperature of 80 K allows population of the CBM $\sim$7 meV before the chemical potential has reached the energy of the CBM. Hence why we see negative values of $E_F - E_c$ at small gate voltages in Table 5.2.

Fig. 5.5 demonstrates how the change in chemical potential between +1.2 and +3 V is found from the calculated carrier concentrations and equation 5.8. As the value of $E_F - E_c$ depends on $E_{QK}$, $E_{QK}$ is varied in equation 5.8 until its value is equal to the change in chemical potential between +1.2 and +3 V, as demonstrated in Fig 5.5 a) for three different values of $E_{QK}$. From Fig. 5.5 b), $E_{QK}$ is found to be $15.1 \pm 0.6$ meV. The error of $\pm 0.6$ meV considers only the error found from the carrier concentrations. The uncertainty in $E_{QK}$ is also dependent on the values used in equation 5.8 for the effective masses, spin-orbit coupling and temperature.

For monolayer MoSe$_2$ the effective mass of K in the conduction band, $m^*_K$, is widely accepted to be $0.57 m_0$ [33], which is the value used in the calculation. Hetero structuring has been shown to modify carrier effective masses in a report by

<table>
<thead>
<tr>
<th>$V_G$ (V)</th>
<th>$n_G$ ($\times 10^{12}$cm$^{-2}$)</th>
<th>$E_F - E_c$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1.2</td>
<td>0.96 ± 0.05</td>
<td>-11.0 ± 0.4</td>
</tr>
<tr>
<td>+1.5</td>
<td>1.82 ± 0.09</td>
<td>-6.2 ± 0.4</td>
</tr>
<tr>
<td>+2.0</td>
<td>3.5 ± 0.2</td>
<td>-1.0 ± 0.5</td>
</tr>
<tr>
<td>+3.0</td>
<td>6.3 ± 0.3</td>
<td>4.1 ± 0.4</td>
</tr>
<tr>
<td>+4.0</td>
<td>9.0 ± 0.4</td>
<td>7.5 ± 0.4</td>
</tr>
</tbody>
</table>

Table 5.2: Carrier concentrations, $n_G$, and $E_F - E_c$ for five different gate voltages, $V_G$, for the MoSe$_2$/WSe$_2$ heterobilayer. The parameters used in equation 5.8 were $m^*_K = 0.57 m_0$ [33], $m^*_Q = 0.80 m_0$ [169], $\Delta_{SO} = 20$ meV [33], $E_{QK} = 15.1$ meV and $T = 80$ K.
Figure 5.5: a) Carrier concentration against $E_F - E_c$ for three different values of $E_{QK}$ where $m_{K}^* = 0.57 \, m_0$ [33], $m_{Q}^* = 0.80 \, m_0$ [169], $\Delta_{SO} = 20 \, \text{meV}$ [33] and $T = 80 \, \text{K}$. The change in chemical potential, $\Delta \mu$, between $+1.2$ and $+3 \, \text{V}$ is marked on each graph. b) The value of $E_{QK}$ is determined from when the value of $E_{QK}$ used in equation 5.8 equals $\Delta \mu$ between $+1.2$ and $+3 \, \text{V}$, marked by the yellow dashed lines.

Sharma et al. [170]. However, we find no change in effective mass of the valence bands at the Brillouin zone corners between the isolated monolayers and monolayers within the heterobilayer (see Table 5.1). Taking this into consideration, Fig. 5.6 a) shows how $E_{QK}$ changes for values of $m_{K}^*$ between 0.35 and 0.60 $m_0$. From the plot in Fig. 5.6 a) we see a very little change of $\pm 0.2 \, \text{meV}$ in the value of $E_{QK}$ across this wide range of values for $m_{K}^*$.

The effective mass of the conduction band at $Q$, $m_{Q}^*$, gives a greater uncertainty on the value of $E_{QK}$ than $m_{K}^*$. The value used for $m_{Q}^*$ is 0.80 $m_0$, which is found from a paper by J. Wang et al. [169]. This value is determined by taking the effective mass of $Q$ from the individual monolayers and averaging over the two materials contribution to the orbital composition of $Q$ within the heterobilayer ($2/3$ MoSe$_2$, $1/3$ WSe$_2$). Values vary in the literature for the effective mass of $Q$ for the monolayers [33, 169]. Therefore, shown in Fig. 5.6 b) is how $E_{QK}$ changes for values of $m_{Q}^*$ between 0.50 and 0.80 $m_0$. Varying $m_{Q}^*$ across this range changes $E_{QK}$ by $\pm 0.8 \, \text{meV}$.

The spin-orbit coupling of the MoSe$_2$ conduction band at $K$, $\Delta_{SO}$, adds another small degree of uncertainty to the value of $E_{QK}$. A value of 20 meV is used,
Figure 5.6: The value of $E_{QK}$ against a) the effective mass of the MoSe$_2$ conduction band at $K$, $m^*_K$, b) the effective mass of the MoSe$_2$ conduction band at $Q$, $m^*_Q$, c) the spin-orbit coupling of the MoSe$_2$ conduction band at $K$, $\Delta_{SO}$, and d) the temperature, $T$. The error bars are equal to $\pm$ 0.6 meV which are from the error in carrier concentration. (The parameters used when not being varied were $m^*_K = 0.57 m_0$ [33], $m^*_Q = 0.80 m_0$ [169], $\Delta_{SO} = 20$ meV [33] and $T = 80$ K).

which is largely agreed upon for the monolayer [33, 171, 172, 173]. Depending on the calculation method used, values for $\Delta_{SO}$ can vary by a few meV [33]. Therefore, Fig. 5.6 c) shows how the value of $E_{QK}$ changes for values of $\Delta_{SO}$ between 15 and 25 meV. The value of $E_{QK}$ only changes by $\pm$ 0.2 meV for the wide range of $\Delta_{SO}$ values.

The largest uncertainty in $E_{QK}$ comes from the sample temperature. The temperature of the sample is measured using a thermocouple connected to the back of the sample holder within the analysis chamber. During these measurements, the thermocouple read 80 K. However, the sample itself is large due to the chip carrier that holds the Si wafer. Therefore, the temperature of the sample during measurements is not well known. Other factors such as the current running through the sample when a gate voltage is applied and heating from the incident photon beam are also likely to increase the sample temperature by a few degrees. The sample temperature is likely to be anywhere between 80 and 100 K. Increasing the temperature in equation 5.8 from 80 to 100 K significantly increases the value of $E_{QK}$ by 3.2 meV, as shown in Fig. 5.6 d).

Adding together all the uncertainties from the carrier concentration, effective mass, spin-orbit coupling and temperature, we determined the uncertainty of $E_{QK}$ to be $\pm$ 4 meV, giving a resultant value of $E_{QK} = 15 \pm$ 4 meV, for the MoSe$_2$/WSe$_2$ heterobilayer.

5.2.4 Determining $E_F$

One challenge when studying the $\mu$ARPES spectra of electron doped semiconductors is defining the Fermi energy, $E_F$. Fig 5.7 a) shows a $\mu$ARPES energy-momentum slice
in kinetic energy for the MoSe$_2$/WSe$_2$ heterobilayer at $+2\, \text{V}$. An EDC was taken over the CBM, which is displayed in Fig 5.7 b). The peak in photoemission intensity from the CBM is highlighted within the black dashed box and is a product of the Fermi edge and a peak in photoemission intensity from the position of the conduction band. Therefore, the EDC is fitted with a product of a Gaussian function, to represent the conduction band edge, and a Sigmoid function, to represent the Fermi edge. Fig. 5.7 c) shows the fitting of the CBM and the fitting equation is

$$f(E) = I_N + \left[ I_0 \exp \left( -\frac{(E - (E_F - E_c))}{w} \right) \right] \frac{1}{1 + \exp((E - E_F)/rate)},$$  \hspace{1cm} (5.9)

where $E$ is the kinetic energy, $I_N$ is the background noise on the detector, $I_0$ is the normalised photoemission intensity of the CBM, $w$ is the width of the Gaussian function and $rate$ is the steepness of the Sigmoid function. The value of $E_F$ is found in kinetic energy and used to convert the energy scale into binding energy. To minimize fitting parameters a Gaussian function was used rather than a Voigt function as the resolution at finite temperature dominates the shape of the bands in the EDC due to atomic vibrations and sample disorder. The same Sigmoid function was used to fit the CBM at different gate voltages on the same sample, as shown in Fig. 5.7 d) (graphs now converted and displayed in binding energy, $E - E_F$). The position in energy of the CBM is shown by the purple dashed line and the position of $E_F$ is shown by the yellow dashed line. Their difference in energy is held fixed at the values calculated for $E_F - E_c$ at each carrier concentration, tabulated in Table 5.2.

The uncertainty in the position of $E_F$ is largely dominated by the value of the $rate$ parameter in the Sigmoid function used to the fit the conduction band. The $rate$ parameter is equivalent to $k_B T$ in the Fermi-Dirac distribution. Fitting the conduction band in the µARPES spectra using the calculated Fermi-Dirac distribution at the experimental temperature of 80 K, produces a very poor fit of the conduction band, as shown by Fig. 5.8 a). By comparing the Fermi-Dirac distribution to a µARPES measurement of a Fermi edge of a metal we can see why.

Fig. 5.8 b) shows a µARPES energy-momentum slice taken on a metal and a Sigmoid fit of the integrated EDC. The Sigmoid fit of the integrated EDC is very broad compared to the Fermi-Dirac distribution. This is because in the µARPES measurement there is broadening due to the resolution of the analyser and the band width of the photon source. However, the Sigmoid fit of the metal Fermi edge does provide a good representation of the data when used in equation 5.9 to fit the conduction band, Fig. 5.8 c).
Figure 5.7: a) µARPES energy-momentum slice of the MoSe$_2$/WSe$_2$ heterobilayer at $V_G = +2\, \text{V}$, along the high symmetry direction defined. The scale bar is 0.2 Å$^{-1}$. b) EDC taken along the blue dashed line in a). The peak in photoemission intensity from the CBM is highlighted in the black dashed box and is plotted in c). c) The fit of the CBM is shown in black, along with the Gaussian and Sigmoid functions used, where $E_F - E_c$ is equal to -1.0 meV. d) EDCs taken over the CBM for the five different gate voltages. The value of $E_F - E_c$ used for each gate voltage is noted above each graph. Insets are a magnified view to show the separation between $E_F$ and $E_c$.

Therefore, to correctly fit the conduction band, the Sigmoid function used in equation 5.9 should be the Fermi-Dirac distribution broadened by the experimental resolution. Allowing the rate parameter to be free in equation 5.9 shows how broadening is also dependent on gate voltage, as shown in Fig 5.8 d). As $w$ and rate both depend on the broadening of the bands in the spectra, the Sigmoid function found for the +2 V fit was chosen to fit the CBM for all five gate voltages (Sigmoid function used in Fig. 5.7). Fig. 5.8 e) compares the +2 V Sigmoid function to the calculated Fermi-Dirac distribution.

Excluding fits using the calculated Fermi-Dirac distribution, due to its poor representation of the data, a comparison of the values found for $E_F$ from using each of different Sigmoid functions are shown in Fig. 5.8 f). From this graph, we conclude that the uncertainty in the position of $E_F$ in our µARPES spectra of conducting semiconductors is ±30 meV.
Figure 5.8: a) Fit of the MoSe\textsubscript{2}/WSe\textsubscript{2} CBM at +2 V, using the calculated Fermi-Dirac distribution, f(E). b) µARPES energy-momentum slice taken at the Fermi energy on a metal. The scale bar is 0.2 Å\textsuperscript{-1}. To the right is the integrated EDC of the spectrum (red line) with a Sigmoid fit over the Fermi energy (blue). N. P. I. stands for normalised photoemission intensity. c) Fit of the MoSe\textsubscript{2}/WSe\textsubscript{2} CBM at +2 V, using the Sigmoid fit for the integrated EDC from the metal Fermi edge image. d) The resultant Sigmoid functions for each gate voltage when allowing all parameters in equation 5.9 to fit freely. e) Comparison between the +2 V Sigmoid fit and the calculated Fermi-Dirac distribution. f) A comparison of the different values of $E_F$ found for the different Sigmoid functions used to fit the CBM.

Fig 5.9 shows how the values used for effective mass, spin-orbit coupling and temperature when calculating $E_F - E_c$, also add a small degree of uncertainty to the position of $E_F$. As described in the previous section, varying the effective mass, spin-orbit coupling, and temperature change the value found for $E_{QK}$ and hence $E_F - E_c$. As seen from Fig. 5.9 a) and b), the effective mass of the bands only change the position in $E_F$ by a couple of meV. The spin-orbit coupling has an even smaller effect on the position of $E_F$, Fig. 5.9 c), and the temperature is the most significant parameter, shifting $E_F$ by a maximum of 3 meV, Fig. 5.9 d). However, all of these uncertainties are far outweighed by the uncertainty from the Sigmoid function used in equation 5.9 to fit the CBM. Therefore, the uncertainty in $E_F$ remains ± 30 meV.
Figure 5.9: a) Change in $E_F$, $\Delta E_F$, against the effective mass of the MoSe$_2$ conduction band at $K$, $m^*_K$, b) the effective mass of the MoSe$_2$ conduction band at $Q$, $m^*_Q$, c) the spin-orbit coupling of the MoSe$_2$ conduction band at $K$, $\Delta SO$, and d) the temperature, $T$. (The parameters used when not being varied were $m^*_K = 0.57 \, m_0$ [33], $m^*_Q = 0.80 \, m_0$ [169], $\Delta SO = 20 \, \text{meV}$ [33] and $T = 80 \, \text{K}$). The rate of the Sigmoid function was held fix as the $+2 \, \text{V}$ Sigmoid function. The legend is displayed on the right.

5.2.5 Band structure changes with electron doping

From the $\mu$ARPES spectra shown in Fig. 5.4 a), changes in band alignment with $V_G$ are studied. Fig. 5.10 a) shows EDCs taken at $\Gamma$ for the MoSe$_2$/WSe$_2$ heterobilayer at each measured gate voltage. Once the heterobilayer has become conducting (+1.2 V), the bands at $\Gamma$ shift to a higher binding energy as $V_G$ is increased to +1.5 V. For any further increase in gate voltage, any band shifts are significantly reduced. No measurable difference was found for $\Delta \Gamma$ across all gate voltages, suggesting the hybridisation between the MoSe$_2$ and WSe$_2$ layers is unchanged with increased electron doping and electric field.

Increasing the carrier concentration in the MoSe$_2$/WSe$_2$ heterobilayer causes a renormalisation of the MoSe$_2$ band structure at $K$. Fig. 5.10 b) shows EDCs extracted at $K$ for each measured gate voltage. Three peaks in photoemission intensity are observed for the valence band; the VBM from the WSe$_2$ layer and the two spin-split MoSe$_2$ bands. The energy of the valence bands are extracted by fitting the valence band with a triple Lorentzian function. The peak in photoemission intensity from the individual bands is displayed below each valence band in purple for WSe$_2$ and green for the two MoSe$_2$ bands. Like $\Gamma$, we observe an initial shift in the band energy between +1.2 and +1.5 V, but only for the MoSe$_2$ bands. As the gate voltage is increased further, the MoSe$_2$ valence bands continue to move to lower binding energies, reducing the valence band offset between the MoSe$_2$ and WSe$_2$ layers at $K$.

Carrier concentration renormalisation of the band structure is observed only for the MoSe$_2$ valence bands due to the electron doping being in that layer, leaving the WSe$_2$ band structure unchanged. Therefore, due to the type II band alignment,
Figure 5.10: a) EDCs taken at $\Gamma$ for the MoSe$_2$/WS$_2$ heterobilayer at multiple gate voltages defined above each EDC. A double Lorentzian fit of the bands is overlaid in black. b) EDCs taken at $K$ of the MoSe$_2$/WS$_2$ heterobilayer at multiple gate voltages defined above each EDC. A triple Lorentzian fit of the bands is overlaid in black. The position of the individual valence bands from the MoSe$_2$ and WSe$_2$ layers are shown by the green and purple single Lorentzian profiles below each EDC. c) Measured band gaps against carrier concentration. To the right, a schematic of the valence band offset defining the intralayer and interlayer band gaps.

The band gap of the heterobilayer remains unchanged with increased carrier concentration. From Fig. 5.10 c) we see the interlayer band gap remains constant around 1.43 eV, whereas the intralayer MoSe$_2$ band gap, $E_G$ MoSe$_2$, decreases by 0.2 eV for an increase in carrier concentration from $1 \times 10^{12}$ to $9 \times 10^{12}$ cm$^{-2}$.

Included in Fig. 5.10 c) is the measured interlayer band gap for the WSe$_2$/MoSe$_2$ heterobilayer. We find the same interlayer band gap even though each TMD layer is at a slightly different potential due to the different stacking order.

### 5.2.6 Doping WS$_2$/MoSe$_2$ heterobilayers

The band structure of a WS$_2$/MoSe$_2$ heterobilayer was also investigated using $\mu$ARPES with in-situ electrostatic gating. The sample was fabricated by Paul...
Nguyen at the University of Washington, using the mechanical exfoliation and PDMS dry transfer technique [51], and has the same sample structure as shown in Fig. 5.1 a) where the hBN dielectric has a thickness of $5.5 \pm 0.5$ nm. An optical image of the two TMD monolayers and the encapsulating graphene flake can be seen in Fig. 5.1 a). The monolayer MoSe$_2$ flake, outlined in green, was fractured into multiple smaller flakes during fabrication. A SPEM image of the region enclosed by the white dashed box is shown in Fig. 5.11 b) and the largest exposed heterobilayer region is labelled HS, from which all µARPES measurements were obtained with a photon energy of 27 eV and a sample temperature of 80 K.

µARPES energy-momentum slices were acquired along the high symmetry directions defined in Fig. 5.11 c) to determine the valence band parameters and band alignments in the undoped WS$_2$/MoSe$_2$ heterobilayer. As WS$_2$ is the top layer of the heterobilayer, the bands originating from the WS$_2$ layer can clearly be resolved. Fig. 5.11 d) shows a µARPES energy-momentum slice along the $\Gamma$-K$_{WS_2}$ direction, with the bands that originate from the WS$_2$ layer, away from $\Gamma$, identified by the overlaid band fits in blue. We find $\Delta_{SO} = 0.44 \pm 0.03$ eV and $m_\star_K = 0.49 \pm 0.05 m_0$, consistent with values found for the WS$_2$ monolayer [118].

Due to the surface sensitivity of ARPES, the electronic bands from the MoSe$_2$ layer are more difficult to resolve. Fig. 5.11 e) shows a µARPES energy-momentum slice along the $\Gamma$-K$_{MoSe_2}$ direction of the heterobilayer region. Mirrored on the left is the same spectrum but with the photoemission intensity displayed in a logarithmic scale. The bands from the MoSe$_2$ layer, away from $\Gamma$ can only be seen using a logarithmic scale and are highlighted by the overlaid green dashed line. The position of the MoSe$_2$ K point within the heterobilayer region was determined from the exposed monolayer region, marked by the pink circle in Fig. 5.11 b). A µARPES energy-momentum slice of the monolayer MoSe$_2$ region is shown in Fig. 5.11 f) and the bands can clearly be resolved. Due to the fracturing of the MoSe$_2$ flake during fabrication the twist angle of the MoSe$_2$ layer with respect to the WS$_2$ layer is likely to differ in the monolayer and heterobilayer regions by $\sim 1-2^\circ$. This adds a small uncertainty in determining the band parameters of the MoSe$_2$ band structure in the heterobilayer.

The VBM of the WS$_2$/MoSe$_2$ heterobilayer is found to be at $\Gamma$, with a binding energy of $1.36 \pm 0.03$ eV. The band edges at $K_{WS_2}$ and $K_{MoSe_2}$ are found to be very close in energy, and within error of one another, with values of $1.41 \pm 0.03$ eV and $1.47 \pm 0.10$ eV, respectively. Multiple optical studies of the WS$_2$/MoSe$_2$ heterobilayer report $K_{MoSe_2}$ to be the valence band edge at $K$ [174, 175, 176, 177, 178]. The discrepancy with our measured values is likely to be due to a combination
Figure 5.11: a) Optical image of the WS$_2$/MoSe$_2$ heterobilayer. b) SPEM image of the white dashed box region in a). The encapsulating graphene flake is outlined in black, the monolayer WS$_2$ is outlined in blue and the monolayer MoSe$_2$ is outlined in green. The scale bar is 5 µm. c) Brillouin zone schematic, defining the high symmetry directions. d) µARPES energy-momentum slice along Γ-K$_{WS_2}$ of the heterobilayer, HS, region. Band fits of the WS$_2$ bands are overlaid in blue. e) On the right, a µARPES energy-momentum slice along Γ-K$_{MoSe_2}$ of the HS region. On the left, a mirror of the right hand side, but with the photoemission intensity displayed in a logarithmic scale. Green dashed line is a line to guide the line for the MoSe$_2$ bands around K$_{MoSe_2}$. f) µARPES energy-momentum slice along Γ-K$_{MoSe_2}$ on the monolayer MoSe$_2$ region identified by the pink circle in b). Band fits are overlaid in green. The scale bars overlaid on the µARPES spectra are 0.2 Å$^{-1}$.

of the poor resolution of the MoSe$_2$ bands in the heterobilayer, resulting in the two spin-split bands being treated as a single band, and the uncertainty in the relative twist angle with WS$_2$.

The CBM in the isolated WS$_2$ and MoSe$_2$ monolayers are predicted to be close to degenerate in energy and located at the Brillouin zone corners. In the heterobilayer, at a carrier concentration of (4.4 ± 0.4) ×10$^{12}$ cm$^{-2}$, we populate the conduction band in both WS$_2$ and MoSe$_2$ layers. This carrier concentration is achieved at a gate voltage of +1.75 V, and is the lowest gate voltage for which photoemission intensity is observed in conduction band of the heterobilayer. Fig. 5.12 a) and b) show µARPES energy-momentum slices acquired at +1.75 V for the Γ-K$_{WS_2}$ and Γ-K$_{MoSe_2}$ directions, respectively. Weak photoemission intensity is observed at the Brillouin zone corner of each layer. The additional replica conduction band seen close to K$_{MoSe_2}$ in Fig. 5.12 a) is consistent with final state photoelectron
Figure 5.12: a) and b) µARPES energy-momentum slices at $V_G = +1.75$ V along the high symmetry directions $\Gamma$-$K_{\text{WS}_2}$ and $\Gamma$-$K_{\text{MoSe}_2}$, respectively. c) and d) µARPES energy-momentum slices at $V_G = +2.5$ V along the high symmetry directions $\Gamma$-$K_{\text{WS}_2}$ and $\Gamma$-$K_{\text{MoSe}_2}$, respectively. Data presented in a black and white colour scale display the photoemission intensity in a logarithmic scale. Band fits of the WS$_2$ bands are overlaid in blue in b) and d). All scale bars are 0.2 Å$^{-1}$. e) µARPES constant energy map at the Fermi energy for $V_G = +2.0$ V. WS$_2$ and MoSe$_2$ Brillouin zones boundaries marked by the blue and green lines respectively.

diffraction, where the CBM in the MoSe$_2$ layer is scattered by the WS$_2$ reciprocal lattice vector when travelling through the encapsulating WS$_2$ layer.

Fig. 5.12 c) and d) show µARPES energy-momentum slices at a higher gate voltage of +2.5 V, where the conduction band in each layer is now more intense. The valence bands at the Brillouin zone corner of the MoSe$_2$ layer are too weak to be observed in the gated µARPES spectra. However, the electronic bands from the WS$_2$ layer can be resolved. An intralayer direct band gap of 1.87 ± 0.04 eV is found for WS$_2$ at $K$, for a carrier concentration of $(8.9 \pm 0.9) \times 10^{12}$ cm$^{-2}$. Assuming no large renormalisation of the MoSe$_2$ bands at $K$, the interlayer band gap of the heterobilayer is found to be indirect as the VBM remains at $\Gamma$.

Determining the conduction band alignment of $K_{\text{MoSe}_2}$ and $K_{\text{WS}_2}$ is challenging as the energy difference is comparable to the energy resolution of the beamline. Considering only the magnitude of the photoemission intensity, it would appear the CBM resides in the MoSe$_2$ layer, rather than WS$_2$. Fig. 5.12 e) shows a µARPES constant energy map at the Fermi energy for $V_G = +2.0$ V. Due to the short acquisition time used for this measurement, photoemission intensity is only observed
at the corners of the MoSe$_2$ Brillouin zone, suggesting a larger carrier concentration is within the MoSe$_2$ layer. As MoSe$_2$ is the lower layer of the heterobilayer and therefore has reduced photoemission intensity compared to the WS$_2$, and we know the WS$_2$ conduction band does have a high cross section for the photon energy and polarisation used, the CBM appears to be within the MoSe$_2$ layer of the heterobilayer, forming a type I band alignment between K points. Type I [174] and type II [176, 177] band alignments have been reported for WS$_2$/MoSe$_2$ heterobilayers, as well as changes in band alignment for increased electron doping [178].

As the conduction band in both layers of the WS$_2$/MoSe$_2$ heterobilayer are populated with an applied gate voltage, we predict both the WS$_2$ and MoSe$_2$ valence bands will renormalise with increased electron doping, changing both the intra- and inter-layer band gaps. From the two gate voltages we have acquired µARPES measurement for, we do see a shift of the valence bands at Γ and K$_{WS_2}$ to lower binding energies for increased V$_G$. Fig. 5.13 shows EDCs taken at each high symmetry position for the two different gate voltages. Comparing the EDCs for each gate voltage, $E_\Gamma - E_K$ is reduced from 0.06 eV, at a carrier concentration of $4.4 \times 10^{12}$ cm$^{-2}$ (+1.75 V), to 0.02 eV, at a carrier concentration of $8.9 \times 10^{12}$ cm$^{-2}$ (+2.5 V). Therefore, $E_\Gamma$ and $E_K$ become close to degenerate in energy as a result of the carrier concentration renormalisation of the WS$_2$ band structure at K.

5.3 Conclusion

This chapter has shown how in-situ electrostatic gating during µARPES measurements can be used to determine band alignments and band gaps of TMD heterobi-
layers and observe changes in band structure with electron doping.

MoSe$_2$/WSe$_2$ and WSe$_2$/MoSe$_2$ are found to be direct band gap semiconductors where the VBM and CBM reside at the Brillouin zone corners of the WSe$_2$ and MoSe$_2$ layers, respectively, forming a type II band alignment. Additionally, the band alignment between high symmetry points $Q$ and $K$ in the MoSe$_2$ conduction band are found by determining the change in chemical potential between the carrier concentrations required to populate each band. Renormalisation of the MoSe$_2$ band structure is observed for increasing carrier concentration in the MoSe$_2$/WSe$_2$ heterobilayer, reducing the valence band offset at $K$ between the two monolayers, while the interlayer band gap remains constant.

Defining the Fermi energy still poses a challenge for determining band energies of electrostatically doped semiconductors. We find an uncertainty of ± 30 meV for the values found for the Fermi energy in our gated µARPES spectra.

For the undoped WS$_2$/MoSe$_2$ heterobilayer, we find the VBM to be at $\Gamma$. We show the CBM is likely to reside in the MoSe$_2$ layer at $K$, however, due to the small energy differences in band alignments within this heterobilayer and that the MoSe$_2$ valence bands at $K$ were not observable when electron doped, further measurements are required to confirm how the band alignments change with increased carrier concentration.

Understanding the changes in band alignment with electron doping is important for the fabrication of optoelectronic devices. Band gap engineering has been studied for other 2D materials such as WSe$_2$ [118], MoS$_2$ [179] and black phosphorus [180], but in contrast to these, the MoSe$_2$/WSe$_2$ heterobilayer provides a unique property where the band gap remains independent of electron doping.
Chapter 6

Moiré effects observed in µARPES spectra of gated 2D heterostructures

6.1 Introduction

Recently, interest has started to grow around the WS$_2$/WSe$_2$ heterobilayer for its optical properties [181], moiré physics [69, 70] and correlated states [182]. Like MoSe$_2$/WSe$_2$, described in the previous chapter, the WS$_2$/WSe$_2$ heterobilayer is expected to have a type II band alignment, where the VBM is well known to reside at the Brillouin zone corners of the WSe$_2$ layer and some confusion falls around whether the CBM is at Q or K in the WS$_2$ layer. Recently, the ground state interlayer exciton has been shown to be the K-Q exciton [181].

Compared to other combinations of semiconducting TMD heterobilayers, the WS$_2$/WSe$_2$ heterobilayer hosts the strongest moiré potential [174]. The strong moiré potential makes this system an ideal platform to study moiré excitons, where there emission energy can be tuned by the relative twist angle between the layers [75, 158]. The energy of the moiré excitons in the WS$_2$/WSe$_2$ heterobilayer has also been shown to be tunable with electron doping [75].

The lattice mismatch between aligned WS$_2$/WSe$_2$ ($a_{WS_2} = 3.16$ Å, $a_{WSe_2} = 3.291$ Å [33]) creates a relatively large moiré period (~8 nm) that does not vary significantly with small changes in twist angle. Due to the large moiré period, flat bands, formed by hybridisation of primary and replica bands, are predicted to persist over a wide range of twist angles. In comparison to TBG, where flat bands are only present near the 'magic' angle (see Section 1.6) and are not well
isolated due to the zero-gap band structure, the WS$_2$/WSe$_2$ heterobilayer provides a promising platform to study strongly correlated states. Fractional electron filling of WS$_2$/WSe$_2$ flat bands has recently shown emergent quantum behaviour. At half filling, one electron per moiré band, evidence of a Mott insulating state has been reported [89]. Away from half filling, many other insulting states have been observed [182], along with additional stripe phases which have also been seen in TBG and other strongly correlated systems [90].

Gated STS has already been used to study the electrical tunability of a WSe$_2$/WS$_2$ moiré superlattice [70], however, STS does not reveal momentum dependence or distinguish high symmetry points. In-situ electrostatic gating during μARPES measurements allows us to directly study the momentum-dependent band structure of the moiré superlattice with electron doping.

In this chapter we use μARPES with in-situ electrostatic gating to study band alignments and moiré effects within twisted WS$_2$/WSe$_2$ heterobilayers, as well as the effect the moiré potential has on neighbouring 2D materials.

6.2 Results and Discussion

6.2.1 WS$_2$/WSe$_2$ sample design and band structure

Three WS$_2$/WSe$_2$ heterobilayer devices, with twist angles of approximately 2°, 6° and 9°, were fabricated by Paul Nguyen and Heonjoon Park at the University of Washington, using mechanical exfoliation and the PDMS dry transfer technique [51].
Figure 6.2: a) SPEM (top) and SPIM (bottom) images of the WS$_2$/WSe$_2$ heterobilayer at multiple gate voltages defined at the top of each SPEM image. The scale bar is 5 µm. The photocurrent of the heterobilayer (red) and the energy of the upper valence band at Γ of the heterobilayer (black) are extracted from the region enclosed by the black dashed box overlaid on each SPEM image and are plotted against gate voltage, $V_G$ in b).

In each device, the WS$_2$/WSe$_2$ heterobilayer is sandwiched between graphene and a thick hBN dielectric with a thickness of 8.3 ± 0.5 nm. The resultant heterostructure is stacked on top of a graphite back gate and placed between two patterned platinum electrodes on a SiO$_2$/Si substrate, as shown in Fig. 6.1 a).

The partially encapsulating graphene flake was cut using AFM into a comb-like structure before stacking, for more effective grounding of the WS$_2$/WSe$_2$ heterobilayer. An optical image of device 1 (6° twist angle) is shown in Fig 6.1 b) and an outline of the graphene flake is shown in black. This comb-like graphene structure exposes WS$_2$/WSe$_2$ heterobilayer regions ∼3 µm in width, from which µARPES measurements were obtained with a photon energy of 27 eV and a sample temperature of 80 K.

The heterobilayer becomes uniformly conducting between the graphene fingers when a sufficiently high gate voltage, $V_G$, is applied to the sample. Fig. 6.2
Figure 6.3: a) Brillouin zone schematic showing the relative orientation of the WS$_2$ and WSe$_2$ layers. b) and c) µARPES energy-momentum slices in the high symmetry directions defined at $V_G = 0$ V and $V_G = +3$ V, respectively. The dotted red, blue and black lines overlaid in b) are fits of the electronic bands. The dashed line is a line to guide the eye, highlighting the position of the lower WSe$_2$ band at K. Overlaid in c) are the fits of the electronic bands in b) shifted by $\Delta E_G = 0.861$ eV. Data presented in a black and white colour scheme shows the photoemission intensity in a logarithmic scale. The scale bars are 0.2 Å$^{-1}$.

a) shows multiple SPEM and scanning photocurrent microscopy (SPIM) images at increasing gate voltages to demonstrate how the photocurrent changes within the heterostructure. In Fig. 6.2 b), the energy of the upper valence band at $\Gamma$ of the heterobilayer, and the photocurrent, are taken from the region outlined by the black dashed box in Fig. 6.2 a) and plotted against $V_G$. As the chemical potential moves through the band gap of the heterobilayer the bands shift linearly down in kinetic energy with increased $V_G$, until the chemical potential becomes aligned with the CBM of the heterobilayer, at which point the heterobilayer becomes conducting. From Fig. 6.2 b) we see that the heterobilayer becomes conducting at around $V_G = +1.75$ V.

Band alignments were investigated for the undoped WS$_2$/WSe$_2$ heterobilayer, in device 1, along the $\Gamma$-$K_{WS_2}$ and $\Gamma$-$K_{WSe_2}$ high symmetry directions, defined in Fig. 6.3 a). µARPES energy-momentum slices of the undoped WS$_2$/WSe$_2$ heterobilayer are shown in Fig. 6.3 b). The lines overlaid in blue and red show the
electronic bands that originate from the WS$_2$ and WSe$_2$ layers, respectively. We find the VBM resides within the WSe$_2$ layer at K, as expected, with a valence band offset of $0.58 \pm 0.04$ eV to the WS$_2$ valence band edge at K. The spin-orbit coupling in the WS$_2$ layer is found to be $0.44 \pm 0.04$ eV, in agreement with values found for the monolayer [118]. The two bands observed at Γ are separated by $0.56 \pm 0.04$ eV in energy due to the hybridisation between the WS$_2$ and WSe$_2$ layers. All band alignments can be found in Table 6.1.

A gate voltage was applied to populate the electronic states within the conduction band and hence determine the CBM. µARPES energy-momentum slices of the electron doped WS$_2$/WSe$_2$ heterobilayer are shown in Fig. 6.3 c). A type II band alignment is found, where the CBM is observed within the WS$_2$ layer at K, and not at Q like the TMD homobilayers [118]. We measure the direct band gap, at a carrier concentration of $(6.4 \pm 0.4) \times 10^{12}$ cm$^{-2}$, to be $1.58 \pm 0.03$ eV. At this carrier concentration, weak photoemission intensity is also observed at the Q point within the WS$_2$ conduction band. We find the Q-K conduction band alignment to be $7.0 \pm 0.8$ meV, using the method described in Section 5.2.3.

A small renormalisation of the WS$_2$ valence bands at K can also be seen by comparing $E_{\Gamma} - E_{K\text{WS}_2}$ for the doped and undoped µARPES spectra. The red, blue and black dotted lines overlaid in Fig. 6.3 b) are the same band fits from the undoped spectra but shifted by the electrostatic shift of the bands at Γ, $\Delta E_{\Gamma} = 0.861$ eV. In the undoped spectra, $E_{\Gamma} - E_{K\text{WS}_2} = -0.15 \pm 0.01$ eV, whereas in the electron doped spectra, $E_{\Gamma} - E_{K\text{WS}_2} = -0.03 \pm 0.01$ eV. The relative position of the electronic bands from the WSe$_2$ layer appear unchanged, giving a smaller valence band offset of $0.46 \pm 0.04$ eV in the doped heterobilayer at $V_G = +3$ V. This renormalisation within the WS$_2$ layer is due to populating the electron states in the WS$_2$ conduction band, as seen for the MoSe$_2$/WSe$_2$ heterobilayer in Section 5.2.5, and has been seen before for alkali doping of WS$_2$ on hBN [117].

6.2.2 Dispersion of the conduction band minimum

Looking more closely at the CBM in device 1, the dispersion of the conduction band is visible. Fig. 6.4 a) shows the same µARPES energy-momentum slice as shown in Fig. 6.3 c) but with no averaging in momentum perpendicular to the direction of the slice. The region around the CBM is enlarged and shown in Fig. 6.4 b). EDCs were extracted at the positions marked by the red ticks at the bottom of Fig. 6.4 b) and are displayed in Fig. 6.4 c). The photoemission intensity observed is a product of the Fermi edge and a peak in photoemission intensity from the position of the conduction band. Therefore, each EDC was fitted using a product of a Gaussian
Figure 6.4: a) µARPES energy-momentum slice along the high symmetry direction defined at $V_G = +3$ V with no averaging in momentum perpendicular to the direction of the slice. The scale bar is 0.2 Å$^{-1}$. The region inside the green dashed box is enlarged in b). The scale bar is 0.05 Å$^{-1}$. The photoemission intensity in a) and b) are displayed in a logarithmic scale. c) EDCs taken across the CBM at the positions marked by the red ticks in b). The blue lines overlaid are the product of a Gaussian function and Sigmoid function. d) The peak in photoemission intensity (red data points) and the position of the CBM (black data points) extracted from the fits in c).

function to represent the conduction band edge and a Sigmoid function to represent the Fermi edge (equation 5.9). The same Sigmoid function was used to fit all EDCs. The extracted values for the expected conduction band edge and the overall peak in photoemission intensity (maximum of the Gaussian-Sigmoid product) are plotted in Fig. 6.4 d) and fitted with a parabola. The parabolic fits of each data set are also overlaid in Fig. 6.4 b). Finding the effective mass from the parabolic fit of the conduction band position gives a value of $0.13 \pm 0.02 m_0$.

The electron effective mass of monolayer WS$_2$ is predicted by first principle calculations to be approximately double that of the value determined by these measurements [33]. Further measurements are required to determine whether the effective mass of the conduction band edge is indeed smaller than expected or whether this is due to a measurement artefact. As the conduction band edge at $\mathbf{K}$ in the TMDs has out-of-plane orbital character (see Section 1.4.1), the effective mass of the band edge could be reduced due to hybridisation between the layers. Furthermore,
curvature of the conduction band edge has not been observed for WS$_2$ monolayers at this carrier concentration, suggesting the effective mass is lower in the WS$_2$/WSe$_2$ heterobilayer.

### 6.2.3 Moiré effects

Further careful inspection of the conduction band in device 1 reveals replica bands of the CBM, despite no evidence of replica bands in the valence band of either the doped or undoped µARPES spectra. Fig. 6.5 a) shows a µARPES constant energy map at the Fermi energy. Three weak replica bands, marked by the orange circles, can be seen around the CBM at positions that correspond to the moiré vector, $\mathbf{G}_M$, of the two TMDs. A µARPES energy-momentum slice is shown in Fig. 6.5 b) along the direction of the vector labeled $\mathbf{G}_M$ in Fig. 6.5 a). The moiré vector is found to be $0.25 \pm 0.04$ Å$^{-1}$ from the average displacement of the replica CBMs from the primary CBM, which using the lattice constants $a_{\text{WS}_2} = 3.16$ Å [33] and $a_{\text{WSe}_2} = 3.291$ Å [33] gives a twist angle of $6 \pm 1^\circ$ [67], in agreement with the relative orientation determined from the valence band structure. Fig. 6.5 c) shows a schematic of the Brillouin zone orientation of device 1, defining $\mathbf{G}_M$ and showing the expected position of the WS$_2$ K point moiré replicas for a twist angle of 6°.
As discussed in Chapter 4, moiré effects are challenging to distinguish from final state photoelectron diffraction. As WS₂ is the top layer of the heterobilayer, we suspect the replica bands observed here are more likely to be intrinsic features of the band structure and not a result of final state photoelectron diffraction. However, from these results alone we cannot rule out the possibility of their creation being due to photoelectron diffraction via scattering off the underlying WSe₂ layer.

PFM can be used to visualise moiré superlattices [71]. PFM phase images of the exposed WS₂/WSe₂ region, and the graphene/WS₂/WSe₂ region, on this heterostructure were acquired by Paul Nguyen and Heonjoon Park at the University of Washington, and are shown in Fig. 6.6. A moiré wavelength of ~2.5 nm can be seen in the exposed WS₂/WSe₂ PFM phase image, which corresponds to a twist angle of ~7° between the TMD layers, in agreement with the twist angle determined from the position of the moiré replica bands observed within the µARPES spectrum. Interesting, the same moiré wavelength is observed in the PFM phase image of the graphene/WS₂/WSe₂ region, suggesting the moiré potential from the underlying WS₂/WSe₂ heterobilayer impinges on the neighbouring graphene layer.

To further investigate this, a second device (2° twist angle) was fabricated with the WS₂ and WSe₂ layers close to alignment, increasing the moiré potential of the superlattice. µARPES energy-momentum slices along the high symmetry direction Γ-K for the undoped and doped heterobilayer are shown in Fig. 6.7 a) and b), respectively. As, expected, we find a type II band alignment with the CBM at K in the WS₂ layer.

Fig. 6.7 c) shows a µARPES constant energy map of the doped heterobilayer at the Fermi energy, where three moiré replica bands around the CBM are observed...
Figure 6.7: a) µARPES energy-momentum slice of device 2 along the high symmetry direction defined at $V_G = 0$ V. Overlaid red and blue lines are fits of bands from the WSe$_2$ and WS$_2$ layers, respectively. b) µARPES energy-momentum slice along the high symmetry direction defined at $V_G = +2.5$ V. c) µARPES constant energy map around the CBM at $E_F$, averaged over 0.4 eV. d) Brillouin zone schematic of the partially graphene encapsulated heterobilayer defining the TMD moiré vector and the expected position of the WS$_2$ K point and graphene Dirac cone moiré replica bands. e) µARPES energy-momentum slices through the graphene Dirac cone on the graphene/WS$_2$/WSe$_2$ region of the sample. f) µARPES constant energy maps around the graphene Dirac cone at energies I = 0.10 eV averaged over 0.2 eV, II = 0.25 eV, III = 0.45 eV and VI = 0.55 eV, averaged over 0.1 eV. Moiré vectors for the three most intense replicas bands are overlaid in orange. The same three moiré vectors are re-centred and overlaid in c). The brown and green lines show the direction of the µARPES energy-momentum slices in e). The data presented in a black and white colour scheme display the photoemission intensity in a logarithmic scale. All scale bars are 0.2 Å$^{-1}$. 
at positions that correspond to the TMD moiré vector. A schematic of the WSe$_2$ and WS$_2$ Brillouin zones can be seen in Fig. 6.7 d), defining the moiré vector, $G_M$, and the expected positions of the moiré replica bands for the WS$_2$ K point (green dashed box). As in the case of device 1, no replica valence bands were observed in either the doped or undoped µARPES spectra. Also included in the schematic is the graphene Brillouin zone relative to the two TMDs for the region of the sample that is partially encapsulated in graphene.

The underlying moiré potential from the WS$_2$/WSe$_2$ heterobilayer is seen to give rise to replica Dirac cones within the encapsulating graphene layer displaced by the moiré vector of the TMD heterobilayer. This phenomenon has also been reported in a study by Xie et al. for a graphene/WS$_2$/WSe$_2$ heterostructure with no electron doping [159].

By electron doping the heterostructure, the primary and replica Dirac cones are shifted $0.26 \pm 0.04$ eV below the Fermi energy for $V_G = +2.5$ V, as shown in Fig. 6.7 e). No hybridisation gaps are observed between the graphene Dirac cones, which is required as strong evidence for an initial state effect [96, 97, 156, 157, 167]. Their absence could be attributed to the energy resolution of the measurement (∼100 meV) being larger than the moiré potential in the graphene layer.

Fig. 6.7 f) shows µARPES constant energy maps around the graphene Dirac cone at the Fermi energy (I), the Dirac point (II) and at two higher binding energies (III and VI). The three most intense replica Dirac cones were used to find an average TMD moiré vector, $G_M = 0.09 \pm 0.01$ Å$^{-1}$. An average was used to find a value for

Figure 6.8: µARPES constant energy maps at $V_G = +2.5$ V a) around the graphene Dirac point, $E_D$, on the graphene/WS$_2$/WSe$_2$ region and b) around the CBM of the WS$_2$/WSe$_2$ region. The white number shows the integrated photoemission intensity within each red box with respect to the primary band in the centre.
Figure 6.9: a) µARPES energy-momentum slice along the high symmetry direction defined for the WS$_2$/MoSe$_2$ heterobilayer encapsulated in graphene. Above - a side view atomic schematic of the top three layers of the heterostructure. b) µARPES energy-momentum slice through the graphene Dirac cone in the direction shown by the green line in c). c) µARPES constant energy maps at binding energies I = 0.0 eV, II = 0.2 eV and III = 0.3 eV, all averaged over 0.1 eV. The orange arrows overlaid in map I show the moiré vector, $\mathbf{G}_M$. Data presented in a black and white colour scheme shows the photoemission intensity in a logarithmic scale. All scale bars are 0.2 Å$^{-1}$.

the moiré vector due to the slight distortion of the mini-Brillouin zone likely due to strain within the layers of the heterostructure [159]. Each of the three vectors are overlaid in orange on map II. The moiré vector can be used to find a value of 2.1 ± 0.3° for the TMD twist angle. With a 19° twist angle between the graphene and WS$_2$ layers, the TMD heterobilayer moiré vector is the only vector that can give the resultant position of the replica Dirac cones observed. The retainment of their angular orientation with respect to the primary Dirac cone, seen in maps III and IV, show each replica must originate from the primary band in the centre labelled $\mathbf{K}_{Gr}$.

The same three moiré vectors are overlaid and re-centred on the heterobilayer CBM in Fig 6.7 b). The same symmetry in photoemission intensity is seen for
both the replica graphene Dirac cones and the replicas of the WS$_2$ CBM. In Fig. 6.8 a), the photoemission intensity is integrated over the primary band and each replica graphene Dirac cone for the areas enclosed by the red boxes. The integrated photoemission intensity is given by the number inside each red box. The same array of red boxes is overlaid on the µARPES constant energy map of the heterobilayer CBM, Fig. 6.8 b). Smaller areas are integrated over to avoid background intensity from the primary CBM. The same symmetry in photoemission intensity is observed and is predicted to be a result of a 60° phase difference between the TMDs in the heterobilayer.

Replica graphene Dirac cones displaced by the moiré vector of an underlying TMD heterobilayer were also observed for a graphene encapsulated WS$_2$/MoSe$_2$ heterobilayer. Fig. 6.9 a) shows a µARPES energy-momentum slice along the Γ-K$_{Gr}$ direction, where faint replica graphene Dirac cones are observed around the primary graphene Dirac cone, and the band structure of the underlying heterobilayer can be seen at Γ. A higher resolution µARPES energy-momentum slice around K$_{Gr}$ is shown in Fig. 6.9 b) with no electron doping. Fig. 6.9 c) shows µARPES constant energy maps around the graphene Dirac cone at the Dirac point (I) and at two higher binding energies (II and III). The replica graphene Dirac cones have the same symmetry in photoemission intensity as seen for the WS$_2$/WSe$_2$ heterobilayer. The three most intense replica Dirac cones were used to find an average TMD moiré vector of $G_M = 0.09 \pm 0.01$ Å$^{-1}$, which gives a twist angle of 2.1 ± 0.3° between the two TMD layers [67], using the lattice constants $a_{WS_2} = 3.16$ Å [33] and $a_{MoSe_2} = 3.289$ Å [33].

**Resolving moiré replica bands**

Moiré replicas of the valence band were not observed in any of the µARPES spectra obtained, despite the fact the moiré potential is expected to be stronger in the valence band than the conduction band. The moiré vector, $G_M$, of the TMD heterobilayer in device 2 is small, due to the small lattice mismatch and small twist angle between the WS$_2$ and WSe$_2$ layers. Fig. 6.10 shows µARPES energy-momentum slices around the high symmetry positions of the TMD heterobilayer band structure, along the direction of the TMD moiré vector. The moiré vector is overlaid in orange in each spectra.

Observing valence band moiré replicas around Γ, Fig. 6.10 a), is challenging due to the large effective mass of the band ($m^*_\Gamma = 1.19 m_0$) combined with the energy resolution of the measurement (~100 meV) and the weak photoemission intensity of the moiré replica bands relative to the primary band. Around the valence band at
Figure 6.10: μARPES energy-momentum slices of the WS$_2$/WSe$_2$ heterobilayer in device 2, taken a) around Γ and b) around K of the heterobilayer with no electron doping, and c) around K of the heterobilayer with electron doping. Each spectra is taken in the direction of the TMD moiré vector. The moiré vector is overlaid in orange in each spectra. The scale bars are 0.2 Å$^{-1}$ and the photoemission intensity is displayed in a logarithmic scale.

K, Fig. 6.10 b), the primary bands from the WSe$_2$ layer are already very weak in photoemission intensity, making it unlikely to observe even weaker replicas, given the high background intensity seen at higher binding energies. The primary valence band at K in the WS$_2$ layer is significantly more intense, but due to the small twist angle, the lower spin-split band of the WSe$_2$ layer hides any weak features close to the WS$_2$ band at K.

Around the CBM at K, Fig. 6.10 c), the background intensity is significantly lower at the Fermi energy, and we measure the effective mass of the CBM to be smaller than the valence band edges, making it easier to observe moiré replica bands at small twist angles. For these reasons we are able to resolve the weak moiré replica bands of the CBM, but not the moiré replica bands within the valence band.

In order to resolve replica bands, the energy resolution of the measurement must be better than the energy separation between the primary and replica bands. To quantify this we can approximate the energy separation between primary and replica bands by $\delta k \frac{\partial E}{\partial k}$, where $\delta k = G_M$ is the moiré vector and $\partial E/\partial k$ is the derivative of the dispersion relation for the corresponding band.

The energy resolution, $\delta E$, can be determined from an EDC, measuring the width of the band. As replica bands have weak photoemission intensity, the band separation should be greater than this. We account for this by a parameter $\alpha$ which will depend on the relative intensity of the primary and replica bands. If they are roughly equal then $\alpha \sim 1$ and for weaker replicas $\alpha \sim 2$ or 3. This gives the condition
\[
\alpha \delta E < \delta k \frac{\partial E}{\partial k},
\]

(6.1)

The derivative of the dispersion relation for a parabolic band can be expressed as:
\[
\frac{\partial E}{\partial k} \sim \delta k \frac{\partial^2 E}{\partial^2 k} = \delta k \frac{\hbar^2}{m_e m^*},
\]

(6.2)

where \(m_e\) is the mass of an electron and \(m^*\) is the effective electron mass. Converting the moiré vector into a moiré wavelength and then expressing as a function of twist angle, \(\theta\), and lattice constants, using equation 1.4, gives the condition:
\[
\alpha \delta E < \frac{16 \pi^2 \hbar^2}{3 m_e m^*} \frac{2(1 + \delta)(1 - \cos \theta) + \delta^2}{(1 + \delta)^2 a^2},
\]

(6.3)

where \(a\) is the lattice constant of one layer and \(\delta\) is the difference in lattice constant between the two layers.

For the WS\(_2\)/WSe\(_2\) heterobilayer in device 2; to resolve moiré replica valence bands at \(\Gamma\) \(\alpha \delta E < 42\) meV, to resolve moiré replica valence bands at \(\mathbf{K}_{\text{WS}_2}\) \(\alpha \delta E < 87\) meV and to resolve moiré replica conduction bands at \(\mathbf{K}_{\text{WS}_2}\) \(\alpha \delta E < 380\) meV. The energy resolution of the measurement is \(\sim 100\) meV; with \(\alpha \sim 2\)-3, only the conduction band moiré replicas should be resolvable within our measurements. This is consistent with the observed spectra.

Increasing the twist angle would separate the replica bands further in energy at the high symmetry positions, but their photoemission intensity would also be reduced at larger twist angles due to a decrease in the moiré potential, hence \(\alpha\) would increase. Therefore, observing replica bands in the valence band of TMDs is challenging.

Replica bands in graphene are easily resolvable due to the linear dispersion of the band structure. The derivative of the dispersion relation is given by \(\partial E/\partial k = \hbar v_F\), giving
\[
\alpha \delta E < \frac{4 \pi \hbar v_F}{\sqrt{3}} \frac{\sqrt{2(1 + \delta)(1 - \cos \theta) + \delta^2}}{(1 + \delta) a}. \]

(6.4)

For the graphene replica bands induced by the moiré potential of the underlying WS\(_2\)/WSe\(_2\) heterobilayer in device 2, at an angle of 2° and a moiré wavelength of 9 nm, \(\alpha \delta E < 530\) meV, therefore easily resolvable within our measurements.

**Final state photoelectron diffraction considerations**

Although final state photoelectron diffraction from the underlying moiré potential can account for the presence of the replica graphene Dirac cones observed in our
Figure 6.11: a) µARPES energy-momentum slice along the high symmetry directions defined for device 3. The overlaid red and blue dotted lines are fits of the bands from the WSe$_2$ and WS$_2$ layers, respectively. The overlaid white dotted lines are fits of the hybridised bands around Γ. The overlaid orange dash-dotted lines are lines to guide the eye highlighting the replica WSe$_2$ band. b) Brillouin zone schematic. c) µARPES constant energy maps at the energy of the VBM. Map to the right in the orange-brown colour scheme is a higher resolution energy map of the map on the left. The red and blue lines mark the Brillouin zone boundaries of the WSe$_2$ and WS$_2$ layers, respectively. d) µARPES energy-momentum slice along the high symmetry direction defined at $V_G = +2.2$ V. The overlaid white and blue dashed lines show the fit of upper valence band at Γ and the valence band edge of WS$_2$ at K. e) µARPES constant energy map at $E_F$ around the CBM, averaged over 0.3 eV. The photoemission intensity is displayed in a logarithmic scale and all scale bars are 0.2 Å$^{-1}$.

µARPES measurements, we do believe these replica bands are intrinsic features of the band structure created by the underlying moiré potential. Firstly, in previous studies of 2D heterostructures under the same experimental conditions, we have not observed multiple replica bands created by photoemitted electrons scattering off the underlying layers. Secondly, we do not observe graphene Dirac cones scattered by the individual TMD layers and thirdly, the observation that the symmetry in the photoemission intensity of the replica WS$_2$ CBMs is the same as that observed for the replica graphene Dirac cones is a strong indication that both sets of replicas are caused by the same periodic potential of the superlattice.

Furthermore, for a third device (device 3) where the WS$_2$ and WSe$_2$ mono-
layers are misaligned by 9°, moiré replicas of the CBM are no longer observed, consistent with the moiré potential disappearing at larger twist angles.

In device 3, we do observe a WSe$_2$ replica valence band due to final state photoelectron diffraction. The photoemitted electrons from the WSe$_2$ layer are scattered through the above WS$_2$ layer upon exiting the sample surface. Fig. 6.11 a) shows a µARPES energy-momentum slice along the high symmetry directions defined in Fig. 6.11 b). The red and blue dashed lines overlaid indicate the bands originating from the WSe$_2$ and WS$_2$ layers, respectively. A replica of the WSe$_2$ valence band is highlighted by the orange dashed line.

Although we can not resolve the angular orientation of the WSe$_2$ valence replica band (see Chapter 4), we determine this band to be due to final state photoelectron diffraction effects, as it is the only replica band observed within the spectrum, Fig. 6.11 c), and its photoemission intensity is significantly more intense than the primary WSe$_2$ band, which is consistent with what we have seen before for final state effects in Chapter 4.

Fig. 6.11 d) shows a µARPES energy-momentum slice of the doped WS$_2$/WSe$_2$ heterobilayer, where the CBM is again observed at the Brillouin zone corners of the WS$_2$ layer. Replicas of the CBM are not observed for this large twist angle, as shown by the µARPES constant energy map in Fig. 6.11 e).

6.2.4 Twist-dependent band alignments

Understanding how the band structure changes as a function of twist angle is important for the emerging field of twistronics. Here, we compare the band structure of the 2°, 6° and 9° twist angle WS$_2$/WSe$_2$ heterobilayers, and compare their band alignments to the individual isolated monolayers.

Fig. 6.12 a) and b) show µARPES energy-momentum slices for isolated monolayer WS$_2$ and WSe$_2$, respectively. Band fits from Γ to K of the isolated monolayers are displayed in Fig. 6.12 c). For monolayer WS$_2$, $\Delta_{SO} = 0.45 \pm 0.03$ eV and $m_k^* = 0.5 \pm 0.1 m_0$ and for monolayer WSe$_2$, $\Delta_{SO} = 0.49 \pm 0.01$ eV and $m_k^* = 0.42 \pm 0.05 m_0$ [118]. The band fits of the isolated monolayers are then compared to the band structure of the 2° twist angle heterobilayer in Fig. 6.12 d). We find the band structure of the WS$_2$ layer is almost retained as in the isolated monolayer, but due to the hybridisation between the layers, we see a separation of the bands at Γ of 0.67 ± 0.04 eV and a reduction in the effective mass of the upper most band at Γ.

A comparison of the band fits for the 2° and 6° WS$_2$/WSe$_2$ heterobilayers are shown in Fig. 6.12 e). For the 6° heterobilayer, the separation of the bands
Figure 6.12: a) and b) µARPES energy-momentum slices along the high symmetry directions defined for monolayer (ML) WS$_2$ and monolayer WSe$_2$, respectively. The overlaid dashed lines are fits of the electronic bands. c) Plot of the monolayer bands fits. d) Comparison of the isolated monolayer band fits to the 2° WS$_2$/WSe$_2$ heterobilayer band fits. e) Comparison of the band fits for the 2° and 6° WS$_2$/WSe$_2$ heterobilayers. All scale bars are 0.2 Å$^{-1}$.

at $\Gamma$ is reduced to 0.56 ± 0.04 eV, suggesting a smaller degree of the hybridisation between the layers than in the 2° misaligned heterobilayer. At each of the Brillouin zone corners the spin-orbit coupling and effective mass remain the same as for the isolated monolayers. The µARPES spectra acquired for each heterobilayer and monolayer are from different samples, therefore, their bands alignment may differ by ∼0.1 eV due to small changes in doping between samples.

Fig. 6.13 shows EDCs for the $\Gamma$ and K high symmetry points of the isolated monolayers and the different twist angle heterobilayers. For the 9° twist angle heterobilayer, a third band is observed at $\Gamma$, highlighted by the green arrow in Fig. 6.13 a). This has been seen before for heterobilayers of MoSe$_2$/WSe$_2$ [110] and WS$_2$/WSe$_2$ [159], where the three bands are described to be a result of an electronic state from each of the individual monolayers and an additional hybridised electronic state. Whether two bands or three bands are observed at $\Gamma$ is due to different domains of the heterobilayer being probed.

Previously, band widths have been reported to increase when moiré effects are present [115]. A previous report by Stansbury et al. studied WSe$_2$/WS$_2$ heterobilayers and found “diffuse” bands due to the formation of moiré replica bands around
Figure 6.13: a) and b) EDCs taken at the high symmetry positions \( \Gamma \) and \( K \), respectively, for monolayer (ML) WS\(_2\) (blue), monolayer WSe\(_2\) (red), and WS\(_2\)/WSe\(_2\) heterobilayers with twist angles of 2° (black), 6° (purple) and 9° (green). The black and purple arrows highlight the peaks in photoemission intensity due to the WSe\(_2\) band at \( K \).

the primary band [115]. Our spectra shows no change in band width between the three different twist angle heterobilayers, or compared to \( \mu \)ARPES measurements of the individual monolayers, where no moiré effects are present. All band widths measured from the EDCs in Fig. 6.13 are \( \sim 0.2 \) eV. Band width strongly depends on sample quality and annealing conditions prior to measurement. Therefore, with high quality samples, and a low enough energy resolution, sharp moiré replica bands should be resolvable in the \( \mu \)ARPES measurements of TMD heterobilayers.

All band parameters for the three different twist angle WS\(_2\)/WSe\(_2\) heterobilayers can be found in Table 6.1.
Table 6.1: Band parameters for the WS$_2$/WSe$_2$ heterobilayers. $\theta$ is the twist angle, $E_K$ is the energy of the VBM, $E_\Gamma - E_K$ is the energy difference between the upper most band at $\Gamma$ and $E_K$, $\Delta_{SO}$ is the spin-orbit coupling of the WS$_2$ layer, VBO is the valence band offset, $\Delta_\Gamma$ is the energy separation of the bands at $\Gamma$, $m^*_K$ is the effective mass of the valence band at $K$ for WS$_2$/WSe$_2$, respectively, and $E_G$ is the interlayer band gap at carrier concentrations of $^1(4.2 \pm 0.5) \times 10^{12}$ cm$^{-2}$, $^2(6.4 \pm 0.4) \times 10^{12}$ cm$^{-2}$ and $^3(2.4 \pm 0.2) \times 10^{12}$ cm$^{-2}$. *The value of $E_K$ used to find the band gap is from the 0 V band fit shifted by the electrostatic potential, $\Delta E_\Gamma$.

<table>
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<th>$\theta$ ($^\circ$)</th>
<th>$E_K$ (eV)</th>
<th>$E_\Gamma - E_K$ (eV)</th>
<th>$\Delta_{SO}$ (eV)</th>
<th>VBO (eV)</th>
<th>$\Delta_\Gamma$ (eV)</th>
<th>$m^*_K$ ($m_0$)</th>
<th>$E_G$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.1 \pm 0.3^*$</td>
<td>0.81 $\pm$ 0.03</td>
<td>0.31 $\pm$ 0.04</td>
<td>0.44 $\pm$ 0.04</td>
<td>0.60 $\pm$ 0.04</td>
<td>0.67 $\pm$ 0.04</td>
<td>0.43 $\pm$ 0.03/0.57 $\pm$ 0.05</td>
<td>1.62 $\pm$ 0.07$^*$</td>
</tr>
<tr>
<td>$6 \pm 1^*$</td>
<td>0.72 $\pm$ 0.03</td>
<td>0.43 $\pm$ 0.04</td>
<td>0.44 $\pm$ 0.04</td>
<td>0.58 $\pm$ 0.04</td>
<td>0.56 $\pm$ 0.04</td>
<td>0.38 $\pm$ 0.01/0.47 $\pm$ 0.02</td>
<td>1.58 $\pm$ 0.03$^*$</td>
</tr>
<tr>
<td>$9 \pm 1^*$</td>
<td>0.92 $\pm$ 0.03</td>
<td>0.30 $\pm$ 0.04</td>
<td>0.43 $\pm$ 0.04</td>
<td>0.52 $\pm$ 0.04</td>
<td>0.61 $\pm$ 0.04</td>
<td>0.4 $\pm$ 0.1/ -</td>
<td>1.58 $\pm$ 0.06$^*$</td>
</tr>
</tbody>
</table>
6.3 Conclusion

In this chapter we have shown that the WS$_2$/WSe$_2$ heterobilayer is a direct band gap semiconductor with a type II band alignment, where the CBM resides at the Brillouin zone corners of the WS$_2$ layer, and not at $Q$ as previously reported. The curvature of the CBM was also visualised in the µARPES spectra and an electron effective mass was determined.

The first direct evidence of moiré replica conduction bands for the WS$_2$/WSe$_2$ superlattice at twist angles of 2.1° and 6° is presented along with strong arguments that these replica bands are moiré-induced and not a result of final state photoelectron diffraction. The evidence consists of the observation of replica graphene Dirac cones in the encapsulating graphene layer which are displaced by the periodicity of the underlying TMD moiré potential and have the same symmetry in photoemission intensity as the WS$_2$ conduction band replicas.

Valence band moiré replicas were not observed in our µARPES measurements due to the energy resolution of the measurements combined with their weak photoemission intensity and the high effective mass of the valence band compared to the conduction band. With the correct combination of energy resolution, twist angle and strength of moiré potential, it may be possible to resolve moiré effects within the valence band of TMD heterobilayers in the future.

Separating the material in which the superlattice is created from the layer of interest, and using proximity to the superlattice potential, gives greater flexibility over the strength and wavelength of the moiré potential that can be induced. Our results demonstrate how graphene, or other 2D materials, could potentially be used as a sensor for changes in dielectric environment.

The gate-dependence of the moiré potential was not explored in these measurements, but gate-tunable artificial moiré superlattices have been reported in a recent study by Xu et al. [183]. It would be interesting to explore whether the strength of moiré potential felt by neighbouring layers could be controlled by an electric field. This could also be a method of increasing the moiré potential felt by the graphene layer stacked on a TMD heterobilayer, which could then in turn increase the hybridisation gaps between primary and replica bands making them more easily visible in µARPES spectra, giving final proof it is indeed an initial state effect.
Chapter 7

Conclusion

The work presented in this thesis aimed to study interlayer interactions in 2D van der Waals heterostructures using µARPES. With the addition of in-situ electrostatic gating, interlayer effects in both the valence band and the conduction band of 2D materials were studied.

In Chapter 3, evidence was provided for a new twistronic effect that has not been previously reported. We showed how strongly coupled hybridised states between two weakly interacting 2D materials undergo Umklapp scattering due to the large lattice-mismatch between the layers. The position of these states in energy and momentum, and the strength of coupling, could be controlled via the twist angle and number of layers. Our µARPES measurements showed this effect for heterostructures of graphene on monolayer and multi-layer PTMCs, but we suspect this phenomena to be present within many other weakly coupled heterostructures, not just unique to the systems studied here.

Chapter 4 showed how replica bands observed in µARPES spectra may appear to be a result of a moiré potential, but in fact are formed by final state photoelectron diffraction effects. In this chapter, heterostructures comprised of hBN and TMDs were studied, where no moiré potential is expected. Our µARPES measurements showed multiple replica bands that first appeared displaced by the moiré vector of the heterostructure. Careful inspection of the replica band’s angular orientation revealed they are actually displaced by the reciprocal lattice vector of the encapsulating 2D material, and therefore, are a measurement artefact, rather than an initial state effect. This explained why no hybridisation gaps were observed within the spectra, despite the large photoemission intensity of the replica bands with respect to the primary bands.

In Chapter 5, the band alignments and band gaps of MoWSeS TMD heter-
obilayers were determined using µARPES with the addition of in-situ electrostatic gating. Conflicting optical measurements were resolved as the CBM in MoSe\(_2\)/WSe\(_2\) was shown to be at \(\mathbf{K}\), and not at \(\mathbf{Q}\). Furthermore, from our µARPES spectra, the \(\mathbf{Q}\)-\(\mathbf{K}\) conduction band alignment of the heterobilayer was determined to be \(15 \pm 4\) meV. Within this chapter, the challenges of fitting the Fermi edge and the CBM in µARPES spectra of gated 2D semiconductors were also discussed. For our measurements, an uncertainty in the Fermi level of \(\pm 30\) meV was found. Electrostatically doping the heterobilayer, allowed the study of band structure changes with increasing carrier concentration. Band gap renormalisation in the layer which held the charge within the conduction band was seen. For the MoSe\(_2\)/WSe\(_2\) heterobilayer this was the MoSe\(_2\) layer, but as the VBM resided within the WSe\(_2\) layer, no overall change in the direct band gap was observed. Similar µARPES measurements were also performed on a WS\(_2\)/MoSe\(_2\) heterobilayer, but more measurements are required to fully characterise how the band structure changes with electron doping.

Chapter 6 studied WS\(_2\)/WSe\(_2\) heterobilayers which are predicted to host the strongest moiré potential out of all the MoWSn TMD heterobilayer combinations. Band alignments and band gaps were determined using µARPES with in-situ electrostatic gating. The CBM was found to be a \(\mathbf{K}\) and its dispersion was also observed. To my knowledge, this is the first µARPES measurement using in-situ electrostatic gating that shows the dispersion of the conduction band in a 2D semiconductor. Moiré effects were also studied within these heterostructures. For small twist angles, moiré replica bands of the CBM were observed. However, there was no evidence of moiré replica valence bands in our µARPES spectra due to the large background photoemission intensity at high binding energies and the energy resolution of the measurement.

Encapsulating the WS\(_2\)/WSe\(_2\) heterobilayer with graphene gave rise to replica graphene Dirac cones displaced by the moiré vector of the TMD superlattice. This showed the moiré potential between 2D materials is not confined to the interacting layers and can impinge upon neighbouring layers, modifying their electronic structure. Therefore, moiré potentials can be induced in any 2D material by placing them in close proximity to a superlattice. Although no hybridisation gaps were observed within these µARPES measurements, there is evidence that these replica bands are a result of a moiré potential and not a result of final state photoelectron diffraction.

To summarise the characteristics of the three twistronic effects studied in this thesis using µARPES: interlayer Umklapp scattering produces hybridisation gaps displaced by a reciprocal lattice vector without the presence of replica bands; photoelectron diffraction gives rise to replica bands displaced by a reciprocal lattice
vector but no hybridisation gaps; and a moiré potential can create both replica bands and hybridisation gaps that are displaced by the moiré vector.

Distinguishing between replica bands created by a moiré potential and replica bands created by final state photoelectron diffraction still remains a challenge, unless there are clear signatures of interactions between the primary and replica bands. Hybridisation gaps formed between replica bands due to a moiré potential have been observed in µARPES measurements of 'magic' angle TBG with magnitudes up to 150 meV [124]. To observe small hybridisation gaps in µARPES measurements, cleaner samples could be fabricated using the current advancements being made in sample fabrication, such as the new inverted polymer stamp technique which has only recently been used to fabricate heterostructures for µARPES experiments [115, 125]. This technique builds heterostructures from the bottom up on the polymer stamp which is then inverted, leaving no polymer residue on the surface. This could improve the resolution seen in µARPES measurements of 2D heterostructures, and therefore, hybridisation gaps within weakly coupled systems may be resolved in the future.

Additionally, improvements in the sample annealing before measurements could dramatically reduce the broadening of the electronic bands, improving the energy resolution of the measurement. To achieve this, lower vapour pressure materials could be used to mount the samples in order to keep the pressure of the vacuum chamber low, preventing particles interacting with the sample surface at high temperature.

Other than improving the measurement resolution to be able to differentiate between final state and initial state effects, another potential method could be to perform µARPES measurements with different light polarisations. Spin-polarised valleys will have different photoemission intensities depending on the polarisation of the light source used to illuminate the sample, therefore, the origin of the replica bands could be determined from their photoemission intensity. These experiments could be performed at Diamond Light Source where they have the capability of changing the polarisation of the photon beam.

A further extension of this work would be to study the effect electron doping has on interlayer interactions. For example, if the strength of the moiré potential could be controlled via the application of an electric field, this would open up a new avenue for tuning interlayer interactions in 2D van der Waals heterostructures. Likewise, for interlayer Umklapp scattering, the band alignments between the layers could be tuned via an applied electric field, changing the position of the strongly coupled states within the band structure.
Additionally, proximity effects could be explored for moiré potentials. Using μARPES, this could be achieved by placing a spacer layer, such as monolayer hBN, between the moiré superlattice and the 2D material you wish to impose the moiré potential on. Comparing the electronic structure of the heterostructure with and without a spacer layer would allow one to study the changes in band structure due to the proximity of the 2D material to the neighbouring moiré potential. Understanding moiré potential proximity effects would allow 2D materials to be used as sensors for changes in dielectric environment.

Furthermore, flat bands are yet to be visualised in μARPES measurements of TMD superlattices. With improved energy resolution, μARPES experiments could reveal flat bands that have been shown to be present in STS measurements of WSe$_2$/WS$_2$ superlattices [70]. In-situ electrostatic gating could be used to bring the vHS into the vicinity of the Fermi energy which could hold many exciting possibilities for 2D devices. The tunability of vHS and hybridisation gaps with electrostatic doping as already been demonstrated in μARPES measurements of TBG [123].

On that idea, μARPES with in-situ electrostatic doping could be used to visualise the opening of a gap at the Fermi level with applied electric field in systems such as twisted monolayer-bilayer graphene. A report by Shi et al. [86] shows that when applying a positive potential to twisted monolayer-bilayer graphene a gap opens at the Fermi energy, due to the potential difference between the layers. This potential difference could be characterised using μARPES measurements by determining the electrostatic shift of the layers with applied gate voltage. Opening gaps at the Fermi level in graphene systems could allow its high carrier mobility to be used in new semiconductor devices.

μARPES can be used to study a wide range of different 2D materials and their heterostructures. A family of 2D materials that have only recently been fabricated are the magnetic 2D materials, such as Cr$_2$Ge$_2$Te$_6$ [184] and CrI$_3$ [185]. Stacking magnetic 2D materials with one another, or with other 2D materials, could change their magnetic order or give rise to new interlayer phenomena which may be tunable via the twist angle or electric field. Typically, these exotic 2D materials are air sensitive, therefore, with the recent advancements being made in 2D heterostructure fabrication, they could be encapsulated with monolayer materials such as hBN or graphene to allow the study of their electronic structure using μARPES.

In this thesis, we have shown μARPES with in-situ electrostatic gating to be a powerful tool in determining band parameters and visualising interlayer effects in twisted 2D heterostructures. Once understood and characterised, these interlayer effects can then go on to be exploited in designing the next generation of quantum
materials.
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