

Imperial College of Science, Technology and Medicine
Department of Materials

Effects of Stacking and Twisting on the Optical and Electronic Properties of Transition Metal Dichalcogenide Bilayers

Miriam Judith Scharnke

Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy
in the Centre for Doctoral Training for the Theory and Simulation of Materials
Department of Materials
Imperial College London
December 2022

Abstract

Moiré lattices formed by bilayers of atomically thin semiconductors with relative twist angle or lattice mismatch host a plethora of novel electronic and optical phenomena. The Bethe–Salpeter equation has been used very successfully to describe optical properties of semiconductors, however, the unit cells of these moiré systems can be very large, including hundreds of atoms. The resulting Bethe–Salpeter basis size is not currently computationally accessible, which means that standard ab initio codes can not yet be used. Using tight-binding instead of DFT as the basis for the Bethe–Salpeter Hamiltonian significantly reduces basis size.

In this work, I use a sophisticated tight-binding model in order to calculate electronic structure and optical properties of MoS₂ monolayers and homobilayers with different high-symmetry stackings and stackings with relative twist angles of 3.89°-21.79°.

I first generalize a tight-binding model with eleven bands per spin and per monolayer unit cell first presented by Fang et al.[1] to include up to sixth-nearest neighbour intralayer hopping. I then use this tight-binding model to calculate band structures of MoS₂ monolayers, and twisted and untwisted bilayers. Finally, I compute exciton binding energies and absorption spectra of these systems in vacuum by using the tight-binding eigenenergies and wavefunctions to set up and solve an effective Bethe–Salpeter Hamiltonian, using the Rytova–Keldysh interaction to describe static dielectric screening in atomically thin semiconductors.

I declare that the work contained in this thesis is my own, unless specifically mentioned otherwise in the text. This work was carried out between July 2018 and December 2022 at Imperial College London under the supervision of Dr Johannes Lischner and Professor Andrew Horsfield. This thesis has not been submitted for a degree or diploma at any other university.

Acknowledgements

First thanks go to Chris, always, for the patience and love with which you supported me through the PhD journey. You are truly the best human.

Thank you to my main supervisor, Johannes Lischner, without whom this would not have been possible, for taking me on in the first place, and for the sheer number of things you have taught me. Thank you to my second supervisor, Andrew Horsfield, for setting my priorities straight and being a source of calm and reassurance whenever it seemed that my project was doomed (which, frankly, happened a lot more often than I care to admit in a document intended for formal examination). Thank you also to Arash Mostofi, for all your help, despite not being my supervisor and me not being your actual responsibility at all! All three of you have taught me some of your own way of doing science, and I hope I have become a better student because of it.

Thank you to Miranda Toora, Annalisa Neri, Darakshan Khan, and everybody else on the administrative staff at Imperial College. You have been incredibly helpful!

Thank you to all the other people involved in this project, in alphabetical order, Indrajit, Kemal, Martik and Valerio. It has been a true pleasure to work with you!

Thank you to Michael Bonitz, for your support and guidance during my undergraduate degree. Thank you to the rest of my CDT cohort, for making me feel a lot less lonely than I otherwise might have been in this endeavour! Thank you to the QFFF crowd, Jamie, Alex, Adam, Sara, and Dan for being all around excellent people, and for believing in me (and telling me so). Thank you to the Cambridge Knitting Club for your friendship and acceptance, and a surprising amount of good academic advice.

Thank you, finally, to my family for setting me up for this truly privileged life.

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution 4.0 International Licence (CC BY).

Under this licence, you may copy and redistribute the material in any medium or format for both commercial and non-commercial purposes. You may also create and distribute modified versions of the work. This on the condition that you credit the author.

When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes.

Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

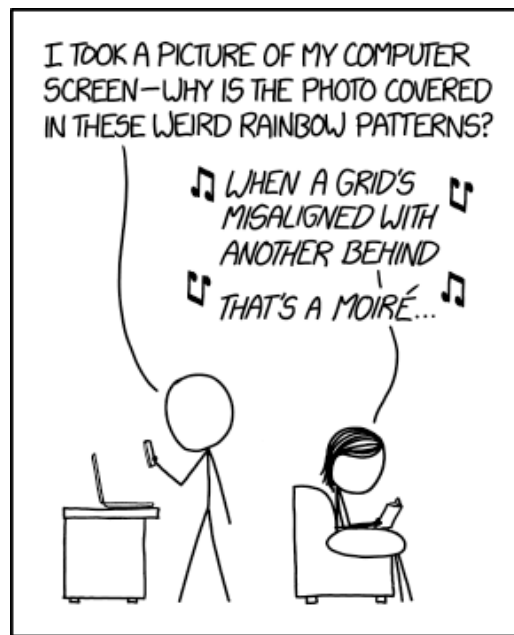


Figure 1: <https://xkcd.com/1814>

Contents

Abstract	i
Acknowledgements	iii
1 Introduction	1
2 Literature review	7
2.1 Experiment	7
2.1.1 Atomically thin semiconductors	7
2.1.2 Transition metal dichalcogenides (TMDs)	8
2.1.3 Optical Properties of TMDs	10
2.1.4 Experimental synthesis of twisted bilayers of atomically thin semiconductors	13
2.2 Theory	15
2.2.1 GW-BSE	15
2.2.2 Effective mass models and $k \cdot p$ -theory	16
2.2.3 The tight-binding approach to solving the BSE	17
3 Methods	19
3.1 Density functional theory	20

3.1.1	Exchange-correlation functional	21
3.1.2	Pseudopotentials	22
3.2	Bloch's theorem	22
3.3	Tight-binding theory	23
3.3.1	Slater–Koster parameters	25
3.4	Wannierization	26
3.5	Rydberg excitons	28
3.6	Bethe–Salpeter equation	31
3.7	BSE in TB basis	36
3.7.1	Exciton wavefunction in real space	38
3.8	Rytova–Keldysh interaction	39
3.9	Optical conductivity	43
3.10	Computational details	47
3.10.1	Density Functional Theory Calculations	47
3.10.2	Cutoff energy for BSE calculations	47
3.10.3	Lattice Fourier transform of the electrostatic interaction on a finite lattice	48
4	Sixth-nearest neighbour tight-binding model	50
4.1	Crystal structure of monolayer transition metal dichalcogenides	51
4.2	Orbital basis	53
4.3	Constructing the tight-binding Hamiltonian	55
4.3.1	Diagonal Elements	57

4.3.2	Off-diagonal elements for orbitals on the same type of atom with the same $\mathcal{M}_2$ -parity	58
4.3.3	Off-diagonal elements for orbitals on the same type of atom with different $\mathcal{M}_2$ -parity	58
4.3.4	Off-diagonal elements for orbitals on different types of atom with the same $\mathcal{M}_2$ -parity	59
4.3.5	Off-diagonal elements for orbitals on different types of atom with different $\mathcal{M}_2$ -parity	59
4.4	$\mathcal{R}_3$ symmetry	60
4.5	Results of $\mathcal{R}_3$ reduction	65
4.6	Spin-orbit coupling	68
4.7	Conclusion	69
5	MoS₂ monolayer	71
5.1	Impact of longer-ranged hoppings on MoS ₂ monolayer band structure	71
5.2	Electron and hole effective masses	74
5.3	Convergence of monolayer optical properties with k-grid fineness and cutoff energy	78
5.4	Impact of longer-ranged hoppings on monolayer optical properties	82
5.5	Conclusion	85
6	Untwisted MoS₂ bilayers	86
6.1	High-symmetry bilayer stackings of semiconducting transition metal dichalcogenides	87
6.2	Interlayer interaction in the tight-binding model	90
6.3	DFT calculations of relaxed structures of high-symmetry stackings	92

6.4	Electronic structure of MoS ₂ homobilayers	93
6.5	Optical properties of MoS ₂ homobilayers	102
6.6	Exciton character of MoS ₂ homobilayers	107
7	Twisted MoS₂ homobilayers	125
7.1	Commensurate lattices and moiré lattice vectors	125
7.2	Atomic relaxation for twisted bilayers	127
7.3	The moiré Brillouin zone	129
7.4	Dependence of electronic structure on twist angle	130
7.5	Dependence of optical spectra on twist angle	135
7.6	Exciton character of twisted MoS ₂ homobilayers	141
7.7	Conclusion	147
8	Conclusion	155
8.1	Convergence	155
8.2	Electronic Properties	156
8.3	Optical Properties	156
8.3.1	MoS ₂ monolayers	157
8.3.2	Stacking configurations	157
8.3.3	Twisted systems	157
8.4	Final thoughts	158
A	Tight-binding parameters	178
B	Orbital character at band edges	181

C	Optically active excitonic states	186
C.1	Untwisted systems	186
D	Most relevant transitions for optically active excitonic states	189
D.1	Untwisted systems	189
D.1.1	AB-stacked MoS ₂ homobilayers	198
D.1.2	AA-stacked MoS ₂ homobilayers	198
D.1.3	B ^{MX} -stacked MoS ₂ homobilayers	198
D.1.4	B ^{MM} -stacked MoS ₂ homobilayers	198
D.1.5	B ^{XX} -stacked MoS ₂ homobilayers	202
D.2	Twisted systems	203
D.2.1	21.79° twisted MoS ₂ homobilayers	203
D.2.2	9.43° twisted MoS ₂ homobilayers	207
D.2.3	7.34° twisted MoS ₂ homobilayers	207
D.2.4	6.01° twisted MoS ₂ homobilayers	209
D.2.5	5.09° twisted MoS ₂ homobilayers	209
D.2.6	4.41° twisted MoS ₂ homobilayers	209
D.2.7	3.89° twisted MoS ₂ homobilayers	209

List of Tables

2.1	Experimental lattice constants for bulk TMDs	12
4.1	Monolayer orbitals	54
4.2	Material-specific Rydberg parameters	54
5.1	Bandstructure information: monolayer	73
5.2	Effective masses: comparison to literature	78
5.3	Comparison of BSE and Rydberg exciton energies (monolayer)	84
6.1	Interlayer distance dependence on stacking configuration	93
6.2	Band structure properties of high symmetry stackings	101
6.3	Stacking dependence of the lowest exciton excitation energy (and corresponding binding energy)	102
7.1	Convergence parameters for twisted systems	127
7.2	Twist angle dependence of band extrema and gaps	134
7.3	Binding energies of lowest energy excitons in twisted systems.	139
7.4	Binding energies of lowest-energy optically active excitons in twisted twisted systems	140
7.5	Minimum BSE matrix sizes for convergence	141

A.1	Hopping parameters for MoS ₂ in eV.	179
A.2	Fitting parameters for $p - p$ -hopping	179
A.3	Fitting parameters for $p_z - d_{z^2}$ -hopping	180
B.1	Band character of monolayer MoS ₂ without spin	182
B.2	Band character: AA stacking	182
B.3	Band character: AB stacking	183
B.4	Band character: B ^{MX} stacking	183
B.5	Band character: B ^{XM} stacking	184
B.6	Band character: B ^{MM} stacking	184
B.7	Band character: B ^{XX} stacking	185
C.1	Optically active excitons: AB stacking	187
C.2	Optically active excitons: AA stacking	187
C.3	Optically active excitons: B ^{MX} stacking	187
C.4	Optically active excitons: B ^{MM} stacking	188
C.5	Optically active excitons: B ^{XX} stacking	188
D.1	Transitions contributing to optically active excitons: AB stacking, peak I	190
D.2	Transitions contributing to optically active excitons: AB stacking, peak II	192
D.3	Transitions contributing to optically active excitons: AB stacking, peak III	192
D.4	Transitions contributing to optically active excitons: AB stacking, peak IV	192
D.5	Transitions contributing to optically active excitons: AB stacking, peak V	193
D.6	Transitions contributing to optically active excitons: AB stacking, peak VI	193

D.7	Transitions contributing to optically active excitons: AB stacking, peak VII . . .	193
D.8	Transitions contributing to optically active excitons: AB stacking, peak VIII . .	194
D.9	Transitions contributing to optically active excitons: AB stacking, peak IX . . .	194
D.10	Transitions contributing to optically active excitons: AA stacking, peak I	194
D.11	Transitions contributing to optically active excitons: AA stacking, peak II . . .	195
D.12	Transitions contributing to optically active excitons: AA stacking, peak III . . .	195
D.13	Transitions contributing to optically active excitons: AA stacking, peak IV . . .	195
D.14	Transitions contributing to optically active excitons: AA stacking, peak V . . .	196
D.15	Transitions contributing to optically active excitons: B ^{MX} stacking, peak I . . .	196
D.16	Transitions contributing to optically active excitons: B ^{MX} stacking, peak II . . .	196
D.17	Transitions contributing to optically active excitons: B ^{MX} stacking, peak III . .	196
D.18	Transitions contributing to optically active excitons: B ^{MX} stacking, peak IV . .	196
D.19	Transitions contributing to optically active excitons: B ^{MX} stacking, peak V . . .	196
D.20	Transitions contributing to optically active excitons: B ^{MX} stacking, peak VI . .	197
D.21	Transitions contributing to optically active excitons: B ^{MX} stacking, peak VII . .	197
D.22	Transitions contributing to optically active excitons: B ^{MX} stacking, peak VIII .	197
D.23	Transitions contributing to optically active excitons: B ^{MX} stacking, peak IX . .	198
D.24	Transitions contributing to optically active excitons: B ^{MX} stacking, peak X . . .	198
D.25	Transitions contributing to optically active excitons: B ^{MM} stacking, peak I . . .	198
D.26	Transitions contributing to optically active excitons: B ^{MM} stacking, peak II . . .	199
D.27	Transitions contributing to optically active excitons: B ^{MM} stacking, peak III . .	199
D.28	Transitions contributing to optically active excitons: B ^{MM} stacking, peak IV . .	199

D.29 Transitions contributing to optically active excitons: B ^{MM} stacking, peak V . . .	200
D.30 Transitions contributing to optically active excitons: B ^{MM} stacking, peak VI . .	200
D.31 Transitions contributing to optically active excitons: B ^{MM} stacking, peak VII . .	201
D.32 Transitions contributing to optically active excitons: B ^{MM} stacking, peak VIII .	201
D.33 Transitions contributing to optically active excitons: B ^{MM} stacking, peak IX . .	202
D.34 Transitions contributing to optically active excitons: B ^{XX} stacking, peak I	202
D.35 Transitions contributing to optically active excitons: B ^{XX} stacking, peak II . . .	202
D.36 Transitions contributing to optically active excitons: B ^{XX} stacking, peak III . . .	202
D.37 Transitions contributing to optically active excitons: B ^{XX} stacking, peak IV . . .	203
D.38 Transitions contributing to optically active excitons: B ^{XX} stacking, peak V . . .	203
D.39 Transitions contributing to optically active excitons: 21.79° twist, peak I	203
D.40 Transitions contributing to optically active excitons: 21.79° twist, peak II	204
D.41 Transitions contributing to optically active excitons: 21.79° twist, peak III . . .	204
D.42 Transitions contributing to optically active excitons: 21.79° twist, peak IV . . .	204
D.43 Transitions contributing to optically active excitons: 21.79° twist, peak V	205
D.44 Transitions contributing to optically active excitons: 9.43° twist, peak I	205
D.45 Transitions contributing to optically active excitons: 9.43° twist, peak II	206
D.46 Transitions contributing to optically active excitons: 9.43° twist, peak III	206
D.47 Transitions contributing to optically active excitons: 9.43° twist, peak IV	206
D.48 Transitions contributing to optically active excitons: 9.43° twist, peak V	207
D.49 Transitions contributing to optically active excitons: 7.34° twist, peak I	207
D.50 Transitions contributing to optically active excitons: 7.34° twist, peak II	207

D.51	Transitions contributing to optically active excitons: 7.34° twist, peak III	208
D.52	Transitions contributing to optically active excitons: 7.34° twist, peak IV	208
D.53	Transitions contributing to optically active excitons: 6.01° twist, peak I	209
D.54	Transitions contributing to optically active excitons: 6.01° twist, peak II	209
D.55	Transitions contributing to optically active excitons: 6.01° twist, peak III	210
D.56	Transitions contributing to optically active excitons: 5.09° twist, peak I	210
D.57	Transitions contributing to optically active excitons: 5.09° twist, peak II	210
D.58	Transitions contributing to optically active excitons: 5.09° twist, peak III	211
D.59	Transitions contributing to optically active excitons: 5.09° twist, peak IV	211
D.60	Transitions contributing to optically active excitons: 4.41° twist, peak I	211
D.61	Transitions contributing to optically active excitons: 3.89° twist, peak I	212

List of Figures

1	https://xkcd.com/1814	v
1.1	Schematic illustration of excitons	3
2.1	Illustration 1T stacked bulk TMDs	9
2.2	Illustration 2H and 3R stacked bulk TMDs	9
3.1	Illustration of Rytova–Keldysh system geometry	39
4.1	Illustration of sixth nearest neighbour vectors	51
4.2	Illustration of symmetry operations necessary to derive relations between hopping parameters $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$. Neighbour vectors $-\boldsymbol{\delta}_2$ and $\boldsymbol{\delta}_3$ (the directions of $t^{(3)}$ and $t^{(2)}$ hopping) relate to neighbour vector $\boldsymbol{\delta}_1$ through $\mathcal{R}_3$ -symmetry, which relates to neighbour vector $-\boldsymbol{\delta}_1$ (the direction of $t^{(1)}$ hopping) through $\mathcal{M}_2$ -symmetry.	62
5.1	Bandstructure comparison: TB3 vs TB6 vs DFT: monolayer (no SOC)	72
5.2	Monolayer effective masses: 2nd order polynomial	76
5.3	Monolayer effective masses: 4th order polynomial	77
5.4	Cutoff convergence of binding energy	79
5.5	K-grid convergence of binding energy	80
5.6	Cutoff convergence of optical spectrum	81

5.7	K-grid convergence of optical spectrum	82
5.8	Absorption of MoS ₂ monolayers	83
6.1	Illustration of high-symmetry stacking configurations	88
6.2	Bandstructure comparison TB3 vs TB6 vs DFT: AA stacking (no SOC)	94
6.3	Close up of bandstructure comparison TB3 vs TB6 vs DFT: AA stacking (no SOC)	95
6.4	Bandstructure comparison TB3 vs TB6 vs DFT: AB stacking (no SOC)	96
6.5	Close up of bandstructure comparison TB3 vs TB6 vs DFT: AB stacking (no SOC)	97
6.6	Bandstructure comparison TB3 vs TB6 vs DFT: B ^{MX} stacking (no SOC)	98
6.7	Close up of bandstructure comparison TB3 vs TB6 vs DFT: B ^{MX} stacking (no SOC)	99
6.8	Bandstructure comparison TB3 vs TB6 vs DFT: B ^{XM} stacking (no SOC)	100
6.9	Close up of bandstructure comparison TB3 vs TB6 vs DFT: B ^{XM} stacking (no SOC)	102
6.10	Bandstructure comparison TB3 vs TB6 vs DFT: B ^{MM} stacking (no SOC)	103
6.11	Close up of bandstructure comparison TB3 vs TB6 vs DFT: B ^{MM} stacking (no SOC)	104
6.12	Bandstructure comparison TB3 vs TB6 vs DFT: B ^{XX} stacking (no SOC)	105
6.13	Close up of bandstructure comparison TB3 vs TB6 vs DFT: B ^{XX} stacking (no SOC)	106
6.14	Interlayer distance dependence of direct and indirect bandgap	107
6.15	Optical spectra of MoS ₂ homobilayers	108
6.16	Stacking dependence of optical spectra	109

6.17 Stacking dependence of optical spectra: literature results	110
6.18 Illustration of the real space distribution of the optically active excitons in AB stacked MoS ₂ bilayers	120
6.19 Illustration of the real space distribution of the optically active excitons in AA stacked MoS ₂ bilayers	121
6.20 Illustration of the real space distribution of the optically active excitons in B ^{MX} stacked MoS ₂ bilayers	122
6.21 Illustration of the real space distribution of the optically active excitons in B ^{MM} stacked MoS ₂ bilayers	123
6.22 Illustration of the real space distribution of the optically active excitons in B ^{XX} stacked MoS ₂ bilayers	124
7.1 Illustration of moiré grids for different twist angles	127
7.2 Bandstructures of twisted MoS ₂ bilayers with $\theta=21.79^\circ$, 9.43° , 7.34° , and 6.09° .	131
7.3 Bandstructures of twisted MoS ₂ bilayers with $\theta=5.09^\circ$, 4.41° , 3.89° , and 3.48° .	132
7.4 Twist angle dependence of interlayer distance and bandgaps	133
7.5 Comparison of optical absorbtion spectrum and exciton DOS for different twist angles.	136
7.6 Band folding illustration	138
7.7 Dependence of exciton binding energy on twist angle	142
7.8 Illustration of the real space distribution of the optically active excitons in 21.79° twisted MoS ₂ bilayers	149
7.9 Illustration of the real space distribution of the optically active excitons in 9.43° twisted MoS ₂ bilayers	150
7.10 Illustration of the real space distribution of the optically active excitons in 7.34° twisted MoS ₂ bilayers	151

7.11	Illustration of the real space distribution of the optically active excitons in 6.01° twisted MoS ₂ bilayers	152
7.12	Illustration of the real space distribution of the optically active excitons in 5.09° twisted MoS ₂ bilayers	153
7.13	Illustration of the real space distribution of the optically active excitons in 4.41° twisted MoS ₂ bilayers	154
7.14	Illustration of the real space distribution of the optically active excitons in 3.89° twisted MoS ₂ bilayers	154
D.1	Index illustration for untwisted Brillouin zone	190
D.2	Index illustration for twisted Brillouin zones	191

Chapter 1

Introduction

The aim of this project is to study the dependence of interlayer and intralayer excitons on stacking configuration in atomically thin transition metal dichalcogenide (TMD) bilayers by performing atomistic calculations.

Atomically thin materials consist of crystals which are periodically extended in two dimensions, but finite in the third. Graphene is perhaps the most famous of these, and the first that was experimentally realized, but there are many more. TMDs are a subset of these materials, and a large number of them are semiconducting.

The general structure of monolayered, semiconducting TMDs is a layer of a transition metal, typically molybdenum or tungsten, sandwiched between two layers of chalcogen atoms, typically sulfur, selenium, or tellurium. The two chalcogen layers are located directly on top of each other and the metal layer is shifted relative to the chalcogen atoms such that a honeycomb structure is formed when viewed from the top.

One of the interesting aspects of having quasi-two-dimensional systems in three-dimensional space is the use of the third dimension: atomically thin materials can be stacked on top of one another, resulting in so-called van der Waals heterostructures, hugely increasing the number of

possible atomically thin materials, and therefore hugely increasing the probability that some set of desired material properties can be achieved. Furthermore, it is possible not only to stack the monolayers on top of each other directly, but also to twist them relative to each other, resulting in an additional tuning parameter, and in large scale moiré lattices.

Atomically thin semiconductors exhibit weak dielectric screening compared to three-dimensional semiconductors. This is a purely geometric effect, since there simply is less material to do the screening. This is true even when a substrate is used, as is necessary in experiments, since one half of the surrounding space is still vacuum (or air). This strongly nonisotropic screening means that even when static screening is assumed, the Coulomb interaction is not screened uniformly, as in the three-dimensional case: $V^{(\epsilon)} = V^{(\epsilon=0)}/\epsilon$, but has to be treated in a more complicated way (see Sec. 3.8 for details).

This weak dielectric screening results in strong exciton binding energies in 2D semiconductors, leading to the low-energy parts of the corresponding optical spectra to be almost entirely governed by excitons[2].

Excitons are bound states between conduction band electrons and valence band holes. Holes are quasiparticles reflecting the fact that a neutrally charged state (as in, the absence of a charged particle) in a negatively charged environment behaves similarly to a positively charged particle in a neutral environment. The finite binding energy resulting from this effectively positive particle and the negatively charged electron means that it takes less energy to excite an electron from a valence band state to a conduction band state than the direct difference between the energies of those two states. This basic concept is illustrated in Fig. 1.1.

Even within this quasiparticle picture, this is a simplified description. In reality, the excitonic states of a semiconducting crystal are a superposition of several of these valence state to conduction state transitions. They do not even have to consist purely of direct transitions, where the relevant valence and conduction states have the same crystal momentum as each

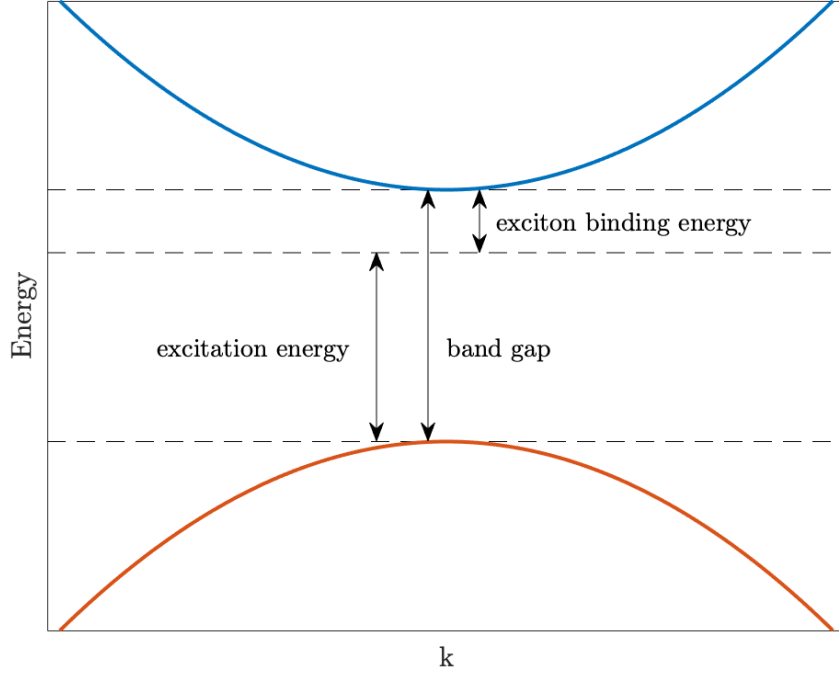


Figure 1.1: Schematic illustration of optically active excitons at direct bandgaps. The excitation energy of the exciton is given by the difference between the bandgap and the binding energy between the composite conduction band electron and valence band holes. The valence band is shown in red and the conduction band in blue.

other. However, since photon momenta are negligibly small compared to the difference in crystal momenta in any resolution included in any of the simulations in this work, I restrict myself to direct transitions only in order to describe the spectra of optical excitations in these materials.

So, in order to describe the low energy parts of the optical spectra of TMD mono- and bilayers, I need to calculate the exciton eigenenergies and eigenfunctions of these systems. This is done by solving the Bethe–Salpeter equation (BSE), which is the equation of motion for the two-particle (electron-hole) Green’s function.

For TMD monolayers, and even for untwisted TMD bilayers with unit cells only twice as large as the monolayer ones, very accurate BSE calculations can be performed using large-scale codes such as BerkeleyGW[3].

However, for twisted TMD bilayers, this is not yet computationally feasible, due to the fact

that, firstly, the resulting unit cells can include hundreds or thousands of atoms, and secondly, very fine k -grids and large cutoff energies for the relevant plane wave bases are needed in order to accurately describe optical spectra.

An alternative approach to modelling excitons in twisted heterostructures is to abandon the atomistic approach and use, for example, effective mass theory or $\mathbf{k} \cdot \mathbf{p}$ -theory.

However, there also exists a medium approach, involving some of the atomistic properties, but still resulting in more computational feasibility. This is to solve the BSE in a tight-binding basis instead of the full GW quasiparticle basis, massively reducing basis size while still allowing for an accurate description of the quasiparticle energies close to the bandgap.

In this work, I use a tight-binding model first introduced by Fang et al.[4] and improved upon by Vitale et al.[5]. I start by further improving this model by including up to sixth-nearest neighbour hopping (instead of the prior second- (and selected third-)nearest neighbour hopping) in order to improve the description of the conduction manifold which is important for the description of excited states. It is worth mentioning that this, and any further, extension of the tight-binding model does not increase the number of bands and therefore does not increase the size of the BSE Hamiltonian matrix, which is the computational bottleneck of this approach.

It is worth noting that, while the rank of the Hamiltonian does not increase due to this approach, its sparsity may be reduced. We do not currently take advantage of sparsity in the code, so this does not impact this model. I did experiment with using sparse matrices in the code at one point to see whether this could yield computational improvement, and it did not significantly do so, particularly in the case of twisted systems, because the resulting BSE Hamiltonians are not sufficiently sparse.

In terms of computational cost (though not, in this case, human labour) the extension of the tight-binding model to include longer-ranged hoppings is therefore a very cheap improve-

ment to make.

Finally, I use this tight-binding model as the basis for BSE calculations of MoS₂ monolayers, and untwisted and twisted MoS₂ homobilayers.

I then use this model to calculate the optical spectra and excitonic character of different high-symmetry stacking geometries of MoS₂ as well as commensurately twisted MoS₂ bilayers. I am able to directly study the layer character of excitons in twisted MoS₂ bilayers, because this approach allows us to calculate the excitonic wavefunctions (which can only be approximated as hydrogen wavefunctions in e.g. effective mass theory). I am also able to show that a frequently used simplification of the TB basis (to not consider the chalcogen orbitals) is justified by including these orbitals and showing that the excitons are still almost exclusively localized on the metal atoms.

The structure of this thesis is as follows. I will start by reviewing the existing literature on both experimental and theoretical work on optical properties of twisted and untwisted TMD bilayers in Ch. 2.

Next, I will introduce the general theoretical methods used in this work in Ch. 3. This will include a brief overview over density functional theory in Sec. 3.1, a more detailed introduction into tight-binding theory in Sec. 3.3, and a very brief explanation of Wannierization in Sec. 3.4, that is, how to obtain tight-binding parameters from DFT calculations without having to resort to using them as fitting parameters. Then, I will explain how to describe excitons in the effective mass model in Sec. 3.5, before explaining how to describe them ab initio with the Bethe–Salpeter equation in Sec. 3.6. Next, I will derive how to express the Bethe–Salpeter equation in a tight-binding basis in Sec. 3.7. Lastly, I will provide the equations for electron-hole interaction in Sec. 3.8, the optical conductivity in Sec. 3.9, and then provide some computational details of the various codes used in this work in Sec. 3.10.

The next four chapters will contain the results of this work. I start in Ch. 4 by explicitly deriving a symmetrized sixth-nearest neighbour tight-binding Hamiltonian for monolayer TMDs. I compare the results of this model to the third-nearest neighbour model on which it is based in Ch. 5, by calculating both electronic structure and optical spectra of monolayer MoS₂, and comparing the latter to ab initio calculations from Qiu et al.[6].

In Ch. 6 I explain how to perform bilayer calculations based on the monolayer model, including atomic relaxation and the interlayer interaction, and then compute electronic structure and optical spectra of the five high-symmetry stackings of MoS₂ homobilayers.

Finally, I present the results (and limitations) of the same model for twisted MoS₂ homobilayers for a range of twist angles between 21.79° and 3.48° in Chapter 7.

Chapter 2

Literature review

This section will provide a brief overview of the literature on excitons in TMD bilayers. Section 2.1 will mention some important experimental results. Section 2.2 will review the ways in which excitons in TMDs are typically modelled, and the advantages and disadvantages of different methods. For this chapter, I have found the recent review paper by Bienek et al.[7] particularly helpful.

2.1 Experiment

2.1.1 Atomically thin semiconductors

There is a class of materials called van der Waals materials which is characterized by strong, covalent bonds in two dimensions, and weak, van der Waals bonds in the third dimension, and which has been known for several decades[8, 9, 10]. In their bulk form, the weak interlayer bonding means they are often useful as dry lubricants[11]. However, more recently, it has been possible to isolate a single layer of these materials[12, 13, 14, 15], opening up an entirely new field of study. The first and perhaps most famous of these materials is graphene, for the discovery of which the Nobel prize in physics was awarded in 2010[16]. Other important examples of this type of materials are hexagonal boron nitride (hBN), which is an insulator with a bandgap

of over 5 eV[17]. Finally, there is the subject of this work, transition metal dichalcogenides (TMDs)—more on those in the next section 2.1.2.

These atomically thin materials are interesting even in their monolayer form, but they also come with the option to stack them on top of one another, massively increasing the number of different potential materials. This was first suggested by Geim et al.[18], with several layers of hBN sandwiched between two layers of graphene as a first proof of concept presented by Ponomarenko et al.[19].

There is yet another tuning parameter inherent in this class of materials: twist angle. When stacking even two identical monolayers on top of each other, it is possible to obtain a moiré material with a much larger unit cell than just two stacked monolayer unit cells through a relative twist angle between the layers. Again, graphene played a leading role in this research[20, 21, 22, 23], exhibiting superconductivity at a specific twist angle of 1.1° [22].

2.1.2 Transition metal dichalcogenides (TMDs)

Transition metal dichalcogenides (TMDs) have a slightly more complicated interlayer structure than the other examples of atomically thin semiconductor mentioned in the previous section. They are formed of a layer of transition metal atoms (usually molybdenum or tungsten) sandwiched between two layers of chalcogen atoms (often sulfur or selenium, and sometimes tellurium) all bound together covalently, and the resulting three-layer sheets of material then adhere to one another through van der Waals interaction in the bulk form. There exist several different geometries of van der Waals TMDs in nature[24, 25]. These different geometries are illustrated in Figs. 2.1 and 2.2. Note these are bulk stackings, so the nomenclature differs to the one used to describe high symmetry stackings of TMD homobilayers in Chapter 6.

1T stacking (shown in Fig. 2.1) has a single-layer repeat, and the top and bottom chalcogen layers are not directly on top of each other. It is metallic.[26]. 3R stacking (shown in the

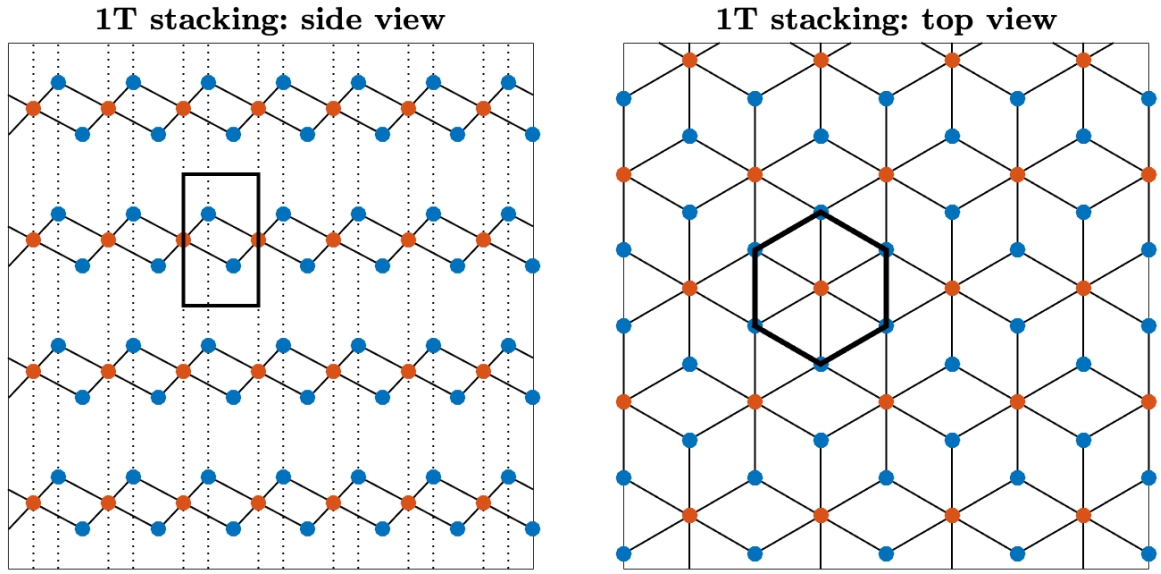


Figure 2.1: Top and side view of 1T stacked TMDs. Red indicates metal atoms, blue indicates chalcogen atoms, and the unit cell is indicated in bold lines.

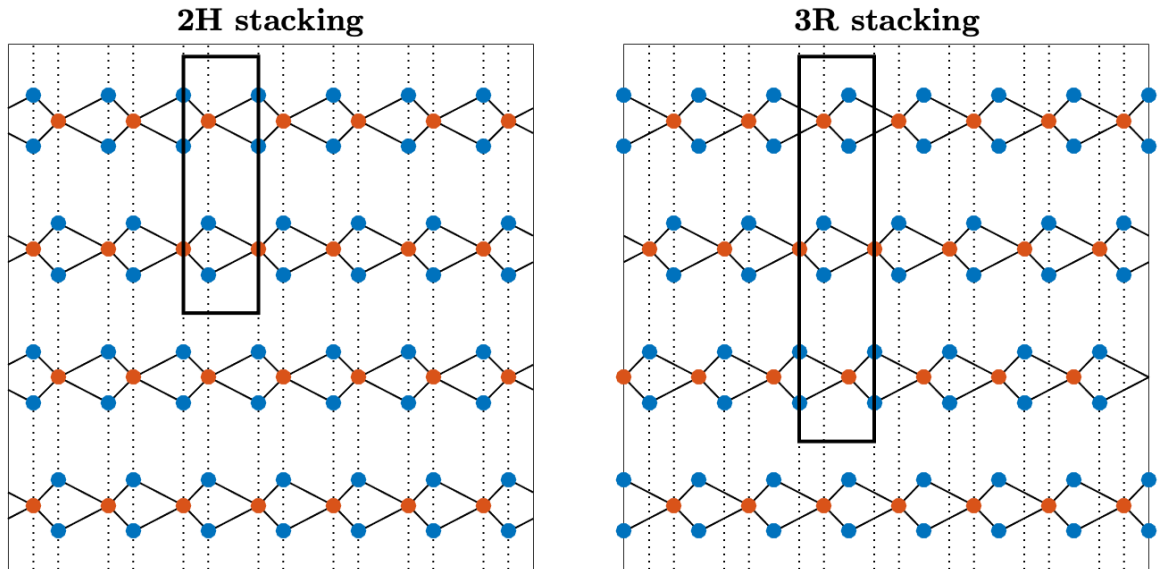


Figure 2.2: Side view of 2H and 3R stacked TMDs. Red indicates metal atoms, blue indicates chalcogen atoms, and the unit cell is indicated in bold lines.

right-hand panel of Fig. 2.2) has a unit cell comprised of three layers which are oriented the same way but shifted relative to each other. 2H stacking (shown in the left-hand panel of Fig. 2.2) has a two-layer repeat, and the two layers are flipped relative to each other but not shifted. Both 2H and 3R stackings are semiconducting[27]. In this work, I will consider semiconducting TMDs, composed of the type of monolayer of which 2H and 3R stacking are comprised, where the top and bottom chalcogen layer within the trilayer structure are directly on top of each other, forming a honeycomb lattice similar to graphene and hBN when viewed from the top.

2.1.3 Optical Properties of TMDs

TMDs first started to be considered as a particularly interesting type of atomically thin semiconductor in 2010, when several papers were published which found that monolayer MoS₂ displayed much stronger photoluminescence than bilayer or bulk MoS₂[28, 29, 30]. The same effect was found in MoSe₂[31], WS₂[32], WSe₂[32, 33], and MoTe₂[33, 34]. It was found that this is due to the fact that n -layer TMDs for $n \geq 2$ are indirect bandgap semiconductors, but monolayer TMDs are direct bandgap semiconductors. This explanation was theoretically predicted by DFT calculations for MoS₂[35] and GW-BSE calculations for MoS₂, MoSe₂, WS₂, WSe₂, and MoTe₂[36] in 2012, and experimentally confirmed in 2013[37] for MoS₂ by photoluminescence spectroscopy of the valence band, confirming the change of order of valence band maxima from Γ being higher in energy in multilayer systems and K/K' being higher in energy in the monolayer system.

In this work, I will only simulate optical spectra for TMDs in vacuum. However, in reality, measuring optical spectra requires the use of a substrate. Our code does include the option for a substrate, but only in the form of a substrate-specific dielectric constant affecting the screened Coulomb interaction, which is a significantly simplified picture. The first measurements of optical properties of atomically thin TMDs used SiO₂ as a substrate[38]. One of the most important technological developments for photoluminescence spectroscopy for atomically thin semiconductors in recent years is the use of high-quality h-BN as a substrate instead[39,

40, 41], which yields significantly sharper optical peaks.

In both monolayer and bilayer systems, the optical spectra of TMDs are governed by excitons[42, 43, 44, 2, 45, 46]. It is possible to differentiate between two qualitatively very different types of excitons: intralayer excitons, in which the composite electron and hole are located in the same layer, and which broadly behave like their monolayer counterparts, and interlayer excitons, in which electron and hole are located in different layers. Interlayer excitons have a dipole moment perpendicular to the heterostructure, since the composite particles have opposite electric charge, and can therefore be identified experimentally relatively straightforwardly by the application of an electric field perpendicular to the heterostructure. This has been done e.g. by Joe et al.[47], Jauregui et al[48], and Calman et al.[49] for MoSe₂/WSe₂, and Lorchat et al.[50] for MoS₂ homobilayers. The spatial separation of electrons and holes in interlayer excitons means they have significantly longer lifetimes (by an order of magnitude) than intralayer excitons, see for instance Rivera et al.[51] for MoSe₂/WSe₂.

Semiconducting transition metal dichalcogenide bilayers broadly fall into two categories, homobilayers (in which both layers contain the same chemical elements) and heterobilayers (in which they do not). In this work, I will consider only MoS₂ homobilayers, but the method is suitable for heterobilayers as well.

Optical properties of MoS₂ homobilayers have been reported on in Refs. [52, 53, 50] for different stacking configurations, and in Refs. [54, 55, 56, 57, 58] for relative twist angles between the layers. The excitation energies of momentum direct excitons in MoS₂ homobilayers has not been found to vary much with twist angle[57], whereas the momentum indirect excitons depend very strongly on twist angle[57].

TMD heterobilayers can again be split into two categories, depending on whether the chalcogen atoms used in the two different layers are the same or different. The lattice parameters of TMDs with the same chalcogen atoms are nearly identical, but the lattice parameters of TMDs

	MoS ₂	MoSe ₂	WS ₂	WSe ₂
a (Å)	3.16	3.29	3.15	3.28
d_{X-X} (Å)	3.17	3.33	3.14	3.34
d_{X-M} (Å)	2.42	2.52	2.40	2.53

Table 2.1: Lattice constant a , distance between chalcogen layers (d_{X-X}), and between metal and chalcogen atoms (d_{X-M}) from experimental bulk data. Data for MoS₂ from Ref. [59], MoSe₂ from Ref. [60], WS₂ from Ref. [61], and WSe₂ from Ref. [62].

with different chalcogen atoms have a more significant mismatch, resulting in a moiré lattice even without a twist angle (see Tab. 2.1 for experimental lattice parameters for bulk TMDs).

For heterobilayers with different chalcogen atoms, Fang et al.[4] investigated the optical properties of WSe₂/MoS₂, with a particular focus on the interlayer distance dependence by creating heterostructures of WSe₂ and MoS₂ separated by varying numbers of layers of hBN, which due to its large bandgap itself does not significantly impact the optical properties at low energies. Kunstmann et al.[63] equally looked at WSe₂/MoS₂ heterobilayers and compared their measured photoluminescence spectra to ab initio calculations. Photoluminescence spectra have also been measured for MoS₂/MoSe₂[64, 65], WS₂/WSe₂[66], and MoSe₂/WS₂ and MoTe₂/MoSe₂[65].

Heterobilayers with the same type of chalcogen atom have garnered a lot of interest, with MoSe₂/WSe₂ as a particular focus[51, 74, 75, 76, 77, 78, 79, 80, 81, 67, 68, 47, 69, 70, 48, 49, 71, 72, 73, 65], and somewhat less work on MoS₂/WS₂[82, 83, 65]. (Of course, this does not claim to be a complete review, so this may be a bias in sampling.)

A lot of the recent literature is focused on interlayer excitons in particular, due to their long life time[70, 48] and room temperature stability[75]. It is worth noting, however, that excitons are rarely purely interlayer or intralayer. Instead, they are often of a hybrid nature, with both interlayer and intralayer contributions[80]. This is true in the purely theoretical case as well. There is no layer character operator or symmetry that commutes with the Hamiltonian to enforce the existence of purely interlayer or intralayer excitons.

In heterobilayers with the same type of chalcogen, the lattice mismatch is significantly smaller and the resulting crystals can locally be approximated well by assuming there is no lattice mismatch. However, it is still possible to obtain moiré crystals through twisting[77, 71, 72, 73], similar to the homobilayer case. Twisting can have a strong effect on the interlayer excitons, in particular on their lifetime[77].

2.1.4 Experimental synthesis of twisted bilayers of atomically thin semiconductors

Finally, it is worth highlighting that the experimental synthesis of twisted bilayers of atomically thin materials is very difficult, since these systems do not typically form in nature. It is even more difficult to create a twisted crystal with a controlled angle, and this represents a significant achievement of engineering.

There are two main steps in the creation of twisted VdW heterobilayers[84]. First, atomically thin materials have to be created. Second, these layers have to be stacked.

There are several different approaches to creating 2D crystals. *Chemical vapour deposition* (CVD) is the process of vapourizing a material by high temperature or low pressure and letting it condense onto a substrate [85]. *Molecular-beam epitaxy* (MBE) is similar in that a 2D crystal is grown onto a substrate. Specifically, a molecular beam of a material is formed by sublimating the material in a chamber which is connected to a vacuum chamber by a small orifice. The molecular vapour expands through the orifice to form a beam of particles which then get deposited onto the substrate[86]. Both these methods allow for the formation of large 2D flakes, but can be vulnerable to undesired impurities and strong coupling to the substrate[87, 88, 89, 90].

A fundamentally different approach is given by *mechanical exfoliation*, which involves tearing off layers of VdW crystals[91, 12, 14, 92, 32]. This technique allows for cleaner stacking

interfaces and less substrate coupling compared to CVD and MBE, but the resulting flakes are smaller[84].

Mechanical exfoliation is often done in air, which can introduce unwanted impurities from the air. One solution is to perform the exfoliation in an oxygen plasma, which has produced good results for graphene and Bi-2212[93, 94]. However, this has been less successful for transition metal dichalcogenides.

Another recent improvement in exfoliation technology is to use an ultrathin gold adhesion layer[95, 96] between 2D crystal and substrate, which allows for the production of larger 2D flakes with diameters up to centimeter scales. However, this can quench the photoluminescence spectrum. Other materials for adhesion layers have been used, such as silver[97], resulting in large 2D flakes with enhanced photoluminescence spectra.

Once the 2D crystals have been synthesized, twisted bilayers can be formed from them. One common approach is to tear, rotate, and stack[98]: a hemispherical handle substrate is formed from a drop of epoxy or PDMS. This handle substrate may be coated with a polymer to act as a sort of glue. This is then used to pick up a 2D flake, rotated at the desired angle, and a second 2D flake is picked up.

For homobilayers, the angle can be particularly well controlled. A single flake can be split into two, ensuring that the initial relative rotations of the two layers with respect to each other is zero, and then the two flakes can be picked up sequentially in the manner described above. The flake can be cut into two with the use of a laser[99], ensuring straight edges and providing additional reference for the measurement of the twist angle.

2.2 Theory

2.2.1 GW-BSE

One of the most sophisticated methods for computing optical properties of crystalline materials is the so-called GW-BSE approach. The general structure is usually to take the Kohn–Sham eigenvalues and eigenfunctions obtained from a density functional theory (DFT) calculation (cf. Sec. 3.1 for a brief overview on DFT) as the starting input for a Dyson equation calculation to obtain single-particle excited states within the GW-approximation, which in turn get used as input into the Bethe–Salpeter equation (cf. Sec. 3.6) to obtain two-particle excited states[3].

There are several large-scale codes which implement this approach[3, 100, 101, 102, 103, 104, 105, 106], and they have been used to calculate the optical properties of a variety of two-dimensional semiconductors[36, 116, 117, 118, 119, 120, 121, 122, 123, 107, 108, 109, 110, 111, 6, 112, 113, 114, 115].

GW-BSE calculations of optical properties of TMDs have confirmed that excitons are an important element of their optical properties[36, 117, 118], due to their strong binding energy, which in turn is due to the weak dielectric screening in atomically thin materials. These calculations are also the origin of one of the most distinctive features of the optical spectra of TMD monolayers: the two large sub-bandgap peaks, called A and B peaks, and which are due to the strong valence band spin-splitting at the K point (where the direct bandgap is located)[124].

Similar calculations have also been carried out on TMD heterostructures[113, 124, 128, 129, 130, 131, 132, 52, 133, 125, 126, 127]. They find A and B peaks similar to the monolayers[113, 124, 128, 131, 132, 52], due to intralayer interaction, but also bilayer specific features, namely interlayer excitons, some of which are optically active[131]. Several studies have been done investigating the effect of stacking configuration and twisting on optical properties, and significant effects have been found[128, 132, 52]. He et al.[128] compared five different high-symmetry

stackings for MoS_2 , and the two bilayer stackings corresponding to the bulk stackings 2H and 3R (which I call AB and B^{MX} stacking in this work, respectively) for MoSe_2 , WS_2 , and WSe_2 . They find that in the stackings in which the chalcogen atoms are situated directly on top of each other (and which, correspondingly, have the largest interlayer separation), the indirect bandgap is located at the K valence band edge and the Q conduction band edge. For all other stackings, they find that it is at the Γ valence band edge and Q conduction band edge. Comparing optical spectra of AB and B^{MX} stacking, they find that AB is spin-degenerate, but B^{MX} is not. Note that AB stacking still exhibits the spin split bands originating from the monolayer, but that due to the inversion symmetry in this stacking, a spin down transition in one layer is equal in energy to a spin up transition in the other layer. The lack of spin degeneracy in B^{MX} stacking results in a greater number of smaller optical peaks nearby each other contributing to the observed optical conductivity peaks, compared to fewer, larger peaks for AB stacking, but that the observed spectra in the resolution measured in their work are still very similar, exhibiting the A and B peaks also present in monolayer spectra.

In contrast, Gerber et al.[52], comparing different high-symmetry stackings of MoS_2 , found that B^{MX} stacked bilayers exhibited the additional, smaller interlayer peak between the A and B peaks compared to AB stacking which has been found in experiments[50].

Lu et al.[132] compared quasiparticle spectra and exciton energies of $\text{MoSe}_2/\text{WSe}_2$ bilayers with small twist angles, and found that the interlayer exciton energies greatly depended on the local stacking configuration of the part of the moiré lattice at which the excitons were localized.

2.2.2 Effective mass models and $k \cdot p$ -theory

The ab initio approach described in the previous section can yield very accurate results. However, they are very computationally challenging. There exist several more computationally tractable approaches which have been used to describe atomically thin TMDs.

The simplest is effective mass theory[44, 140, 141, 142, 143, 144, 145, 146, 147, 134, 135, 136, 137, 138, 139] (cf. Sec. 3.5), which I use in this work to compare to results from more complicated calculations, to see whether any of the observed trends can be explained from just the band edge curvatures alone.

Another slightly more complex and frequently used technique is $\mathbf{k} \cdot \mathbf{p}$ -theory[148, 151, 109, 152, 153, 154, 155, 156, 157, 149, 150], which is a perturbative tight-binding approach, in which the Schrödinger equation for crystal electrons,

$$\left[\mathcal{H}_0 + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} \right] u_{\lambda\mathbf{k}}(\mathbf{r}) = \bar{E}_{\lambda\mathbf{k}} u_{\lambda\mathbf{k}}(\mathbf{r}) , \quad (2.1)$$

is solved in second-order perturbation theory in $\mathbf{k}$ (the first order expansion vanished due to symmetry)[158]. Here, $\mathcal{H}_0 = p^2/2m_0 + V_0(\mathbf{r})$, $\bar{E}_{\lambda\mathbf{k}} = E_\lambda - \hbar^2 k^2/2m_0$, and m_0 is the electron mass. $u_{\lambda\mathbf{k}}$ is the lattice-periodic part of the electronic wavefunction, and V_0 is the periodic potential. λ labels the eigenstates.

These methods can be very instructive, and they can cover very large system sizes, but they are by nature very approximate.

2.2.3 The tight-binding approach to solving the BSE

One compromise between the atomistic nature of GW-BSE theory and the numerical feasibility of $\mathbf{k} \cdot \mathbf{p}$ -theory or effective mass approaches is to construct and diagonalize a Bethe–Salpeter Hamiltonian in a tight-binding basis. This approach is described in detail in Sec. 3.7. There exist several implementations of this approach in literature, some with minimal two- or three-band tight-binding Hamiltonians, eg. Ref.[159] for both two and three band-models for general TMDs, and Ref.[160] and Ref.[161] for MoS₂, and Ref. [162] for a six-band model. Others use a larger basis, including all the valence orbitals on the relevant atoms, that is, five d -orbitals on the metal atoms and 3 p -orbitals each on the two chalcogen atoms[163, 164, 165].

Even though these models are based on eleven-orbital (22 including spin) tight-binding Hamiltonians, they still differ in some key aspects. The first is the nature of dielectric screening. The most common approach is to use the Rytova–Keldysh interaction (cf. Sec. 3.8) and assume static screening[161, 164, 163, 162], others use a dielectric function extracted from DFT[165]. The other difference is the way in which the tight-binding parameters are obtained. In some models, the parameters are directly fitted to ab initio bandstructures[163], in others, the parameters are obtained from projecting the DFT Hamiltonian into a localized Wannier basis (cf. Sec. 3.4) and extracting the hopping parameters directly from the new, localized Hamiltonian, assuming the Wannier orbitals and atomic orbitals are similar[164, 162, 1]. The resulting Hamiltonian can be truncated and the number of free parameters reduced by symmetry[1], or the entire Hamiltonian can be used as is[165].

It is possible to construct tight-binding Hamiltonians for twisted (and untwisted) TMD bilayers on the basis of the monolayer models used in the TB-BSE models above[5]. The goal of this work is to use the TB-BSE approach with a twisted TMD tight-binding model based on an eleven-orbital monolayer model[5] to study the character of the optical spectra of MoS₂ bilayers with a particular focus on the layer character of the excitons characterizing the sub-bandgap spectra.

Chapter 3

Methods

In this chapter, I will provide overviews over all the different methods that are employed in this work. I will start by describing the electronic structure calculations required for the tight-binding model described in Chapter 4: I will briefly introduce density functional theory (DFT) in Sec. 3.1, then Bloch's theorem in Sec. 3.2. Then, following from that, I will provide a brief overview of tight-binding theory in Sec. 3.3. In Sec. 3.4, I will explain how to obtain tight-binding parameters from DFT calculations by Wannierization.

Next, I will talk about how to model excitons. For comparison, I will mention hydrogen-like excitons (in atomically thin materials specifically) in Sec. 3.5. Next, in Sec. 3.6, I will talk about the Bethe–Salpeter equation (BSE), and derive the effective Bethe–Salpeter Hamiltonian in a tight-binding basis in Sec. 3.7. The details of the electrostatic screening in atomically thin semiconductors deserve their own section, Sec. 3.8. In Sec. 3.9, I will talk about how to obtain optical spectra from the results of the BSE calculations.

Finally, in Sec. 3.10, I will talk about the computational details of the various calculations done in this work. I will provide details about the DFT calculations we have used, as well as convergence parameters of the BSE calculations, and talk about finite lattice effects on the electrostatic interaction.

3.1 Density functional theory

The full quantum mechanical Hamiltonian $\hat{H}$ for a many body system can be expressed in general as

$$\hat{H} = \hat{T} + \hat{U} + \hat{V} , \quad (3.1)$$

where $\hat{T}$ describes the kinetic energy of all constituent particles, $\hat{U}$ describes the electrostatic interaction between all constituent particles, and $\hat{V}$ is the external potential, describing everything else. This last term can be understood to define a system, since the other two terms are system-independent except for the number of particles included.

Frequently, $\hat{T}$ and $\hat{U}$ will only include electrons, and the atomic nuclei will be considered as part of the external potential. This is known as the Born–Oppenheimer approximation, and it is based on the fact that electrons are several orders of magnitude lighter (and therefore faster) than the nuclei, and that the nuclei can therefore be considered to be stationary on the time scales of electronic motion.

Density functional theory (DFT) is based on two theorems. Firstly, the Hohenberg–Kohn theorem[166], which states that there is a bijection between the ground state electron-density $n(\mathbf{r})$ and the external potential $V(\mathbf{r})$ —and therefore states that a system is fully determined by the ground state density.

And secondly, the Kohn–Sham theorem[167], which gives a mapping between a fully interacting many-body system with ground state electron density $n(\mathbf{r})$, and a *noninteracting* effective Hamiltonian $\hat{H}_{\text{KS}}$,

$$\hat{H}_{\text{KS}} = \hat{T} + \hat{V}_{\text{KS}} \quad (3.2)$$

with the same ground state density. (This is not a contradiction to the Hohenberg–Kohn theorem, since this effective Hamiltonian does not include electron-electron interactions; which is also what makes it computationally solvable). The Kohn–Sham potential $\hat{V}_{\text{KS}}$ is often written as

$$\hat{V}_{\text{KS}}(\mathbf{r}) = \hat{V}(\mathbf{r}) + \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \hat{V}_{\text{XC}}[n(\mathbf{r})](\mathbf{r}) , \quad (3.3)$$

where the first term is just the external potential from Eq. (3.1), the second term is the Hartree potential, which describes the Coulomb interaction of a single electron with the ground state density (which includes itself), and $\hat{V}_{\text{XC}}$ is the exchange-correlation potential, which includes everything not described by the other two terms, and which needs to be approximated in practical DFT calculations.

3.1.1 Exchange-correlation functional

The simplest approximation to the exchange-correlation functional is the local-density approximation (LDA)[168], in which the potential is described by an integral over an energy density ϵ_{XC} which depends on the local electron density only,

$$E_{\text{XC}}^{\text{LDA}}[n(\mathbf{r})] = \int d^3\mathbf{r}' n(\mathbf{r}') \epsilon_{\text{XC}}(n(\mathbf{r}')) . \quad (3.4)$$

The simplest way of including non-local effects is provided by the generalized gradient approximation (GGA)[168], in which the energy density under the integral depends on the local value of the first derivative of the electronic density as well as the local value of the density itself,

$$E_{\text{XC}}^{\text{GGA}}[n(\mathbf{r})] = \int d^3\mathbf{r}' f(n(\mathbf{r}'), \nabla n(\mathbf{r}')) . \quad (3.5)$$

The precise nature of the functional dependence of the energy densities in the LDA and GGA exchange-correlation functionals is rarely analytically known. Different codes approximate them in different ways.

3.1.2 Pseudopotentials

Another common approximation in DFT calculations is the use of pseudopotentials[169]. They provide a way to significantly reduce basis size, and therefore computational effort. The basic assumption is that not all electrons in a solid have to be treated equally. The core electrons of the constituent atoms are approximated by an effective potential. Only the valence electrons are modelled explicitly. Furthermore, the valence electron wavefunctions are approximated by wavefunctions with fewer nodes. This allows for the use of a plane wave basis, where a computationally tractable number of plane waves suffices to describe the wavefunctions.

The pseudopotentials used in DFT calculations nowadays are typically norm-conserving[170]. This means they fulfil the following criteria: inside a given cutoff radius r_c , the norm of the pseudowavefunction ϕ_i^{PP} has to be equal to the norm of the corresponding all-electron wavefunction ϕ_i^{full} , that is[171]

$$\int_{|\mathbf{r}| < r_c} d^3\mathbf{r} (\phi_i^{\text{PP}})^* \phi_j^{\text{PP}} = \int_{|\mathbf{r}| < r_c} d^3\mathbf{r} (\phi_i^{\text{full}})^* \phi_j^{\text{full}} , \quad (3.6)$$

and above this radius, ϕ_i^{PP} and ϕ_i^{full} have to be identical.

3.2 Bloch's theorem

Bloch's theorem lies at the centre of condensed matter theory, allowing for the ab initio calculation of macroscopically large systems through use of translational symmetry. Wavefunctions in periodic solids are eigenfunctions of the discrete translation operator. Based on this, Bloch's theorem can be derived. It states that eigenfunctions of a periodic solid $\psi_{n\mathbf{k}}(\mathbf{r})$ can be written in terms of the crystal momentum $\mathbf{k}$ (which can be interpreted as a quantum number associated with the translation operator) and a lattice periodic function $u(\mathbf{r})$ as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) , \quad (3.7)$$

such that

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R})\psi_{n\mathbf{k}}(\mathbf{r}) , \quad (3.8)$$

where $\mathbf{R}$ is a lattice vector.

3.3 Tight-binding theory

This section will give an overview over tight-binding theory in general, as well as some of the methods used in the model which is the basis of our calculations. Details of that model will be presented later, in Chapter 4, since some of the details are the result of my own work. The key assumption of tight-binding theory is that the wavefunction $\psi_{n\mathbf{k}}(\mathbf{r})$ can always be written in as a linear combination of basis states orbitals $\tilde{\chi}_{A\mathbf{k}}$,

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_A C_{nA\mathbf{k}} \tilde{\chi}_{A\mathbf{k}}(\mathbf{r}) , \quad (3.9)$$

which in turn can be written as a linear combination of specific atomic orbitals ϕ_A at different lattice sites,

$$\tilde{\chi}_{A\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \phi_A(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_A) , \quad (3.10)$$

chosen to obey Bloch's theorem (3.7),

$$\tilde{\chi}_{A\mathbf{k}}(\mathbf{r} + \mathbf{R}') = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \phi_A(\mathbf{r} + \mathbf{R}' - \mathbf{R} - \boldsymbol{\tau}_A) \quad (3.11)$$

$$= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}''=\mathbf{R}-\mathbf{R}'} \exp(i\mathbf{k} \cdot (\mathbf{R}'' + \mathbf{R}')) \phi_A(\mathbf{r} - \mathbf{R}'' - \boldsymbol{\tau}_A) \quad (3.12)$$

$$= \exp(i\mathbf{k} \cdot \mathbf{R}') \tilde{\chi}_{A\mathbf{k}}(\mathbf{r}) . \quad (3.13)$$

Here, n is the band index, A is the orbital index (which includes the spin index), $C_{nA\mathbf{k}}$ are the tight-binding coefficients and $\phi_A(\mathbf{r})$ is the A -th atomic orbital, $\boldsymbol{\tau}_A$ is the unit cell coordinate of

the atom around which $\phi_A(\mathbf{r})$ is localized, and N is the number of unit cells in the crystal.

Combining Eqs. (3.9) and (3.10) yields

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}, A} \exp(i\mathbf{k} \cdot \mathbf{R}) C_{nA\mathbf{k}} \phi_A(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_A) . \quad (3.14)$$

Note that it is possible to chose a single-particle basis in such a way as to make the location of the relevant orbital within the unit cell more explicit,

$$\chi_{A\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\tau}_A)) \phi_A(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_A) . \quad (3.15)$$

Both Eq. (3.10) and (3.15) are commonly used conventions. We will be using (3.15) in the remainder of this work.

The tight-binding eigenvectors $C_{nA\mathbf{k}}$ obey the eigenvalue problem

$$\sum_B H_{AB}(\mathbf{k}) C_{nB\mathbf{k}} = E_{n\mathbf{k}} C_{nA\mathbf{k}} , \quad (3.16)$$

and the tight-binding Hamiltonian matrix elements can be written as

$$H_{AB}(\mathbf{k}) = \langle \chi_{A\mathbf{k}} | \hat{H} | \chi_{B\mathbf{k}} \rangle \quad (3.17)$$

$$= \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'} \exp(i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R} + \boldsymbol{\tau}_B - \boldsymbol{\tau}_A)) \langle \phi_{A\mathbf{R}} | \hat{H} | \phi_{B\mathbf{R}'} \rangle \quad (3.18)$$

$$= \sum_{\Delta\mathbf{R}} \exp(i\mathbf{k} \cdot (\Delta\mathbf{R} + \boldsymbol{\tau}_B - \boldsymbol{\tau}_A)) \underbrace{\langle \phi_{A\Delta\mathbf{R}} | \hat{H} | \phi_{B0} \rangle}_{(*)} , \quad (3.19)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 - \sum_{Ri} \frac{Z_i e^2}{|\mathbf{r} - \mathbf{R} - \boldsymbol{\tau}_i|} , \quad (3.20)$$

where i sums over the atoms in the unit cell and $\mathbf{R}$ sums over all the unit cells. Z_i is the number of protons in the nucleus of atom i , e is the electric charge of the electron, and m_e is

the electron mass. Note that when we fit to DFT, we assume the Hamiltonian also includes electron-electron interaction at the mean-field level.

There are two facts which make tight-binding methods efficient. Firstly, the overlap between orbitals located on different atoms is assumed to decrease rapidly with distance, so that the full Hamiltonian matrix (3.19) can be approximated by restricting the sum to a finite number of terms. This is a reasonable assumption for semiconductors. Secondly, instead of calculating the hopping integrals (*) explicitly, they are often used as fitting parameters in order to reproduce band structures from more complex electronic structure calculations while reducing basis size—sometimes drastically.

3.3.1 Slater–Koster parameters

One way of parameterizing tight-binding band structures is to use Slater–Koster parameters, which we will do for the interlayer hoppings. This section will provide a brief summary of this method.

The single-particle Hamiltonian (3.20) includes a sum over nuclear potentials centered at all the atomic sites in the crystal. This means each integral in Eq. (3.19) has contributions from three different locations: the position of the two atomic orbitals $\phi_{A\Delta\mathbf{R}}$ and ϕ_{B0} , and the location of the atom on which the potential term is centred. The central idea of the two-centre approximation, as introduced by Slater and Koster in 1954[172], is to include only those integrals which have contributions from at most two locations: the on-site integrals, in which both atomic orbitals and the potential are all located around the same site, and the two-centre integrals, in which the atoms are on different sites and the interaction is centred around one of those two sites.¹

The resulting integrals are dependent on $\Delta\mathbf{R}$ and the type of orbitals involved—more specifically, the angular momentum of the types of orbitals involved. Therefore the full Hamiltonian

¹There is a third type of term which would appear to fulfil the requirements, where the atomic orbitals are on the same site but the interaction is centred around a different site. This is also disregarded.

can be expressed in terms of integrals of the type

$$V_{ab\gamma} = \langle \phi_{a\gamma} | \hat{H}^{2C} | \phi_{b\gamma} \rangle , \quad (3.21)$$

where $\hat{H}^{2C}$ is the two-centre part of the single-particle Hamiltonian (3.20), including only the kinetic energy and the nuclear potentials centred on the atoms on which orbitals $|\phi_{a\gamma}\rangle$ and $|\phi_{b\gamma}\rangle$ are located. Here, a and b denote the angular momentum quantum numbers and γ describes the symmetry of the bonds.

This technique reduces the complexity of the system to a very small number of parameters which relate to the hopping matrices through a relatively small number of equations which are readily available in the literature, e.g. Table 1 in Ref. [172].

This is a very useful choice for the interlayer hoppings, because we are interested in a large number of systems each with slightly different interlayer configurations. In a twisted bilayer, the types of orbitals we consider are the same regardless of twist angle, but their relative distance and orientation is highly dependent on the twist angle and the position in the moiré unit cell. We are able to find analytic fitting functions to describe the distance dependence of the relevant Slater–Koster parameters, allowing us to, in principle, simulate arbitrary twist angles and stacking configurations based on a small number of parameters.

3.4 Wannierization

In this work, I will use tight-binding parameters derived directly from ab initio calculations by way of Wannier functions. The purpose of this section is to give a brief overview of this procedure. I found Dr. Z. Goodwin’s PhD thesis[173] particularly useful in writing this.

Wannier functions $|w_n \mathbf{R}\rangle$ provide an alternative, real-space basis for solid state systems, related

to Bloch functions $\psi_{n\mathbf{k}}$ by a lattice Fourier transform,

$$|w_n\mathbf{R}\rangle = \frac{1}{\sqrt{N_{\mathbf{k}}}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n\mathbf{k}}\rangle . \quad (3.22)$$

These functions are not unique, because the Bloch functions are only defined up to a complex phase which can itself be $\mathbf{k}$ -dependent,

$$\psi_{n\mathbf{k}} \rightarrow e^{i\phi_n(\mathbf{k})} \psi_{n\mathbf{k}} , \quad (3.23)$$

which can have a significant impact on the form of the Wannier functions due to the sum over $\mathbf{k}$ in Eq. (3.22).

More generally, given a set of bands separated in energy from all other bands, any unitary transform $U_{nm}^{(\mathbf{k})}$ between the constituent Bloch states will result in the same bandstructure, but completely different Wannier functions[174],

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = \sum_{m=1}^{n_{\text{bands}}} U_{nm}^{(\mathbf{k})} |\psi_{n\mathbf{k}}\rangle , \quad (3.24)$$

and

$$|w_n\mathbf{R}\rangle = \frac{1}{\sqrt{N_{\mathbf{k}}}} \sum_{\mathbf{k}} \sum_{m=1}^{n_{\text{bands}}} e^{-i\mathbf{k}\cdot\mathbf{R}} U_{nm}^{(\mathbf{k})} |\psi_{n\mathbf{k}}\rangle . \quad (3.25)$$

The choice of Wannier functions is therefore not unique, and different choices can be made for different applications. Frequently, what is desired are Wannier functions that are maximally localized, that is, which minimize the spread around the site at which they are centered. This can be treated as an optimization problem, by treating the spread as a functional of the unitary matrix $U_{nm}^{(\mathbf{k})}$ in Eq. (3.25).

Optimization algorithms require initial guesses, and a good choice of initial guess can make the computation more efficient, but also result in a particular local minimum. For Wannier functions, one can use atomic orbitals $|g_n\rangle$ to obtain an initial guess (particularly an orbital

with specific angular momentum quantum number), and start by projecting the Bloch states $|\psi_{m\mathbf{k}}\rangle$ onto this orbital, resulting in

$$\phi_{n\mathbf{k}} = \sum_{m=1}^{n_{\text{bands}}} |\psi_{m\mathbf{k}}\rangle \langle \psi_{m\mathbf{k}} | g_n \rangle \equiv \sum_{m=1}^{n_{\text{bands}}} |\psi_{m\mathbf{k}}\rangle A_{mn}^{\mathbf{k}} . \quad (3.26)$$

The overlap matrix $A^{\mathbf{k}}$ in Eq. (3.26) is not unitary, so this projection does not result in a set of orthonormal states. It is, however, possible to orthonormalize the resulting set by

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = \sum_{m=1}^{n_{\text{bands}}} |\phi_{m\mathbf{k}}\rangle \left(S_{\mathbf{k}}^{-1/2} \right)_{mn} , \quad (3.27)$$

where

$$(S_{\mathbf{k}})_{mn} = \left(A_{\mathbf{k}}^{\dagger} A_{\mathbf{k}} \right)_{mn} . \quad (3.28)$$

The set $|\tilde{\psi}_{n\mathbf{k}}\rangle$, called Löwdin-orthonormalized Bloch-like states, have smooth gauge in $\mathbf{k}$. They can be wannierized using Eq. (3.22), resulting in well-localized functions.

The resulting functions are not atomic orbitals, but they can be very similar to atomic orbitals. It is then possible to take an effective, ab-initio Hamiltonian obtained from, e.g., DFT and its Bloch states, choose a set of atomic orbitals to use as starting guesses, obtain the corresponding Wannier functions as described in this section, express the DFT Hamiltonian in the basis of Wannier functions, and extract relevant tight-binding parameters from it. In this way, the resulting tight-binding model can be said to be ab initio: we do not fit parameters to a bandstructure but instead compute the hoppings directly.

3.5 Rydberg excitons

The lowest energy excitonic states in semiconductors are generally composed of holes located at the valence band maximum and electrons at the conduction band minimum. In the case of a direct bandgap, this is true for the lowest energy optically active excitons. In the case of

an indirect bandgap, this can still be somewhat true for the optically active excitons, if the smallest direct gap is a transition from a local valence band maximum to a local conduction band minimum. In all these cases, it is possible to approximate the lowest energy excitons through the effective mass model.

Energy bands near band extrema can always be approximated locally by a parabolic dispersion. In that case, it may therefore be possible to describe an exciton as a bound state of a negatively charged free particle and a positively charged free particle with effective masses m_e^* and m_h^* . These effective masses can be obtained from the local band curvature by free particle dispersion,

$$E(\mathbf{k}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m^*} \Rightarrow m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial \mathbf{k}^2}} . \quad (3.29)$$

These excitons are known as Rydberg excitons. Rydberg exciton energies and wavefunctions can then be obtained by solving the hydrogenic Schrödinger equation,

$$\left[-\frac{\nabla^2}{2\mu^*} + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E_n \psi(\mathbf{r}) , \quad (3.30)$$

where V is the electrostatic interaction between electron and hole and μ^* is the effective reduced mass,

$$\mu^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*} . \quad (3.31)$$

In three dimensions, in a semiconductor or insulator, the dielectrically screened Coulomb interaction is given by

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0\epsilon|\mathbf{r}|} , \quad (3.32)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, and ϵ is the background dielectric constant. The eigenenergies of the bound states of the three-dimensional hydrogen atom are

well known,

$$E_n^{3D} = -\frac{\mu^* e^4}{2(4\pi\epsilon_0\epsilon)^2 \hbar^2} \frac{1}{n^2}, \quad (3.33)$$

for integer n .

It is possible, albeit somewhat less well known, to solve the hydrogen atom in a purely two-dimensional system[175]. In a universe with two spatial dimensions, the eigenenergies of the bound hydrogen states are given by,

$$E_n^{2D} = -\frac{\mu^* e^4}{2(4\pi\epsilon_0\epsilon)^2 \hbar^2} \frac{1}{\left(n - \frac{1}{2}\right)^2}. \quad (3.34)$$

However, two-dimensional materials are not two-dimensional universes—the electric fields lines extend into three dimensions, even if the particles are confined to two dimensions. And yet, describing excitons in two-dimensional materials as three-dimensional hydrogen does not work well either. This is because the screening is not as uniform as the single dielectric constant ϵ in Eq. (3.32) implicitly assumes. See Fig. 3.1 for an illustration of this.

Electrostatic screening in flat sheets of material in three-dimensional universes can be described well by the Keldysh interaction (more on that later, in Sec. 3.8),

$$W(\mathbf{r}) = \frac{\pi e^2}{2\epsilon r_0} \left[\mathbf{H}_0 \left(\frac{r}{r_0} \right) - \mathbf{Y}_0 \left(\frac{r}{r_0} \right) \right], \quad (3.35)$$

where $\mathbf{H}_0$ is a Struve function, $\mathbf{Y}_0$ is a Bessel function of second kind, r_0 is an effective screening length classically proportional to layer thickness, and related to the polarizability α^{2D} by $r_0 = 2\pi\alpha^{2D}$ [176]. To my knowledge, no closed-form solution to the hydrogen atom with this type of screening is known—given the complexity of the real-space expression of the Keldysh interaction, a lack of an closed-form solution would perhaps not be surprising. However, it is not computationally difficult to find numerical solutions. Furthermore, an approximate closed-form solution to the lowest exciton binding energy has been found by Olsen et al.[146], by

calculating the average screening felt by an exciton, resulting in

$$E_0^{\text{quasi 2D}} \approx \frac{8\mu^*}{\left(1 + \sqrt{1 + 32\pi\alpha\mu^*/3}\right)^2}. \quad (3.36)$$

This is a useful expression for some quick sanity checks when trying to understand binding energy behaviour from more complicated calculations in later chapters.

Note that one consequence of Eq. (3.36) is the limiting case $\mu^* \rightarrow \infty$, corresponding to flat bands. In this case,

$$\lim_{\mu^* \rightarrow \infty} E_0^{\text{quasi 2D}} \approx \frac{3}{4\pi\alpha}, \quad (3.37)$$

which for the case of MoS₂ bilayers is equal to about 600 meV (see Sec. 3.8 for details of the parameters). Importantly, this predicts a constant exciton binding energy for systems with very flat bands.

3.6 Bethe–Salpeter equation

Formally, excitons can be described by the electron-hole correlation function L and its equation of motion, the Bethe–Salpeter equation. I will give a brief derivation here, following Rohlfing et al.[177].

The equation of motion for the electron-hole correlation function L can be written as

$$L(12; 1'2') = L_0(12; 1'2') + \int d(3456) L_0(14; 13') K(35; 46) L(62; 52'), \quad (3.38)$$

where $i \equiv (\mathbf{x}_i, t_i) \equiv (\mathbf{r}_i, \sigma_i, t_i)$ is the conventional way of abbreviating position, spin, and time coordinates, and the integral over $\mathbf{x}$ includes the integral over real space and summation over

spin indices,

$$\int d\mathbf{x} \equiv \sum_{\sigma} \int d^3\mathbf{r} . \quad (3.39)$$

Equation (3.38) is the formal equivalent of the Dyson equation for the single particle Green's function. L_0 is the free correlation function and can be written as

$$L_0(12; 1'2') = G_1(1, 2')G_1(2, 1') , \quad (3.40)$$

where $G_1(i, j)$ is the interacting single-particle Green's function. K is the electron-hole interaction kernel, given by

$$K(35; 46) = \frac{\partial}{\partial G_1(6, 5)} [v_{\text{coul}}(3)\delta(3, 4) + \Sigma(3, 4)] , \quad (3.41)$$

where Σ is the selfenergy operator.

We will need several approximations in order to bring Eq. (3.38) into a computationally convenient form. First, L depends on four different time coordinates. However, we are only interested in optical transitions, in which the electron and hole are created at the same time, leaving only two time coordinates. Furthermore, since we do not consider external fields, this can be further reduced to only one coordinate, corresponding to the difference between the remaining two time coordinates. This is commonly Fourier-transformed to result in an energy-dependence instead of a time-dependence, and the electron-hole correlation function is expressed as $L(12, 1'2'; \omega)$, where $i \equiv (\mathbf{r}_i, \sigma_i)$ no longer contains time.

L_0 can be written in terms of electron and hole quasiparticle energies $E_{v/c}$ and wave functions $\psi)_{v/c}$ as

$$L_0(12, 1'2'; \omega) = i \sum_{v,c} \left[\frac{\psi_c(\mathbf{x}_1)\psi_v^*(\mathbf{x}'_1)\psi_v(\mathbf{x}_2)\psi_c^*(\mathbf{x}'_2)}{\omega - (E_c - E_v) + i0^+} - \frac{\psi_v(\mathbf{x}_1)\psi_c^*(\mathbf{x}'_1)\psi_c(\mathbf{x}_2)\psi_v^*(\mathbf{x}'_2)}{\omega + (E_c - E_v) + i0^+} \right] , \quad (3.42)$$

where c and v note the unoccupied and occupied electronic quasiparticle states, respectively. In this work, we will approximate these quasiparticle states by tight-binding states, which will be discussed in more detail in the next section, Sec. 3.7.

The symbol 0^+ in the denominators of Eq. (3.42) is short hand for a positive, infinitesimally small real number, implying a limit which will only get executed after any integral that includes L_0 as a term in its integrand.

The next assumption is that excitons, too, can be described as quasiparticles with wavefunctions χ_M and energies Ω_M , in which case L can be expressed in a form similar to Eq. (3.42),

$$L(12, 1'2'; \omega) = i \sum_M \left[\frac{\chi_M(\mathbf{x}_1, \mathbf{x}'_1) \chi_M^*(\mathbf{x}_2, \mathbf{x}'_2)}{\omega - \Omega_M + i0^+} - \frac{\chi_M(\mathbf{x}_1, \mathbf{x}'_1) \chi_M^*(\mathbf{x}_2, \mathbf{x}'_2)}{\omega + \Omega_M + i0^+} \right], \quad (3.43)$$

where the exciton amplitudes χ_M can be written in second quantization as

$$\chi_M(\mathbf{x}, \mathbf{x}') = \sum_v^{\text{occ}} \sum_c^{\text{empty}} A_{vc}^M \psi_c(\mathbf{x}) \psi_v^*(\mathbf{x}') + B_{vc}^M \psi_v(\mathbf{x}) \psi_c^*(\mathbf{x}'). \quad (3.44)$$

With all of this, the Bethe–Salpeter equation (3.38) turns into a generalized eigenvalue problem,

$$(E_c - E_v) A_{vc}^M + \sum_{v'c'} K_{vc;v'c'}^{AA}(\Omega_M) A_{v'c'}^M + \sum_{v'c'} K_{vc;v'c'}^{AB}(\Omega_M) B_{v'c'}^M = \Omega_M A_{vc}^M, \quad (3.45)$$

$$(E_c - E_v) B_{vc}^M + \sum_{v'c'} K_{vc;v'c'}^{BA}(\Omega_M) A_{v'c'}^M + \sum_{v'c'} K_{vc;v'c'}^{BB}(\Omega_M) B_{v'c'}^M = -\Omega_M B_{vc}^M, \quad (3.46)$$

where

$$K_{vc;v'c'}^{AA}(\Omega_M) = i \int d(3456) \psi_v(\mathbf{x}_4) \psi_c^*(\mathbf{x}_3) K(35, 46; \Omega_M) \psi_{v'}^*(\mathbf{x}_5) \psi_{c'}(\mathbf{x}_6), \quad (3.47)$$

$$K_{vc;v'c'}^{AB}(\Omega_M) = i \int d(3456) \psi_v(\mathbf{x}_4) \psi_c^*(\mathbf{x}_3) K(35, 46; \Omega_M) \psi_{v'}^*(\mathbf{x}_6) \psi_{c'}(\mathbf{x}_5) \quad (3.48)$$

etc. The off-block-diagonal terms K^{AB} and K^{BA} , which link the amplitudes A^M and B^M are typically small compared to K^{AA} and K^{BB} , and will be neglected. This is known as the Tamm–Dancoff approximation. This decouples Eqs. (3.45) and (3.46), and makes them equivalent up

to the sign of the energy, resulting in an effective Hamiltonian $\mathcal{H}_{\text{BSE}}$, such that

$$\mathcal{H}_{\text{BSE}}A^M = \Omega_M A^M, \quad (3.49)$$

$$\mathcal{H}_{\text{BSE}}B^M = -\Omega_M B^M. \quad (3.50)$$

This can be understood as the equations for exciton creation and annihilation, which are equivalent up to the sign of the eigenenergy.

In order to obtain a simplified expression for the interaction kernel K , Eq. (3.41), we employ the GW approximation for the selfenergy Σ , that is

$$\Sigma = iG_1 W, \quad (3.51)$$

corresponding to the first order expansion of the selfenergy in terms of powers of W . With this, we find

$$K(35; 46) = -i\delta(3, 4)\delta(5^-, 6)v(3, 6) + i\delta(3, 6)\delta(4, 5)W(3^+, 4) \quad (3.52)$$

$$\equiv K^x(35; 46) + K^d(35; 46). \quad (3.53)$$

Note that in this expression, the coordinates (3, 4, etc.) include time coordinates, and the + or – superscripts indicate infinitesimally small deviations from the time coordinate to ensure well-defined time-ordering. The interaction kernel is now expressed as two different terms, a direct term K^d and an exchange term K^x .

Inserting this expression into Eqs. (3.47) results in

$$\begin{aligned} \langle vc|K^{AA,d}(\Omega_M)|v'c'\rangle &= \int d\mathbf{x}d\mathbf{x}' \psi_c^*(\mathbf{x})\psi_{c'}(\mathbf{x})\psi_v(\mathbf{x}')\psi_{v'}^*(\mathbf{x}) \\ &\times \frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} W(\mathbf{r}, \mathbf{r}'; \omega) \left[\frac{1}{\Omega_M - \omega - (E_{c'} - E_v) + i0^+} + \frac{1}{\Omega_M + \omega - (E_{c'} - E_v) + i0^+} \right], \end{aligned} \quad (3.54)$$

and

$$\langle v c | K^{AA,x}(\Omega_M) | v' c' \rangle = \int d\mathbf{x} d\mathbf{x}' \psi_c^*(\mathbf{x}) \psi_v(\mathbf{x}) v(\mathbf{r}, \mathbf{r}') \psi_{c'}(\mathbf{x}') \psi_{v'}^*(\mathbf{x}') , \quad (3.55)$$

noting that the expression for the direct term includes a frequency integration over the interaction since it includes energy-dependent screening, whereas the exchange term includes the bare Coulomb interaction, which is energy independent.

The next approximation involves neglecting the energy dependence of the screened interaction, known as the static screening approximation, resulting in

$$\langle v c | K^{AA,d} | v' c' \rangle = - \int d\mathbf{x} d\mathbf{x}' \psi_c^*(\mathbf{x}) \psi_{c'}(\mathbf{x}) W(\mathbf{r}, \mathbf{r}') \psi_v(\mathbf{x}') \psi_{v'}^*(\mathbf{x}') . \quad (3.56)$$

At this point, I will change notation somewhat. So far, c and v have been used to indicate specific conduction and valence states, respectively. Going forward, since I am only evaluating the BSE for the specific case of a periodic solid, I will only work in reciprocal space, and will indicate quasiparticle states by energy band index (as the newly defined meaning of c and v) and reciprocal lattice vector $\mathbf{k}$.

The Hamiltonian in Eq. (3.49) can be expressed as

$$\langle v c \mathbf{k} \mathbf{Q} | \mathcal{H}_{\text{BSE}} | v' c' \mathbf{K}' \mathbf{Q} \rangle = \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k} \mathbf{K}' \mathbf{Q}} (E_{\mathbf{k}+\mathbf{Q}c} - E_{\mathbf{k}v}) - (D - X)_{vv'}^{cc'}(\mathbf{k} \mathbf{K}' \mathbf{Q}) , \quad (3.57)$$

where

$$\begin{aligned} (D_{\mathbf{k} \mathbf{K}' \mathbf{Q}})_{vv'}^{cc'} &= \langle v c \mathbf{k} \mathbf{Q} | K^{\text{eh}, d} | v' c' \mathbf{K}' \mathbf{Q} \rangle \\ &= - \int d\mathbf{x} d\mathbf{x}' \psi_{c\mathbf{k}+\mathbf{Q}}^*(\mathbf{x}) \psi_{c'\mathbf{K}'+\mathbf{Q}}(\mathbf{x}) W(\mathbf{r}, \mathbf{r}') \psi_{v\mathbf{k}}(\mathbf{x}') \psi_{v'\mathbf{K}'}^*(\mathbf{x}') , \end{aligned} \quad (3.58)$$

$$\begin{aligned} (X_{\mathbf{k} \mathbf{K}' \mathbf{Q}})_{vv'}^{cc'} &= \langle v c \mathbf{k} \mathbf{Q} | K^{\text{eh}, x} | v' c' \mathbf{K}' \mathbf{Q} \rangle \\ &= - \int d\mathbf{x} d\mathbf{x}' \psi_{c\mathbf{k}+\mathbf{Q}}^*(\mathbf{x}) \psi_{v\mathbf{k}}(\mathbf{x}) V(\mathbf{r}, \mathbf{r}') \psi_{c'\mathbf{K}'+\mathbf{Q}}(\mathbf{x}') \psi_{v'\mathbf{K}'}^*(\mathbf{x}') . \end{aligned} \quad (3.59)$$

Here, $\mathbf{Q}$ corresponds to the difference in crystal momentum between electron and hole.

3.7 Bethe–Salpeter equation in a tight-binding basis

In this section, I will express the Bethe–Salpeter Hamiltonian (3.57) in terms of quasiparticle energies and wavefunctions obtained from tight-binding theory.

Inserting the equation for tight-binding wavefunctions in terms of atomic orbitals, Eq. (3.14), into the above equation for the direct term, Eq. (3.58), yields

$$\begin{aligned}
 (D_{\mathbf{k}\mathbf{K}'}^{cc'})_{vv'} &= \frac{1}{N^2} \sum_{\substack{\mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 \mathbf{R}_4 \\ A_1 A_2 A_3 A_4}} \exp(-i\mathbf{k} \cdot \mathbf{R}_1) \exp(i\mathbf{K}' \cdot \mathbf{R}_2) \exp(i\mathbf{k} \cdot \mathbf{R}_3) \exp(-i\mathbf{K}' \cdot \mathbf{R}_4) \\
 &\quad \times C_{cA_1\mathbf{k}+\mathbf{Q}}^* C_{c'A_2\mathbf{K}'+\mathbf{Q}} C_{vA_3\mathbf{k}} C_{v'A_4\mathbf{K}'}^* \\
 &\quad \times \int d\mathbf{r} d\mathbf{r}' \underbrace{\phi_{A_1}(\mathbf{r} - \mathbf{R}_1 - \boldsymbol{\tau}_{A_1}) \phi_{A_2}(\mathbf{r} - \mathbf{R}_2 - \boldsymbol{\tau}_{A_2})}_{(*)} W(\mathbf{r}, \mathbf{r}') \\
 &\quad \times \underbrace{\phi_{A_3}(\mathbf{r} - \mathbf{R}_3 - \boldsymbol{\tau}_{A_3}) \phi_{A_4}(\mathbf{r} - \mathbf{R}_4 - \boldsymbol{\tau}_{A_4})}_{(*)} . \tag{3.60}
 \end{aligned}$$

Note that we assume the atomic orbitals are real, which is a choice of basis we can always make.

The atomic orbitals are strongly localized. We therefore assume that the starred products are only non-zero if $\mathbf{R}_1 + \boldsymbol{\tau}_{a_1} = \mathbf{R}_2 + \boldsymbol{\tau}_{a_2}$ and $\mathbf{R}_3 + \boldsymbol{\tau}_{a_3} = \mathbf{R}_4 + \boldsymbol{\tau}_{a_4}$, which is equivalent to $\mathbf{R}_1 = \mathbf{R}_2$, $\boldsymbol{\tau}_{a_1} = \boldsymbol{\tau}_{a_2}$, $\mathbf{R}_3 = \mathbf{R}_4$, $\boldsymbol{\tau}_{a_3} = \boldsymbol{\tau}_{a_4}$, since the two atoms inside the same unit cell are closer together than any lattice vector by definition. We further assume that these products are only non-negligible for the case $A_1 = A_2$ and $A_3 = A_4$. This would be exact given the previous approximation if the two integrals over $\mathbf{r}$ and $\mathbf{r}'$ were independent, since the atomic orbitals are (or can always chosen to be) orthogonal to each other.

Inserting this into Eq. (3.60) gets rid of half the summations and simplifies the expression

significantly,

$$\begin{aligned}
(D_{\mathbf{k}\mathbf{K}'}^{cc'})_{vv'} &= \frac{1}{N^2} \sum_{\substack{\mathbf{R}_1 \mathbf{R}_3 \\ A_1 A_3}} \exp(-i(\mathbf{k} - \mathbf{K}') \cdot \mathbf{R}_1) \exp(i(\mathbf{k} - \mathbf{K}') \cdot \mathbf{R}_3) \\
&\times C_{cA_1\mathbf{k}+\mathbf{Q}}^* C_{c'A_1\mathbf{K}'+\mathbf{Q}} C_{vA_3\mathbf{k}} C_{v'A_3\mathbf{K}'}^* \\
&\times \int d\mathbf{r} d\mathbf{r}' (\phi_{A_1}(\mathbf{r} - \mathbf{R}_1 - \boldsymbol{\tau}_{A_1}))^2 W(\mathbf{r}, \mathbf{r}') (\phi_{A_3}(\mathbf{r} - \mathbf{R}_3 - \boldsymbol{\tau}_{A_3}))^2 . \quad (3.61)
\end{aligned}$$

Since the integrals are over all $\mathbb{R}^3$, both integration variables can be shifted by a constant value, $\mathbf{r}^{(\prime)} \rightarrow \mathbf{r}^{(\prime)} + \mathbf{R}_1$. Further defining $\Delta\mathbf{R} \equiv \mathbf{R}_3 - \mathbf{R}_1$, and assuming that $W(\mathbf{r}, \mathbf{r}') \equiv W(\mathbf{r} - \mathbf{r}')$, one finds

$$\begin{aligned}
(D_{\mathbf{k}\mathbf{K}'}^{cc'})_{vv'} &= \frac{1}{N} \sum_{\substack{\Delta\mathbf{R} \\ A_1 A_3}} \exp(i(\mathbf{k} - \mathbf{K}') \cdot \Delta\mathbf{R}) \\
&\times C_{cA_1\mathbf{k}+\mathbf{Q}}^* C_{c'A_1\mathbf{K}'+\mathbf{Q}} C_{vA_3\mathbf{k}} C_{v'A_3\mathbf{K}'}^* W(\Delta\mathbf{R} + \boldsymbol{\tau}_{A_1} - \boldsymbol{\tau}_{A_3}) . \quad (3.62)
\end{aligned}$$

Similarly, inserting Eq. (3.9) into Eq. (3.59), and doing the same manipulations, yields

$$\begin{aligned}
(X_{\mathbf{k}\mathbf{K}'}^{cc'})_{vv'} &= \frac{1}{N} \sum_{\substack{\Delta\mathbf{R} \\ A_1 A_3}} \exp(i\mathbf{Q} \cdot \Delta\mathbf{R}) \\
&\times C_{cA_1\mathbf{k}+\mathbf{Q}}^* C_{vA_1\mathbf{k}} C_{c'A_3\mathbf{K}'+\mathbf{Q}} C_{v'A_3\mathbf{K}'}^* V(\Delta\mathbf{R} + \boldsymbol{\tau}_{A_1} - \boldsymbol{\tau}_{A_3}) . \quad (3.63)
\end{aligned}$$

Note that in the case of only one atom per unit cell, or in the case where only orbitals on one atom per unit cell are part of the tight-binding basis, these expressions simplify even further to the form found in e.g. Wu et al.[161],

$$\begin{aligned}
(D_{\mathbf{k}\mathbf{K}'}^{cc'})_{vv'} &= \frac{1}{N} \sum_{A_1} C_{cA_1\mathbf{k}+\mathbf{Q}}^* C_{c'A_1\mathbf{K}'+\mathbf{Q}} \sum_{A_3} C_{vA_3\mathbf{k}} C_{v'A_3\mathbf{K}'}^* \\
&\sum_{\Delta\mathbf{R}} \exp(i(\mathbf{k} - \mathbf{K}') \cdot \Delta\mathbf{R}) W(\Delta\mathbf{R}) \quad (3.64)
\end{aligned}$$

$$= \left(C_{\mathbf{k}+\mathbf{Q}}^\dagger C_{\mathbf{K}'+\mathbf{Q}} \right)_{cc'} \left(C_{\mathbf{K}'}^\dagger C_{\mathbf{k}} \right)_{v'v} W(\mathbf{k} - \mathbf{K}') , \quad (3.65)$$

where the reciprocal space interaction is defined via a discrete Fourier transform,

$$W(\mathbf{k}) = \frac{1}{N} \sum_{\Delta \mathbf{R}} \exp(i\mathbf{k} \cdot \Delta \mathbf{R}) W(\Delta \mathbf{R}) . \quad (3.66)$$

Similarly, the exchange term becomes²

$$(X_{\mathbf{k}\mathbf{K}'})_{vv'}^{cc'} = \left(C_{\mathbf{k}+\mathbf{Q}}^\dagger C_{\mathbf{k}} \right)_{cv} \left(C_{\mathbf{K}'}^\dagger C_{\mathbf{K}'+\mathbf{Q}} \right)_{v'c'} V(\mathbf{Q}) . \quad (3.67)$$

3.7.1 Exciton wavefunction in real space

It can be instructive to consider the exciton wave function in real space, particularly for the purpose of determining whether any given exciton is an interlayer, intralayer, or hybrid exciton.

In real space, the exciton wavefunction can be written as

$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{v\mathbf{k}} A_{cv\mathbf{k}}^M \psi_{c\mathbf{k}} \psi_{v\mathbf{k}}^* , \quad (3.68)$$

which in terms of the tight-binding model becomes

$$\begin{aligned} \Psi(\mathbf{r}_e, \mathbf{r}_h) &= \frac{1}{N} \sum_{v\mathbf{k}} A_{cv\mathbf{k}}^M \sum_{\substack{\mathbf{R}_A \mathbf{R}_B \\ AB}} \exp(i\mathbf{k} \cdot (\mathbf{R}_A + \boldsymbol{\tau}_A - \mathbf{R}_B - \boldsymbol{\tau}_B)) C_{cA\mathbf{k}} C_{vB\mathbf{k}}^* \\ &\quad \times \phi_A(\mathbf{r}_e - \mathbf{R}_A - \boldsymbol{\tau}_A) \phi_B(\mathbf{r}_h - \mathbf{R}_B - \boldsymbol{\tau}_B) \end{aligned} \quad (3.69)$$

$$\begin{aligned} &\approx \frac{1}{N} \sum_{v\mathbf{k}} A_{cv\mathbf{k}}^M \sum_{\substack{\mathbf{R}_A \mathbf{R}_B \\ AB}} \exp(i\mathbf{k} \cdot (\mathbf{R}_A + \boldsymbol{\tau}_A - \mathbf{R}_B - \boldsymbol{\tau}_B)) C_{cA\mathbf{k}} C_{vB\mathbf{k}}^* \\ &\quad \times \delta(\mathbf{r}_e - \mathbf{R}_A - \boldsymbol{\tau}_A) \delta(\mathbf{r}_h - \mathbf{R}_B - \boldsymbol{\tau}_B) . \end{aligned} \quad (3.70)$$

Here, $\mathbf{r}_e$ and $\mathbf{r}_h$ are real space coordinates corresponding to electron and hole, respectively. In the last step, I approximate the atomic orbitals as points on the atomic sites. This greatly simplifies the calculation in practice and is sufficiently accurate for my purpose, since I am mostly interested in the layer distribution of the excitons.

²This expression is given with the screened interaction instead of the bare Coulomb interaction in Wu et al.[161].

3.8 Rytova–Keldysh interaction

Next, I will consider the nature of the screening electrostatic interaction in the direct interaction term in Eq. (3.65).

The most widely used form of dielectric screening in 2D materials is the Rytova–Keldysh interaction, describing two particles confined to a flat sheet of width d with dielectric constant ϵ , sandwiched between two semi-infinite substrates with dielectric constants ϵ_1 and ϵ_2 , respectively, as illustrated in Fig. 3.1.

Following Keldysh[178], the screened interaction between two particles with electric charges e

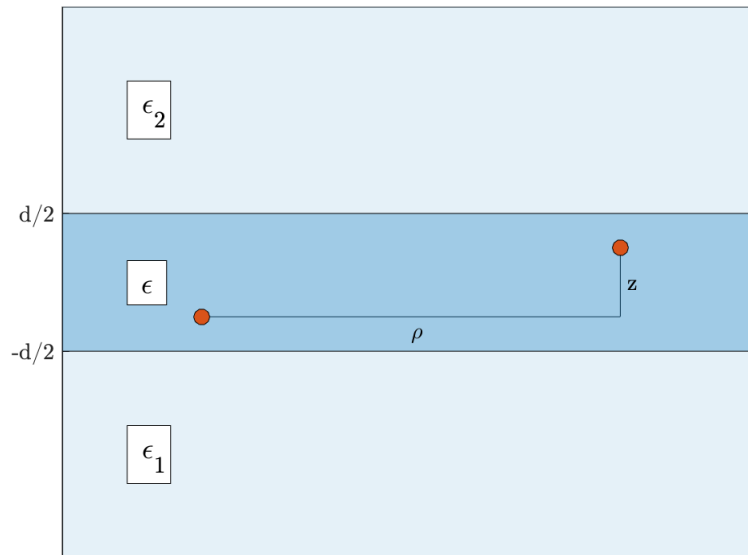


Figure 3.1: Illustration of the system geometry which exhibits Rytova–Keldysh screening as explained in Sec. 3.8. It consists of a layer of thickness d and with dielectric constant ϵ sandwiched between two semi-infinite layers with dielectric constants ϵ_1 and ϵ_1 . Two particles with unit charge are confined in the middle layer, a horizontal distance ρ and a vertical distance z apart.

and e' is given by

$$V(\boldsymbol{\rho}, z, z') =$$

$$\frac{4\pi ee'}{\epsilon} \int \frac{d^2 \mathbf{k}}{(2\pi)^2} \exp(2\mathbf{k} \cdot \boldsymbol{\rho}) \frac{\cosh\left(|\mathbf{k}| \left(\frac{d}{2} - z\right) + \eta_2\right) \cosh\left(|\mathbf{k}| \left(\frac{d}{2} + z'\right) + \eta_1\right)}{|\mathbf{k}| \sinh(|\mathbf{k}|d + \eta_1 + \eta_2)}, \quad (3.71)$$

where

$$\eta_i = \frac{1}{2} \ln \left(\frac{\epsilon + \epsilon_i}{\epsilon - \epsilon_i} \right). \quad (3.72)$$

and $\mathcal{J}_0$ is a Bessel function of first kind. Assuming that $\epsilon_i \ll \epsilon$ (as is the case for MoS₂ in vacuum or on a SiO₂ substrate), this reduces to

$$V(\boldsymbol{\rho}) = \frac{2ee'}{\epsilon d} \int_0^\infty dt \frac{\mathcal{J}_0(t)}{t + \frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{|\boldsymbol{\rho}|}{d}} \quad (3.73)$$

$$= \frac{\pi ee'}{\epsilon d} \left[\mathcal{H}_0 \left(\frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{|\boldsymbol{\rho}|}{d} \right) - \mathcal{N}_0 \left(\frac{\epsilon_1 + \epsilon_2}{\epsilon} \frac{|\boldsymbol{\rho}|}{d} \right) \right], \quad (3.74)$$

where $\mathcal{H}_0$ is a Struve function and $\mathcal{N}_0$ is a Neumann function, now more commonly called Bessel function of second type and denoted with Y_0 .

The problem with this expression is that the layer thickness of an atomically thin sheet of material is difficult to define. It is possible to use the layer thickness as a fitting parameter to reproduce experimental optical spectra, as is done in e.g. Ref. [163]. Perhaps not surprisingly, the layer thickness obtained for monolayer MoS₂ in that work turns out to be roughly 6 Å, which is equal to the interlayer separation of bulk MoS₂.

However, Cudazzo et al. [176] have found an expression identical in functional form to Eq. (3.74) by computing the static screening in a truly two-dimensional, i.e., infinitely thin, sheet of material in vacuum, where the material parameters can be expressed solely in terms of two-dimensional polarizability α_{2D} .

They solve the Poisson equation,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi n(\mathbf{r}) , \quad (3.75)$$

where $n(\mathbf{r}) = n_{\text{ext}}(\mathbf{r}) + n_{\text{ind}}(\mathbf{r})$, $n_{\text{ext}}(\mathbf{r}) = e\delta(\mathbf{r})$, and the induced charge density $n_{\text{ind}}(\mathbf{r})$ is localized on the 2D plane. In the long wavelength limit,

$$n_{\text{ind}} = -\nabla \cdot \mathbf{P}_{2D} , \quad (3.76)$$

where

$$\mathbf{P}_{2D}(\boldsymbol{\rho}) = -\alpha_{2D} \nabla_{\boldsymbol{\rho}} \phi(\boldsymbol{\rho}, z) . \quad (3.77)$$

This leads to

$$n_{\text{ind}}(\mathbf{r}) = \delta(z) \alpha_{2D} \nabla_{\boldsymbol{\rho}}^2 \phi(\boldsymbol{\rho}, z=0) . \quad (3.78)$$

In turn,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi e \delta(\mathbf{r}) - 4\pi \alpha_{2D} \nabla_{\boldsymbol{\rho}}^2 \phi(\boldsymbol{\rho}, z=0) \delta(z) , \quad (3.79)$$

which, when Fourier-transformed, results in

$$(|\mathbf{q}|^2 + k_z^2) \phi(\mathbf{q}, k_z) = 4\pi e - 4\pi \alpha_{2D} |\mathbf{q}|^2 \underbrace{\int \frac{dk_z}{2\pi} \phi(\boldsymbol{\rho}, k_z)}_{\phi_{2D}(\mathbf{q})} . \quad (3.80)$$

This can be solved for $\phi_{2D}(\mathbf{q})$ to result in

$$\phi_{2D}(\mathbf{q}) = \frac{2\pi e}{|\mathbf{q}| (1 + 2\pi \alpha_{2D} |\mathbf{q}|)} . \quad (3.81)$$

Fourier-transforming $e\phi_{2D}(\mathbf{q})$ back to real space yields the effective screened interaction,

$$W(\boldsymbol{\rho}) = \frac{e^2}{4\alpha_{2D}} \left[\mathcal{H}_0 \left(\frac{|\boldsymbol{\rho}|}{r_0} \right) - Y_0 \left(\frac{|\boldsymbol{\rho}|}{r_0} \right) \right], \quad (3.82)$$

where

$$r_0 = 2\pi\alpha_{2D}. \quad (3.83)$$

Equation (3.82) can be generalized to include substrates[179]. If the infinitely thin sheet of dielectric material is sandwiched between two substrates with permittivities ϵ_{top} and ϵ_{bottom} , Eq. (3.82) becomes

$$W(\boldsymbol{\rho}) = \frac{\pi e^2}{2\epsilon r_0} \left[\mathcal{H}_0 \left(\frac{|\boldsymbol{\rho}|}{r_0} \right) - Y_0 \left(\frac{|\boldsymbol{\rho}|}{r_0} \right) \right], \quad (3.84)$$

where $r_0 = 2\pi\alpha_{2D}/\epsilon$ and $\epsilon = (\epsilon_{\text{top}} + \epsilon_{\text{bottom}})/2$. Note that in this convention, the screening length r_0 includes the effect of the substrates. Sometimes, another convention is used, such as in Van Tuan et al.[180],

$$W(\boldsymbol{\rho}) = \frac{\pi e^2}{2r_0} \left[\mathcal{H}_0 \left(\frac{|\boldsymbol{\rho}|\epsilon}{r_0} \right) - Y_0 \left(\frac{|\boldsymbol{\rho}|\epsilon}{r_0} \right) \right], \quad (3.85)$$

where $r_0 = 2\pi\alpha_{2D}$.

We use $r_0 = 33.875\text{\AA}/\epsilon$ to describe the effective screening length of monolayer MoS₂[161], and $r_0 = 67.750\text{\AA}/\epsilon$ for MoS₂ bilayers. This last is slightly ad hoc, reflecting the fact that in Keldysh's original work, r_0 is proportional to the layer thickness. We do not include a substrate in the calculations presented in this work, that is, we model MoS₂ in vacuum, $\epsilon = 1$, in order to compare our results to ab initio calculations which have also been performed with $\epsilon = 1$.

Equation (3.84) has been used very successfully to describe static dielectric screening in TMD monolayers[6, 161, 181, 111]. However, in TMD bilayers, the situation becomes more complex. In these systems, electrons and holes can be localized in different layers. If the out-of-plane

distance of the electron and the hole becomes comparable to or larger than their in-plane distance, then the approximations resulting in Eq. (3.84) are no longer valid. Furthermore, the interaction can become unphysically large for electrons and holes that are situated on top of each other. In this case, their actual distance might be several Angstroms, but their in-plane distance $|\boldsymbol{\rho}|$ might approach zero.

The simplest solution to this is to replace the 2D distance $|\boldsymbol{\rho}|$ with the 3D distance $\sqrt{|\boldsymbol{\rho}|^2 + D^2}$, where D is the interlayer separation, as is done in Ref. [182]. This is somewhat ad hoc, but often a very simple improvement, and this is what will be used in this work.

3.9 Optical conductivity

In order to determine the optical absorption spectrum, we calculate the diagonal component of the real part of the optical conductivity in linear response, which is equal to absorption[163],

$$\text{Re}\sigma_{xx}(\omega) = \frac{e^2\pi}{m^2\hbar\omega A} \sum_M \left| \langle \text{FS} | \hat{P}_x | M \rangle \right|^2 \delta(\omega - \Omega_M), \quad (3.86)$$

where

$$|M\rangle = \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^M a_{c\mathbf{k}}^\dagger a_{v\mathbf{k}} |\text{FS}\rangle. \quad (3.87)$$

Here, $A = A_c n_k^2$ is the total area of the crystal that is modelled (finite due to the finite number of k-points n_k), A_c is the area of the crystal unit cell, $\hat{P}_x$ is the many-body momentum operator (in x -direction), $|M\rangle$ is the exciton wavefunction, $|\text{FS}\rangle$ is the many-body ground state, Ω_M is the exciton eigenenergy of $|M\rangle$, and $a_{c\mathbf{k}}^\dagger$, $a_{v\mathbf{k}}$ are electron and hole creation operators, respectively. Combined, it is

$$\text{Re}\sigma_{xx}(\omega) = \frac{e^2\pi}{m^2\hbar\omega A} \sum_M \left| \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^M \langle \text{FS} | \hat{P}_x a_{c\mathbf{k}}^\dagger a_{v\mathbf{k}} | \text{FS} \rangle \right|^2 \delta(\omega - \Omega_M). \quad (3.88)$$

Following Ref. [163], the many-body momentum operator $\hat{P}_x$ can be expressed in terms of the single-particle momentum operator $\hat{p}_x$ as

$$\hat{P}_x = \sum_{pq} \langle p | \hat{p}_x | q \rangle a_p^\dagger a_q , \quad (3.89)$$

and therefore

$$\langle \text{FS} | \hat{P}_x a_s^\dagger a_r | \text{FS} \rangle = \sum_{pq} \langle p | \hat{p}_x | q \rangle \underbrace{\langle \text{FS} | a_p^\dagger a_q a_s^\dagger a_r | \text{FS} \rangle}_{(*)} . \quad (3.90)$$

Due to orthogonality, $(*)$ can only be non-zero if either $p = q$ and $s = r$, or $p = r$ and $q = s$. Noting from Eq. 3.88 that $p \equiv c\mathbf{k}$ and $q \equiv v\mathbf{k}$, $p \neq q$ in all cases. We further make use of the fermionic commutation relations,

$$[a_p^\dagger, a_q^\dagger] = [a_p, a_q] = 0 , \quad (3.91)$$

$$[a_p, a_q^\dagger] = \delta_{pq} , \quad (3.92)$$

and obtain

$$\langle \text{FS} | a_p^\dagger a_q a_s^\dagger a_r | \text{FS} \rangle = \delta_{pr} \delta_{qs} \langle \text{FS} | a_p^\dagger a_q a_q^\dagger a_p | \text{FS} \rangle \quad (3.93)$$

$$= \delta_{pr} \delta_{qs} \langle \text{FS} | a_p^\dagger a_p (1 - a_q^\dagger a_q) | \text{FS} \rangle \quad (3.94)$$

$$= f_p (1 - f_q) , \quad (3.95)$$

where f_n is the Fermi occupation number of state $|n\rangle$. At zero temperature in a semiconductor, $f_{c\mathbf{k}} = 0$ and $f_{v\mathbf{k}} = 1$, and we obtain

$$\text{Re}\sigma_{xx}(\omega) = \frac{e^2 \pi}{m^2 \hbar \omega A} \sum_M \left| \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^M \langle v\mathbf{k} | \hat{p}_x | c\mathbf{k} \rangle \right|^2 \delta(\omega - \omega_M) . \quad (3.96)$$

Up to this point, the derivation has been relatively straightforward and uncontroversial. However, contradicting literature exists regarding the evaluation of the momentum matrix element in Eq. (3.96)[183]. Frequently, the expression

$$\mathbf{p} \rightarrow \frac{m_e}{\hbar} \nabla_{\mathbf{k}} H(\mathbf{k}) \quad (3.97)$$

is given. Sometimes, such as in Ref. [184], Eq. (3.97) is treated as exact. For an analysis on the qualitative and quantitative differences between different approaches, see for example Read et al.[185]. A more rigorous approach starts from

$$\mathbf{p} = m_e \mathbf{v} = m_e \frac{d\mathbf{r}}{dt} = \frac{im_e}{\hbar} [H, \mathbf{r}] . \quad (3.98)$$

In the tight-binding basis, the matrix elements are found to be

$$\langle n\mathbf{k} | \mathbf{p} | m\mathbf{k} \rangle = \frac{1}{N} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \sum_{\mathbf{R}\mathbf{R}'} \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \langle B\mathbf{R}' | \mathbf{p} | A\mathbf{R} \rangle \quad (3.99)$$

$$= \frac{im_e}{\hbar N} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \sum_{\mathbf{R}\mathbf{R}'} \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \langle B\mathbf{R}' | [H, \mathbf{r}] | A\mathbf{R} \rangle . \quad (3.100)$$

Consider for a moment just the last term in Eq. (3.100),

$$\langle B\mathbf{R}' | [H, \mathbf{r}] | A\mathbf{R} \rangle \quad (3.101)$$

$$= \langle B\mathbf{R}' | H\mathbf{r} | A\mathbf{R} \rangle - \langle B\mathbf{R}' | \mathbf{r}H | A\mathbf{R} \rangle . \quad (3.102)$$

Add a unity operator, $\mathbb{1} = \sum_{C\mathbf{R}''} |C\mathbf{R}''\rangle \langle C\mathbf{R}''|$. The expression becomes

$$\sum_{C\mathbf{R}''} \langle B\mathbf{R}' | H | C\mathbf{R}'' \rangle \langle C\mathbf{R}'' | \mathbf{r} | A\mathbf{R} \rangle - \langle B\mathbf{R}' | \mathbf{r} | C\mathbf{R}'' \rangle \langle C\mathbf{R}'' | H | A\mathbf{R} \rangle . \quad (3.103)$$

The overlap between orbitals localized on different atoms is negligibly small, therefore

$$\langle B\mathbf{R}' | \mathbf{r} | A\mathbf{R} \rangle \approx (\mathbf{R}\delta_{AB} + \mathbf{d}_{BA})\delta_{\mathbf{R}\mathbf{R}'} , \quad (3.104)$$

where

$$\mathbf{d}_{BA} = \langle B0|\mathbf{r}|A0\rangle \quad (3.105)$$

is the intraatomic contribution.

With that, Eq. (3.100) becomes

$$\begin{aligned} \langle n\mathbf{k}|\mathbf{p}|m\mathbf{k}\rangle &\approx \frac{im_e}{\hbar N} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \sum_{\mathbf{R}\mathbf{R}'} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')) \\ &\quad \times (\mathbf{R} - \mathbf{R}') \langle B\mathbf{R}'|H|A\mathbf{R}\rangle \\ &\quad + \frac{im_e}{\hbar N} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \sum_{\mathbf{R}\mathbf{R}'} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')) \\ &\quad \times \sum_C (\langle B\mathbf{R}'|H|C\mathbf{R}\rangle \mathbf{d}_{CA} - \mathbf{d}_{BC} \langle C\mathbf{R}'|H|A\mathbf{R}\rangle) . \end{aligned} \quad (3.106)$$

Further taking advantage of the fact that

$$\exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}'))(\mathbf{R} - \mathbf{R}') = -i\nabla_{\mathbf{k}} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')) , \quad (3.107)$$

and that

$$\sum_{A\mathbf{R}} \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')) C_{nA\mathbf{k}} \hat{H}|A\mathbf{R}\rangle = \hat{H}(\mathbf{k})|n\mathbf{k}\rangle = E_{n\mathbf{k}}|n\mathbf{k}\rangle , \quad (3.108)$$

we obtain

$$\begin{aligned} \langle n\mathbf{k}|\mathbf{p}|m\mathbf{k}\rangle &\approx \frac{m_e}{\hbar} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \nabla_{\mathbf{k}} \langle B\mathbf{k}|\hat{H}(\mathbf{k})|A\mathbf{k}\rangle \\ &\quad + \frac{im_e}{\hbar} [E_{n\mathbf{k}} - E_{m\mathbf{k}}] \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \mathbf{d}_{BA} . \end{aligned} \quad (3.109)$$

Going forward, we neglect the intraatomic contribution, resulting in

$$\langle n\mathbf{k}|\mathbf{p}|m\mathbf{k}\rangle \approx \frac{m_e}{\hbar} \sum_{AB} C_{nB\mathbf{k}}^* C_{mA\mathbf{k}} \nabla_{\mathbf{k}} \langle B\mathbf{k}|\hat{H}(\mathbf{k})|A\mathbf{k}\rangle . \quad (3.110)$$

Inserting Eq. (3.110) into Eq. (3.96), we obtain the final expression for the optical absorption,

$$\text{Re}\sigma_{xx}(\omega) = \frac{e^2}{4\hbar} \frac{4\pi}{\hbar\omega A} \sum_M \left| \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^M \sum_{AB} C_{vA\mathbf{k}}^* C_{cB\mathbf{k}} \nabla_{k_x} \langle \phi_A | \hat{H}(\mathbf{k}) | \phi_B \rangle \right|^2 \times \delta(\omega - \omega_M). \quad (3.111)$$

3.10 Computational details

3.10.1 Density Functional Theory Calculations

Density Functional Theory (DFT) calculations were used in three separate ways in this project. First, TMD monolayer bandstructures were calculated in order to obtain monolayer tight-binding parameters through wannierization, cf. Sec. 3.4. Furthermore, TMD homobilayer bandstructures were calculated for different interlayer separations and rigid horizontal shifts between layers in order to obtain Slater–Koster parameters for the interlayer hoppings in the tight-binding model, cf. Sec. 6.2. Lastly, different high-symmetry stacking bandstructures were calculated in order to test the validity of the tight-binding model, cf. Ch. 6.

In all these cases, the DFT calculations were carried out using the Quantum Espresso code package[186]. For all of these, the exchange-correlation potential which was used was the optB88 generalized gradient approximation, and we used pseudopotentials that have been generated from ONCVPSP (optimized norm-conserving Vanderbilt pseudopotential) by Hamann et al.[187], and the plane wave cutoff was 70 Ry. For the monolayer calculations, a $25 \times 25 \times 1$ k-grid was used, and for the bilayer calculations, a $12 \times 12 \times 1$ k-grid was used.

3.10.2 Cutoff energy for BSE calculations

For a 30×30 k-grid, the BSE basis for an untwisted bilayer calculation would include $n_k \times n_c \times n_v = 30^2 \times 28 \times 16 = 403,200$ transitions, which is impractically large. (Here, n_k is the number of k-points, and n_c and n_v are the number of conduction and valence bands included in our model, respectively.) Since transitions between the lowest energy valence states and the highest

energy conduction bands are unlikely to significantly contribute to the low-energy excitons we are interested in, we can introduce an energy cutoff and only consider transitions which have a smaller energy. There are several ways of implementing such a cutoff — commonly, the number of bands included in the calculation can be restricted, or a limit to the allowed transition energies can be introduced, or else all transitions between some minimum energy and some maximum energy can be considered. We use a somewhat hybrid approach, following Ref. [188]. At every $\mathbf{k}$ -point, we include all transitions between $E_{c\mathbf{k}}^{(\min)} - e_c$ and $E_{v\mathbf{k}}^{(\max)} + e_c$, where $E_{c\mathbf{k}}^{(\min)}$ is the conduction band minimum at that $\mathbf{k}$ -point, $E_{v\mathbf{k}}^{(\max)}$ is the valence band maximum, and e_c is the cutoff energy. With this definition, we find that generally, a cutoff of 0.5 eV above the direct gap at K is sufficient for convergence of the exciton binding energies (this corresponds to a value of 2.3 eV for the MoS₂ monolayer, since the band gap is roughly 1.8 eV).

3.10.3 Lattice Fourier transform of the electrostatic interaction on a finite lattice

The direct and exchange terms of the BSE Hamiltonian matrix elements, Eqs. (3.65) and (3.67) include lattice Fourier transforms of the electrostatic interaction (3.66). Using finitely large crystals, i.e., finitely fine $\mathbf{k}$ -grids, complicates this calculation in two ways.

Firstly, the Coulomb interaction diverges as $\mathbf{r} \rightarrow 0$ (regardless of whether or not it is screened). Therefore, $V(\mathbf{r} = 0)$ needs to be regularized to result in finite Hamiltonian matrix elements. We follow the approach of e.g. Ref. [161] and set

$$V(\mathbf{r} = 0) \approx V(\mathbf{r}_0) , \quad (3.112)$$

$$W(\mathbf{r} = 0) \approx W(\mathbf{r}_0) , \quad (3.113)$$

where $\mathbf{r}_0$ is distance between nearest-neighbour atoms.

Secondly, the expression (3.66) is dependent on the choice of lattice points, because it is not

periodic. The number of unit cells we include in the lattice sum is dependent on the k -grid fineness, and we recenter the grid so that the origin is at the center. However, the grid is constructed to be diamond shaped, so for small lattices, this can result in broken symmetries.

Chapter 4

Symmetry-adapted eleven-band sixth-nearest neighbour tight-binding model for monolayer transition metal dichalcogenides

The following chapter describes the details of the tight-binding model which forms the basis of the simulations performed in this work.

The starting point for this tight-binding model is an eleven-band tight-binding model with up to third-nearest neighbour hoppings which was first introduced by Fang et al.[4]. The model was extended to twisted bilayers by Vitale et al.[5].

I have extended the tight-binding model for the monolayers to include up to sixth-nearest neighbour model hoppings, which significantly improves the description of the band structure in general and the conduction band manifold in particular.

I start by deriving the full symmetry-adapted sixth-nearest neighbour Hamiltonian. I first describe the crystal structure of transition metal dichalcogenide monolayers and then the orbital

basis used in Fang et al.[4]. I then construct the Hamiltonian matrix elements, taking advantage of both mirror symmetries of the system, which relate various hopping integrals to each other through either a factor of 1 or -1 due to the convenient choice of orbital basis. Lastly, I summarize how to make use of the three-fold rotational symmetry to further reduce the number of required parameters, and then give the explicit equations resulting from this analysis.

4.1 Crystal structure of monolayer transition metal dichalcogenides

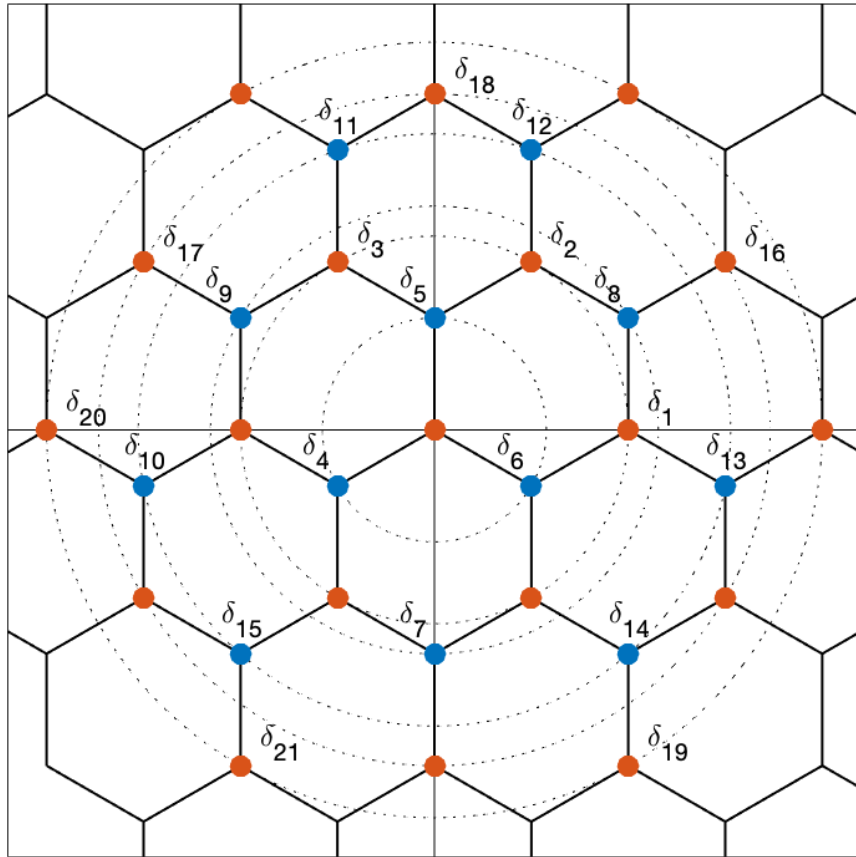


Figure 4.1: Neighbour vectors up to sixth-nearest neighbours in monolayer TMDs, illustrated for a metal atom at the origin. Red: metal atoms, blue: chalcogen atoms. The distance of different atoms to the origin is indicated with dotted concentric circles.

As mentioned in Sec. 1, semiconducting monolayer transition metal dichalcogenides of 2H type consist of a layer of transition metal atoms sandwiched between two layers of chalcogen atoms. When viewed from the top, the chalcogen atoms are directly on top of each other, and the crystal forms a honeycomb structure[189], as illustrated in Fig. 4.1

Our choice of lattice vectors is

$$\mathbf{a}_1 = a\hat{\mathbf{e}}_x , \quad (4.1)$$

$$\mathbf{a}_2 = -\frac{a}{2}\hat{\mathbf{e}}_x + \frac{\sqrt{3}a}{2}\hat{\mathbf{e}}_y , \quad (4.2)$$

where a is the lattice constant and $\hat{\mathbf{e}}_x$ and $\hat{\mathbf{e}}_y$ are the unit vectors in x and y -direction, respectively, in the orientation illustrated in Fig. 4.1. For the case of MoS₂, we use $a = 3.183 \text{ \AA}$ [5].

We include hoppings up to sixth nearest neighbours. The vectors connecting an atom at the origin to all relevant neighbours are given by:

$$\begin{aligned} \boldsymbol{\delta}_1 &= \mathbf{a}_1 , & \boldsymbol{\delta}_{12} &= \frac{1}{3}(4\mathbf{a}_1 + 5\mathbf{a}_2) , \\ \boldsymbol{\delta}_2 &= \mathbf{a}_1 + \mathbf{a}_2 , & \boldsymbol{\delta}_{13} &= \frac{1}{3}(4\mathbf{a}_1 - \mathbf{a}_2) , \\ \boldsymbol{\delta}_3 &= \mathbf{a}_2 , & \boldsymbol{\delta}_{14} &= \frac{1}{3}(\mathbf{a}_1 - 4\mathbf{a}_2) , \\ \boldsymbol{\delta}_4 &= -\frac{1}{3}(2\mathbf{a}_1 + \mathbf{a}_2) , & \boldsymbol{\delta}_{15} &= -\frac{1}{3}(5\mathbf{a}_1 + 4\mathbf{a}_2) , \\ \boldsymbol{\delta}_5 &= \frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) , & \boldsymbol{\delta}_{16} &= 2\mathbf{a}_1 + \mathbf{a}_2 , \\ \boldsymbol{\delta}_6 &= \frac{1}{3}(\mathbf{a}_1 - \mathbf{a}_2) , & \boldsymbol{\delta}_{17} &= -\mathbf{a}_1 + \mathbf{a}_2 , \\ \boldsymbol{\delta}_7 &= -\frac{2}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) , & \boldsymbol{\delta}_{18} &= 2\mathbf{a}_2 + \mathbf{a}_1 , \\ \boldsymbol{\delta}_8 &= \frac{2}{3}(2\mathbf{a}_1 + \mathbf{a}_2) , & \boldsymbol{\delta}_{19} &= -2\mathbf{a}_2 , \\ \boldsymbol{\delta}_9 &= \frac{2}{3}(\mathbf{a}_2 - \mathbf{a}_1) , & \boldsymbol{\delta}_{20} &= -2\mathbf{a}_1 , \\ \boldsymbol{\delta}_{10} &= -\frac{1}{3}(5\mathbf{a}_1 + \mathbf{a}_2) , & \boldsymbol{\delta}_{21} &= -2\mathbf{a}_1 - 2\mathbf{a}_2 . \\ \boldsymbol{\delta}_{11} &= \frac{1}{3}(\mathbf{a}_1 + 5\mathbf{a}_2) , \end{aligned}$$

The neighbour vectors are illustrated in Fig. 4.1.

Note that atoms of the same type are always separated by a lattice vector, atoms of different types are always separated by a vector that is not a lattice vector. The latter statement can be seen from the fact that any sum of lattice vectors results in another lattice vector. Consequently, the sum of a lattice vector and a vector which is not a lattice vector cannot result in a lattice vector. The nearest neighbour separation is not a lattice vector. Therefore, the vector between two arbitrary atoms A and B of different type can be expressed as a lattice vector (the distance between atom A and one of the same type atoms neighbouring atom B, and the nearest neighbour distance). It therefore cannot be a lattice vector.

Apart from translation symmetry, the symmetries of this crystal structure are

- $\mathcal{R}_3$: rotation by $2\pi/3$ around the z -axis,
- $\mathcal{M}_1$: mirror symmetry with respect to the xy -plane,
- $\mathcal{M}_2$: mirror symmetry with respect to the yz -plane.

4.2 Orbital basis

We start from a monolayer tight-binding model without spin. We include five d-orbitals located on the transition metal atoms, and six p-orbitals, three for each of the chalcogen atoms in the unit cell, as listed in Table 4.1. The p-orbitals are included as symmetric and antisymmetric superpositions of top and bottom layer p-orbitals of the same type. This results in an orbital basis in which every orbital is either fully symmetric or fully antisymmetric with respect to both $\mathcal{M}_1$ and $\mathcal{M}_2$ symmetry.

It is useful to provide the full expressions for the angle dependent part of these orbitals, that is the relevant spherical harmonic functions, which allow us to explicitly calculate the relations

Index	Basis Function	$\mathcal{M}_1$	$\mathcal{M}_2$
1	d_{xz}	—	—
2	d_{yz}	—	+
3	$(p_z^{\text{top}} + p_z^{\text{bottom}})/\sqrt{2}$	—	+
4	$(p_x^{\text{top}} - p_x^{\text{bottom}})/\sqrt{2}$	—	—
5	$(p_y^{\text{top}} - p_y^{\text{bottom}})/\sqrt{2}$	—	+
6	d_{z^2}	+	+
7	d_{xy}	+	—
8	$d_{x^2-y^2}$	+	+
9	$(p_z^{\text{top}} - p_z^{\text{bottom}})/\sqrt{2}$	+	+
10	$(p_x^{\text{top}} + p_x^{\text{bottom}})/\sqrt{2}$	+	—
11	$(p_y^{\text{top}} + p_y^{\text{bottom}})/\sqrt{2}$	+	+

Table 4.1: Monolayer orbitals classified according to whether they are symmetric or antisymmetric under $\mathcal{M}_1$ and $\mathcal{M}_2$. From: Table 2 in Fang et al [1].

Atom	Z	n	Atom	Z	n
Mo	42	4	S	16	3
W	74	4	Se	34	4

Table 4.2: Parameters for the hydrogen-like orbitals included in our model.

between hoppings related by rotational symmetry. Hydrogen-like orbitals can be written as

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi), \quad (4.3)$$

where Y_{lm} are spherical harmonic functions, and

$$R_{nl}(r) = -\sqrt{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \exp\left(-\frac{Zr}{na_\mu}\right) \left(-\frac{2Zr}{na_\mu}\right)^l L_{n-l-1}^{(2l+1)}\left(-\frac{2Zr}{na_\mu}\right), \quad (4.4)$$

where $L_n^{(\alpha)}(x)$ are generalized Laguerre polynomials, $a_\mu = 4\pi\epsilon_0\hbar^2/\mu e^2$, $\mu = m_N m_e/(m_N + m_e)$, m_N is the mass of the nucleus, m_e the mass of the electron, and Z the atomic number. Since we deal with relatively heavy atoms (sulfur is the lightest, at about 32u), the reduced mass μ is roughly equal to the electron mass, and $a_\mu \approx a_0$, where a_0 is the Bohr radius.

The relevant parameters for the orbitals included in our model are given in Table 4.2. The

spherical harmonic parts of the orbitals included in our model are[190]

$$p_z \rightarrow Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos(\theta) , \quad (4.5)$$

$$p_x \rightarrow \frac{1}{\sqrt{2}} (Y_{1,-1} - Y_{1,1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin(\theta) \cos(\phi) , \quad (4.6)$$

$$p_y \rightarrow \frac{i}{\sqrt{2}} (Y_{1,-1} + Y_{1,1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin(\theta) \sin(\phi) , \quad (4.7)$$

$$d_{z^2} \rightarrow Y_{2,0} = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2(\theta) - 1) , \quad (4.8)$$

$$d_{xy} \rightarrow \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) = \frac{1}{4} \sqrt{\frac{15}{\pi}} \sin^2(\theta) \sin(2\phi) , \quad (4.9)$$

$$d_{x^2-y^2} \rightarrow \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) = \frac{1}{4} \sqrt{\frac{15}{\pi}} \sin^2(\theta) \cos(2\phi) , \quad (4.10)$$

$$d_{xz} \rightarrow \frac{1}{\sqrt{2}} (Y_{2,-1} - Y_{2,1}) = \frac{1}{4} \sqrt{\frac{15}{\pi}} \sin(2\theta) \cos(\phi) , \quad (4.11)$$

$$d_{yz} \rightarrow \frac{i}{\sqrt{2}} (Y_{2,-1} + Y_{2,1}) = \frac{1}{4} \sqrt{\frac{15}{\pi}} \sin(2\theta) \sin(\phi) . \quad (4.12)$$

4.3 Constructing the tight-binding Hamiltonian

In order to maintain the same naming convention as in Fang et al[1], we define the hopping integrals as

$$t_{ij}^{(1)} = \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} + \boldsymbol{\delta}_1) \rangle = \pm \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} - \boldsymbol{\delta}_1) \rangle , \quad (4.13)$$

$$t_{ij}^{(2)} = \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} + \boldsymbol{\delta}_2) \rangle = \pm \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} + \boldsymbol{\delta}_3) \rangle , \quad (4.14)$$

$$t_{ij}^{(3)} = \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} - \boldsymbol{\delta}_3) \rangle = \pm \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} - \boldsymbol{\delta}_2) \rangle , \quad (4.15)$$

where $\hat{H}^{\text{sp}}$ is the single-particle Hamiltonian given in Eq. (3.20). The negative signs appear for orbitals with different $\mathcal{M}_2$ -parity, and the positive signs appears for orbitals with the same $\mathcal{M}_2$ -parity.

For all other hoppings, we define

$$t_{ij}^{(\pm n)} = \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} \mp \boldsymbol{\delta}_n) \rangle. \quad (4.16)$$

As in Eqs. (4.13)-(4.15), $\mathcal{M}_2$ mirror symmetry allows us to relate hoppings with the same/different $\mathcal{M}_2$ -parity with a positive/negative sign,

$$t_{ij}^{(n)} = \pm t_{ij}^{(m)}, \quad (4.17)$$

for hoppings in $\mathcal{M}_2$ -symmetric directions, that is, for $(n, m) \in \{(4, 6), (8, 9), (10, 13), (11, 12), (14, 15), (16, 17), (-16, -17), (19, 21), (-19, -21), (20, -20)\}$, where the sign is negative if ϕ_i and ϕ_j have different parities under $\mathcal{M}_2$, and positive if they have the same parity under $\mathcal{M}_2$.

Furthermore, it is possible to relate hoppings $t_{ij}^{(18)}$ and $t_{ij}^{(-18)}$, taking advantage of the fact that $\pm \boldsymbol{\delta}_{18}$ are related through translational symmetry, as well as the fact that the hopping integrals are real. For any two orbitals i and j ,

$$t_{ij}^{(18)} = \langle \phi_i(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r} - \boldsymbol{\delta}_{18}) \rangle \quad (4.18)$$

$$= \langle \phi_i(\mathbf{r} + \boldsymbol{\delta}_{18}) | \hat{H}^{\text{sp}} | \phi_j(\mathbf{r}) \rangle \quad (4.19)$$

$$= \langle \phi_j(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_i(\mathbf{r} + \boldsymbol{\delta}_{18}) \rangle \quad (4.20)$$

$$= t_{ji}^{(-18)}. \quad (4.21)$$

This makes no difference to the number of parameters needed for the off-diagonal Hamiltonian matrix elements, but it reduces the number of parameters required for the diagonal elements by eleven, since it follows that $t_{ii}^{(18)} = t_{ii}^{(-18)}$.

With all this, we can now write down the tight-binding Hamiltonian. We can classify five different types of Hamiltonian matrix elements, according to symmetry. Again, we follow the logic of Fang et al. and generalize the matrix elements to include longer-distance hoppings while taking advantage of Eqs. (4.13)–(4.17).

4.3.1 Diagonal Elements

The diagonal terms include on-site energies and hoppings between the same type of atoms, e.g., along directions $\pm\boldsymbol{\delta}_1, \pm\boldsymbol{\delta}_2, \pm\boldsymbol{\delta}_3, \pm\boldsymbol{\delta}_{16}, \pm\boldsymbol{\delta}_{17}, \pm\boldsymbol{\delta}_{18}, \pm\boldsymbol{\delta}_{19}, \pm\boldsymbol{\delta}_{20}$, and $\pm\boldsymbol{\delta}_{21}$. Since the diagonal elements by definition only include hoppings between the same type of orbital, the parities of these orbitals under $\mathcal{M}_2$ are the same, and the above identities (4.13)–(4.15) and (4.17) hold with positive sign. We obtain

$$\begin{aligned}
H_{ii}(\mathbf{k}) &= \epsilon_i + t_{ii}^{(1)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_1}) + t_{ii}^{(2)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3}) \\
&\quad + t_{ii}^{(3)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3}) + t_{ii}^{(16)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{16}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{17}}) \\
&\quad + t_{ii}^{(-16)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{16}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{17}}) \\
&\quad + t_{ii}^{(18)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{18}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{18}}) \\
&\quad + t_{ii}^{(20)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{20}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{20}}) + t_{ii}^{(19)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{19}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{21}}) \\
&\quad + t_{ii}^{(-19)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{19}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{21}}) \\
&= \epsilon_i + 2t_{ii}^{(1)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_1) + t_{ii}^{(2)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3}) \\
&\quad + t_{ii}^{(3)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_3}) \\
&\quad + t_{ii}^{(16)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{16}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{17}}) + t_{ii}^{(-16)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{16}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{17}}) \\
&\quad + t_{ii}^{(18)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{18}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{18}}) \\
&\quad + 2t_{ii}^{(20)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{20}) + t_{ii}^{(19)} (e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{19}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{21}}) \\
&\quad + t_{ii}^{(-19)} (e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{19}} + e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{21}}) . \tag{4.22}
\end{aligned}$$

The diagonal elements of the Hamiltonian have to be real, because the Hamiltonian has to be Hermitian (the hopping elements $t_{ij}^{(n)}$ are all real because the atomic orbitals are chosen to be real.). This is only satisfied for all $\mathbf{k}$ if $t_{ii}^{(2)} = t_{ii}^{(3)}$, $t_{ii}^{(16)} = t_{ii}^{(-16)}$, and $t_{ii}^{(19)} = t_{ii}^{(-19)}$, which yields

$$\begin{aligned}
H_{ii}(\mathbf{k}) &= \\
&\epsilon_i + 2t_{ii}^{(1)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_1) + 2t_{ii}^{(2)} (\cos(\mathbf{k} \cdot \boldsymbol{\delta}_2) + \cos(\mathbf{k} \cdot \boldsymbol{\delta}_3))
\end{aligned}$$

$$\begin{aligned}
& + 2t_{ii}^{(18)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{18}) + 2t_{ii}^{(16)} (\cos(\mathbf{k} \cdot \boldsymbol{\delta}_{16}) + \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{17})) \\
& + 2t_{ii}^{(20)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{20}) + 2t_{ii}^{(19)} (\cos(\mathbf{k} \cdot \boldsymbol{\delta}_{19}) + \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{21})) .
\end{aligned} \tag{4.23}$$

4.3.2 Off-diagonal elements for orbitals on the same type of atom with the same $\mathcal{M}_2$ -parity

These are given by $(i, j) \in \{(3, 5), (6, 8), (9, 11)\}$ (for the inverse pairs (j, i) use again that the Hamiltonian has to be Hermitian) and the matrix elements are found to be

$$\begin{aligned}
H_{ij}(\mathbf{k}) = & 2t_{ij}^{(1)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_1) + 2t_{ij}^{(20)} \cos(\mathbf{k} \cdot \boldsymbol{\delta}_{20}) \\
& + t_{ij}^{(2)} (e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_2} + e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_3}) + t_{ij}^{(3)} (e^{i\mathbf{k} \cdot \boldsymbol{\delta}_2} + e^{i\mathbf{k} \cdot \boldsymbol{\delta}_3}) \\
& + t_{ij}^{(-16)} (e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{16}} + e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{17}}) + t_{ij}^{(16)} (e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{16}} + e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{17}}) \\
& + t_{ij}^{(18)} e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{18}} + t_{ji}^{(18)} e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{18}} \\
& + t_{ij}^{(19)} (e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{19}} + e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{21}}) + t_{ij}^{(-21)} (e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{19}} + e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{21}}) .
\end{aligned} \tag{4.24}$$

4.3.3 Off-diagonal elements for orbitals on the same type of atom with different $\mathcal{M}_2$ -parity

These are given by $(i, j) \in \{(1, 2), (3, 4), (4, 5), (6, 7), (7, 8), (9, 10), (10, 11)\}$ and yields

$$\begin{aligned}
H_{ij}(\mathbf{k}) = & -2it_{ij}^{(1)} \sin(\mathbf{k} \cdot \boldsymbol{\delta}_1) + 2t_{ij}^{(20)} \sin(\mathbf{k} \cdot \boldsymbol{\delta}_{20}) \\
& + t_{ij}^{(2)} (e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_2} - e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_3}) + t_{ij}^{(3)} (-e^{i\mathbf{k} \cdot \boldsymbol{\delta}_2} + e^{i\mathbf{k} \cdot \boldsymbol{\delta}_3}) \\
& + t_{ij}^{(-16)} (e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{16}} - e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{17}}) + t_{ij}^{(16)} (e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{16}} - e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{17}}) \\
& + t_{ij}^{(19)} (e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{19}} - e^{i\mathbf{k} \cdot \boldsymbol{\delta}_{21}}) + t_{ij}^{(-21)} (-e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{19}} + e^{-i\mathbf{k} \cdot \boldsymbol{\delta}_{21}}) .
\end{aligned} \tag{4.25}$$

The terms including δ_{18} disappear because, due to $\mathcal{M}_2$ antisymmetry,

$$t_{ij}^{(18)} = -t_{ij}^{(18)} = 0 , \quad (4.26)$$

$$t_{ij}^{(-18)} = -t_{ij}^{(-18)} = 0 . \quad (4.27)$$

4.3.4 Off-diagonal elements for orbitals on different types of atom with the same $\mathcal{M}_2$ -parity

These are given by $(i, j) \in \{(4, 1), (3, 2), (5, 2), (9, 6), (11, 6), (10, 7), (9, 8), (11, 8)\}$ and yields

$$\begin{aligned} H_{ij}(\mathbf{k}) = & \\ & t_{ij}^{(4)} (e^{i\mathbf{k} \cdot \delta_4} + e^{i\mathbf{k} \cdot \delta_6}) + t_{ij}^{(5)} e^{i\mathbf{k} \cdot \delta_5} \\ & + t_{ij}^{(7)} e^{i\mathbf{k} \cdot \delta_7} + t_{ij}^{(8)} (e^{i\mathbf{k} \cdot \delta_8} + e^{i\mathbf{k} \cdot \delta_9}) + t_{ij}^{(14)} (e^{i\mathbf{k} \cdot \delta_{14}} + e^{i\mathbf{k} \cdot \delta_{15}}) \\ & + t_{ij}^{(10)} (e^{i\mathbf{k} \cdot \delta_{10}} + e^{i\mathbf{k} \cdot \delta_{13}}) + t_{ij}^{(12)} (e^{i\mathbf{k} \cdot \delta_{11}} + e^{i\mathbf{k} \cdot \delta_{12}}) . \end{aligned} \quad (4.28)$$

4.3.5 Off-diagonal elements for orbitals on different types of atom with different $\mathcal{M}_2$ -parity

These are given by $(i, j) \in \{(3, 1), (5, 1), (4, 2), (10, 6), (9, 7), (11, 7), (10, 8)\}$ and yields

$$\begin{aligned} H_{ij}(\mathbf{k}) = & \\ & t_{ij}^{(4)} (e^{i\mathbf{k} \cdot \delta_4} - e^{i\mathbf{k} \cdot \delta_6}) \\ & + t_{ij}^{(8)} (e^{i\mathbf{k} \cdot \delta_8} - e^{i\mathbf{k} \cdot \delta_9}) + t_{ij}^{(14)} (e^{i\mathbf{k} \cdot \delta_{14}} - e^{i\mathbf{k} \cdot \delta_{15}}) \\ & + t_{ij}^{(10)} (e^{i\mathbf{k} \cdot \delta_{10}} - e^{i\mathbf{k} \cdot \delta_{13}}) + t_{ij}^{(12)} (-e^{i\mathbf{k} \cdot \delta_{11}} + e^{i\mathbf{k} \cdot \delta_{12}}) . \end{aligned} \quad (4.29)$$

4.4 $\mathcal{R}_3$ symmetry

It is possible to reduce the number of free parameters yet further by making use of $\mathcal{R}_3$ -symmetry.

The crystal Hamiltonian is invariant under $\mathcal{R}_3$, that is, the transformation $\phi \rightarrow \phi + \frac{2\pi}{3}$. Let us first examine the transformations of the orbitals in Eqs. (4.5)-(4.12) under that rotation.

Both d_{z^2} and p_z transform into themselves,

$$d_{z^2} \xrightarrow{\phi+2\pi/3} d_{z^2} , \quad (4.30)$$

$$p_z \xrightarrow{\phi+2\pi/3} p_z . \quad (4.31)$$

The ϕ -dependence of the other orbitals is given by either sines and cosines, therefore it is useful to recall that

$$\sin\left(\phi + \frac{2\pi}{3}\right) = -\frac{1}{2}\sin(\phi) + \frac{\sqrt{3}}{2}\cos(\phi) , \quad (4.32)$$

$$\sin\left(\phi + \frac{4\pi}{3}\right) = -\frac{1}{2}\sin(\phi) - \frac{\sqrt{3}}{2}\cos(\phi) , \quad (4.33)$$

$$\cos\left(\phi + \frac{2\pi}{3}\right) = -\frac{\sqrt{3}}{2}\sin(\phi) - \frac{1}{2}\cos(\phi) , \quad (4.34)$$

$$\cos\left(\phi + \frac{4\pi}{3}\right) = \frac{\sqrt{3}}{2}\sin(\phi) - \frac{1}{2}\cos(\phi) . \quad (4.35)$$

From this, we can easily see that

$$p_x \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}p_x - \frac{\sqrt{3}}{2}p_y \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y , \quad (4.36)$$

$$p_y \xrightarrow{+\frac{2\pi}{3}} \frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y \xrightarrow{+\frac{2\pi}{3}} -\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y , \quad (4.37)$$

$$d_{xy} \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}d_{xy} - \frac{\sqrt{3}}{2}d_{x^2-y^2} \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}d_{xy} + \frac{\sqrt{3}}{2}d_{x^2-y^2} , \quad (4.38)$$

$$d_{x^2-y^2} \xrightarrow{+\frac{2\pi}{3}} \frac{\sqrt{3}}{2}d_{xy} - \frac{1}{2}d_{x^2-y^2} \xrightarrow{+\frac{2\pi}{3}} -\frac{\sqrt{3}}{2}d_{xy} - \frac{1}{2}d_{x^2-y^2} , \quad (4.39)$$

$$d_{xz} \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}d_{xz} - \frac{\sqrt{3}}{2}d_{yz} \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}d_{xz} + \frac{\sqrt{3}}{2}d_{yz} , \quad (4.40)$$

$$d_{yz} \xrightarrow{+\frac{2\pi}{3}} \frac{\sqrt{3}}{2}d_{xz} - \frac{1}{2}d_{yz} \xrightarrow{+\frac{2\pi}{3}} -\frac{\sqrt{3}}{2}d_{xz} - \frac{1}{2}d_{yz} . \quad (4.41)$$

Since the linear combinations of p -orbitals which are used in the basis are sums of equivalent orbitals oriented along the z -axis, the same transformation under ϕ -rotation applies to them in the same way as to the plain atomic orbitals, even though their r and θ -dependence is much more complicated. To summarize, for pairs $(\alpha, \beta) \in \{(1, 2), (4, 5), (7, 8), (10, 11)\}$, the transformation is given by

$$\phi_\alpha \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}\phi_\alpha - \frac{\sqrt{3}}{2}\phi_\beta \xrightarrow{+\frac{2\pi}{3}} -\frac{1}{2}\phi_\alpha + \frac{\sqrt{3}}{2}\phi_\beta , \quad (4.42)$$

$$\phi_\beta \xrightarrow{+\frac{2\pi}{3}} \frac{\sqrt{3}}{2}\phi_\alpha - \frac{1}{2}\phi_\beta \xrightarrow{+\frac{2\pi}{3}} -\frac{\sqrt{3}}{2}\phi_\alpha - \frac{1}{2}\phi_\beta . \quad (4.43)$$

This notation is useful—the orbitals labelled α all have even parity under $\mathcal{M}_2$, and the orbitals labelled β have odd $\mathcal{M}_2$ parity. They all transform similarly. The last class of orbitals (designated in the following as γ) are invariant under $\mathcal{R}_3$ and have even $\mathcal{M}_2$ parity.

Let us consider the on-site energies first. $\mathcal{R}_3$ -symmetry dictates they have to be invariant under rotation by $\pm 2\pi/3$, that is

$$\epsilon_\alpha = \langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r}) \rangle \quad (4.44)$$

$$= \left(-\frac{1}{2} \langle \phi_\alpha(\mathbf{r}) | \pm \frac{\sqrt{3}}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(-\frac{1}{2} | \phi_\alpha(\mathbf{r}) \rangle \pm \frac{\sqrt{3}}{2} | \phi_\beta(\mathbf{r}) \rangle \right) \quad (4.45)$$

$$= \frac{1}{4} \epsilon_\alpha + \frac{3}{4} \epsilon_\beta \pm \frac{\sqrt{3}}{4} \left(\langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r}) \rangle + \langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r}) \rangle \right) \quad (4.46)$$

$$= \frac{1}{4} \epsilon_\alpha + \frac{3}{4} \epsilon_\beta , \quad (4.47)$$

where the last identity can be seen to be true in two different ways. Mathematically, it follows that

$$\frac{\sqrt{3}}{4} \left(\langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r}) \rangle + \langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r}) \rangle \right) \quad (4.48)$$

$$= -\frac{\sqrt{3}}{4} \left(\langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r}) \rangle + \langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r}) \rangle \right) = 0 . \quad (4.49)$$

Physically, we know that the additional terms describe hopping between orbitals on the same atoms, which are forbidden due to orthogonality of the orbitals.

From the above identity we can see that

$$\epsilon_\alpha = \epsilon_\beta . \quad (4.50)$$

Next, let us consider the hopping integrals corresponding to second-nearest neighbours, as

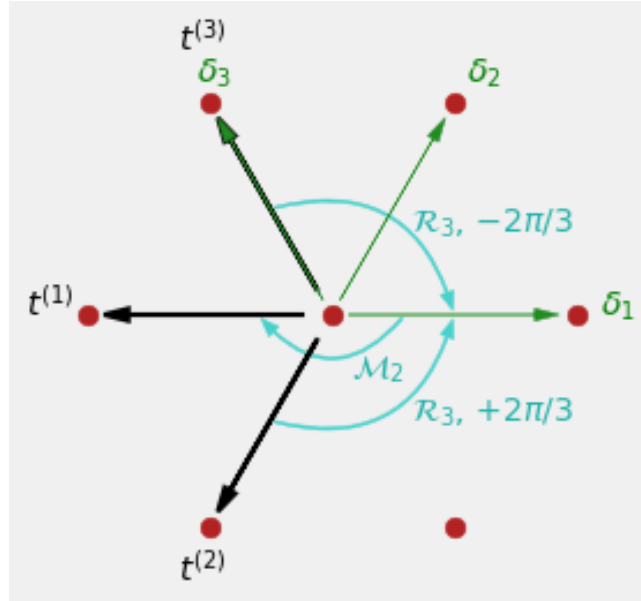


Figure 4.2: Illustration of symmetry operations necessary to derive relations between hopping parameters $t^{(1)}$, $t^{(2)}$, and $t^{(3)}$. Neighbour vectors $-\delta_2$ and δ_3 (the directions of $t^{(3)}$ and $t^{(2)}$ hopping) relate to neighbour vector δ_1 through $\mathcal{R}_3$ -symmetry, which relates to neighbour vector $-\delta_1$ (the direction of $t^{(1)}$ hopping) through $\mathcal{M}_2$ -symmetry.

illustrated in Fig. 4.2. The three neighbour vectors included in Eqs. (4.24) and (4.25) are not directly equivalent under $\mathcal{R}_3$ -symmetry. However, they are equivalent if $\mathcal{M}_2$ -symmetry is also considered. For $t^{(2)}$ and $t^{(3)}$, the coordinate system is first rotated by $-2\pi/3$ and $+2\pi/3$, respectively, and then inverted along the yz -plane, as illustrated in Fig. 4.2, in order to relate

both of them to $t^{(1)}$. This results in

$$t_{\alpha\alpha}^{(2)} = \langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r} + \boldsymbol{\delta}_2) \rangle \quad (4.51)$$

$$\stackrel{\mathcal{R}_3}{=} \left(-\frac{1}{2} \langle \phi_\alpha(\mathbf{r}) | + \frac{\sqrt{3}}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(-\frac{1}{2} | \phi_\alpha(\mathbf{r} - \boldsymbol{\delta}_1) \rangle + \frac{\sqrt{3}}{2} | \phi_\beta(\mathbf{r} - \boldsymbol{\delta}_1) \rangle \right) \quad (4.52)$$

$$\stackrel{\mathcal{M}_2}{=} \left(\frac{1}{2} \langle \phi_\alpha(\mathbf{r}) | + \frac{\sqrt{3}}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(\frac{1}{2} | \phi_\alpha(\mathbf{r} + \boldsymbol{\delta}_1) \rangle + \frac{\sqrt{3}}{2} | \phi_\beta(\mathbf{r} + \boldsymbol{\delta}_1) \rangle \right), \quad (4.53)$$

recalling that the α -orbitals are odd under $\mathcal{M}_2$, whereas the β -orbitals are even under $\mathcal{M}_2$.

Therefore,

$$t_{\alpha\alpha}^{(2)} = \frac{1}{4} t_{\alpha\alpha}^{(1)} + \frac{3}{4} t_{\beta\beta}^{(1)} + \underbrace{\frac{\sqrt{3}}{4} (t_{\alpha\beta}^{(1)} + t_{\beta\alpha}^{(1)})}_{=0, \text{ antisym.}}. \quad (4.54)$$

The antisymmetry of those last two terms can be seen from

$$t_{\alpha\beta}^{(1)} = \langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r} + \boldsymbol{\delta}_1) \rangle \quad (4.55)$$

$$= \langle \phi_\alpha(\mathbf{r} - \boldsymbol{\delta}_1) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r}) \rangle, \quad (4.56)$$

which can be seen by a change of coordinates in the integration and the fact that $\boldsymbol{\delta}_1$ is a lattice vector and that the Hamiltonian has translational symmetry. From there,

$$\langle \phi_\alpha(\mathbf{r} - \boldsymbol{\delta}_1) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r}) \rangle = \left(\langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r} - \boldsymbol{\delta}_1) \rangle \right)^* \quad (4.57)$$

$$= \left(-\langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r} + \boldsymbol{\delta}_1) \rangle \right)^* \quad (4.58)$$

$$= -(t_{\beta\alpha}^{(1)})^* = -t_{\beta\alpha}^{(1)}. \quad (4.59)$$

Finally,

$$t_{\alpha\alpha}^{(2)} = \frac{1}{4} t_{\alpha\alpha}^{(1)} + \frac{3}{4} t_{\beta\beta}^{(1)}. \quad (4.60)$$

Similarly,

$$t_{\beta\beta}^{(2)} = \langle \phi_\beta(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r} + \delta_2) \rangle \quad (4.61)$$

$$\stackrel{\mathcal{R}_3}{=} \left(-\frac{\sqrt{3}}{2} \langle \phi_\alpha(\mathbf{r}) | -\frac{1}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(-\frac{\sqrt{3}}{2} | \phi_\alpha(\mathbf{r} - \delta_1) \rangle - \frac{1}{2} | \phi_\beta(\mathbf{r} - \delta_1) \rangle \right) \quad (4.62)$$

$$\stackrel{\mathcal{M}_2}{=} \left(\frac{\sqrt{3}}{2} \langle \phi_\alpha(\mathbf{r}) | -\frac{1}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(\frac{\sqrt{3}}{2} | \phi_\alpha(\mathbf{r} + \delta_1) \rangle - \frac{1}{2} | \phi_\beta(\mathbf{r} + \delta_1) \rangle \right) , \quad (4.63)$$

and therefore

$$t_{\beta\beta}^{(2)} = \frac{3}{4} t_{\alpha\alpha}^{(1)} + \frac{1}{4} t_{\beta\beta}^{(1)} . \quad (4.64)$$

Next,

$$t_{\gamma\beta}^{(2)} = \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r} + \delta_2) \rangle \quad (4.65)$$

$$\stackrel{\mathcal{R}_3}{=} \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} \left(-\frac{\sqrt{3}}{2} | \phi_\alpha(\mathbf{r} - \delta_1) \rangle - \frac{1}{2} | \phi_\beta(\mathbf{r} - \delta_1) \rangle \right) \quad (4.66)$$

$$\stackrel{\mathcal{M}_2}{=} \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} \left(\frac{\sqrt{3}}{2} | \phi_\alpha(\mathbf{r} + \delta_1) \rangle - \frac{1}{2} | \phi_\beta(\mathbf{r} + \delta_1) \rangle \right) \quad (4.67)$$

$$= \frac{\sqrt{3}}{2} t_{\gamma\alpha}^{(1)} - \frac{1}{2} t_{\gamma\beta}^{(1)} , \quad (4.68)$$

where we used that the γ -orbitals are even under $\mathcal{M}_2$. $t_{\gamma\beta}^{(3)}$ can be derived the same way, the only difference is that the $\mathcal{R}_3$ -rotation has to be counterclockwise instead of clockwise, which changes the sign of the $\frac{\sqrt{3}}{2}$ -term, so

$$t_{\gamma\beta}^{(3)} = -\frac{\sqrt{3}}{2} t_{\gamma\alpha}^{(1)} - \frac{1}{2} t_{\gamma\beta}^{(1)} . \quad (4.69)$$

Similarly,

$$t_{\gamma\alpha}^{(2)} = \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\alpha(\mathbf{r} + \delta_2) \rangle \quad (4.70)$$

$$\stackrel{\mathcal{R}_3}{=} \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} \left(-\frac{1}{2} | \phi_\alpha(\mathbf{r} - \delta_1) \rangle + \frac{\sqrt{3}}{2} | \phi_\beta(\mathbf{r} - \delta_1) \rangle \right) \quad (4.71)$$

$$\stackrel{\mathcal{M}_2}{=} \langle \phi_\gamma(\mathbf{r}) | \hat{H}^{\text{sp}} \left(\frac{1}{2} |\phi_\alpha(\mathbf{r} + \boldsymbol{\delta}_1)\rangle + \frac{\sqrt{3}}{2} |\phi_\beta(\mathbf{r} + \boldsymbol{\delta}_1)\rangle \right) \rangle \quad (4.72)$$

$$= \frac{1}{2} t_{\gamma\alpha}^{(1)} + \frac{\sqrt{3}}{2} t_{\gamma\beta}^{(1)} , \quad (4.73)$$

and

$$t_{\gamma\alpha}^{(3)} = \frac{1}{2} t_{\gamma\alpha}^{(1)} - \frac{\sqrt{3}}{2} t_{\gamma\beta}^{(1)} . \quad (4.74)$$

Lastly,

$$t_{\alpha\beta}^{(2)} = \langle \phi_\alpha(\mathbf{r}) | \hat{H}^{\text{sp}} | \phi_\beta(\mathbf{r} + \boldsymbol{\delta}_2) \rangle \quad (4.75)$$

$$\stackrel{\mathcal{R}_3}{=} \left(-\frac{1}{2} \langle \phi_\alpha(\mathbf{r}) | + \frac{\sqrt{3}}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(-\frac{\sqrt{3}}{2} |\phi_\alpha(\mathbf{r} - \boldsymbol{\delta}_1)\rangle - \frac{1}{2} |\phi_\beta(\mathbf{r} - \boldsymbol{\delta}_1)\rangle \right) \quad (4.76)$$

$$\stackrel{\mathcal{M}_2}{=} \left(\frac{1}{2} \langle \phi_\alpha(\mathbf{r}) | + \frac{\sqrt{3}}{2} \langle \phi_\beta(\mathbf{r}) | \right) \hat{H}^{\text{sp}} \left(\frac{\sqrt{3}}{2} |\phi_\alpha(\mathbf{r} + \boldsymbol{\delta}_1)\rangle - \frac{1}{2} |\phi_\beta(\mathbf{r} + \boldsymbol{\delta}_1)\rangle \right) \quad (4.77)$$

$$= \frac{\sqrt{3}}{4} (t_{\alpha\alpha}^{(1)} - t_{\beta\beta}^{(1)}) - \frac{1}{4} t_{\alpha\beta}^{(1)} + \frac{3}{4} t_{\beta\alpha}^{(1)} \quad (4.78)$$

$$= \frac{\sqrt{3}}{4} (t_{\alpha\alpha}^{(1)} - t_{\beta\beta}^{(1)}) - t_{\alpha\beta}^{(1)} , \quad (4.79)$$

since $t_{\alpha\beta}^{(1)} = -t_{\beta\alpha}^{(1)}$, and equivalently,

$$t_{\alpha\beta}^{(3)} = -\frac{\sqrt{3}}{4} (t_{\alpha\alpha}^{(1)} - t_{\beta\beta}^{(1)}) - t_{\alpha\beta}^{(1)} . \quad (4.80)$$

The same procedure can be applied to all the other hopping integrals included in our model.

4.5 Results of $\mathcal{R}_3$ reduction

In summary, for $(\alpha = 1, \beta = 2), (\alpha = 4, \beta = 5, \gamma = 3), (\alpha = 7, \beta = 8, \gamma = 6), (\alpha = 10, \beta = 11, \gamma = 9)$, we find that

$$\epsilon_\alpha = \epsilon_\beta , \quad (4.81)$$

$$t_{\alpha\alpha}^{(2)} = \frac{1}{4}t_{\alpha\alpha}^{(1)} + \frac{3}{4}t_{\beta\beta}^{(1)}, \quad (4.82)$$

$$t_{\beta\beta}^{(2)} = \frac{3}{4}t_{\alpha\alpha}^{(1)} + \frac{1}{4}t_{\beta\beta}^{(1)}, \quad (4.83)$$

$$t_{\gamma\gamma}^{(2)} = t_{\gamma\gamma}^{(1)}, \quad (4.84)$$

$$t_{\gamma\beta}^{(2,3)} = \pm \frac{\sqrt{3}}{2}t_{\gamma\alpha}^{(1)} - \frac{1}{2}t_{\gamma\beta}^{(1)}, \quad (4.85)$$

$$t_{\gamma\alpha}^{(2,3)} = \frac{1}{2}t_{\gamma\alpha}^{(1)} \pm \frac{\sqrt{3}}{2}t_{\gamma\beta}^{(1)}, \quad (4.86)$$

$$t_{\alpha\beta}^{(2,3)} = \pm \frac{\sqrt{3}}{4}(t_{\alpha\alpha}^{(1)} - t_{\beta\beta}^{(1)}) - t_{\alpha\beta}^{(1)}. \quad (4.87)$$

Furthermore, for $(n, m) \in \{(16, -18), (-16, 18)\}$,

$$t_{\alpha\alpha}^{(n)} = \frac{1}{4}t_{\alpha\alpha}^{(m)} + \frac{3}{4}t_{\beta\beta}^{(m)}, \quad (4.88)$$

$$t_{\beta\beta}^{(n)} = \frac{3}{4}t_{\alpha\alpha}^{(m)} + \frac{1}{4}t_{\beta\beta}^{(m)}, \quad (4.89)$$

$$t_{\gamma\gamma}^{(n)} = t_{\gamma\gamma}^{(m)}, \quad (4.90)$$

$$t_{\gamma\alpha}^{(n)} = -\frac{\sqrt{3}}{2}t_{\gamma\beta}^{(m)}, \quad (4.91)$$

$$t_{\gamma\beta}^{(n)} = -\frac{1}{2}t_{\gamma\beta}^{(m)}, \quad (4.92)$$

$$t_{\alpha\beta}^{(n)} = -\frac{\sqrt{3}}{4}(t_{\alpha\alpha}^{(m)} - t_{\beta\beta}^{(m)}), \quad (4.93)$$

and

$$t_{\alpha\alpha}^{(19)} = \frac{1}{4}t_{\alpha\alpha}^{(20)} + \frac{3}{4}t_{\beta\beta}^{(20)}, \quad (4.94)$$

$$t_{\beta\beta}^{(19)} = \frac{3}{4}t_{\alpha\alpha}^{(20)} + \frac{1}{4}t_{\beta\beta}^{(20)}, \quad (4.95)$$

$$t_{\gamma\gamma}^{(19)} = t_{\gamma\gamma}^{(20)}, \quad (4.96)$$

$$t_{\gamma\alpha}^{(\pm 19)} = \mp \frac{1}{2}t_{\gamma\alpha}^{(20)} - \frac{\sqrt{3}}{2}t_{\gamma\beta}^{(20)}, \quad (4.97)$$

$$t_{\gamma\beta}^{(\pm 19)} = \pm \frac{\sqrt{3}}{2}t_{\gamma\alpha}^{(20)} - \frac{1}{2}t_{\gamma\beta}^{(20)}, \quad (4.98)$$

$$t_{\alpha\beta}^{(\pm 19)} = -\frac{\sqrt{3}}{4}(t_{\alpha\alpha}^{(20)} - t_{\beta\beta}^{(20)}) \pm t_{\alpha\beta}^{(20)}. \quad (4.99)$$

For $(\alpha = 1, \beta = 2, \alpha' = 4, \beta' = 5, \gamma' = 3), (\alpha = 7, \beta = 8, \alpha' = 10, \beta' = 11, \gamma' = 9)$, we find that for $(n, m) \in \{(4, 5), (8, 7)\}$,

$$t_{\alpha'\alpha}^{(n)} = \frac{1}{4}t_{\alpha'\alpha}^{(m)} + \frac{3}{4}t_{\beta'\beta}^{(m)}, \quad (4.100)$$

$$t_{\beta'\beta}^{(n)} = \frac{3}{4}t_{\alpha'\alpha}^{(m)} + \frac{1}{4}t_{\beta'\beta}^{(m)}, \quad (4.101)$$

$$t_{\beta'\alpha}^{(n)} = t_{\alpha'\beta}^{(n)} = -\frac{\sqrt{3}}{4}(t_{\alpha'\alpha}^{(m)} - t_{\beta'\beta}^{(m)}), \quad (4.102)$$

$$t_{\gamma'\alpha}^{(n)} = -\frac{\sqrt{3}}{2}t_{\gamma'\beta}^{(m)}, \quad (4.103)$$

$$t_{\gamma'\beta}^{(n)} = -\frac{1}{2}t_{\gamma'\beta}^{(m)}, \quad (4.104)$$

$$t_{96}^{(n)} = t_{96}^{(m)}, \quad (4.105)$$

$$t_{106}^{(n)} = -\frac{\sqrt{3}}{2}t_{116}^{(m)}, \quad (4.106)$$

$$t_{116}^{(n)} = -\frac{1}{2}t_{116}^{(m)}. \quad (4.107)$$

And, finally,

$$t_{\alpha'\alpha}^{(12,14)} = \frac{1}{4}t_{\alpha'\alpha}^{(10)} + \frac{3}{4}t_{\beta'\beta}^{(10)} \mp \frac{\sqrt{3}}{4}(t_{\alpha'\beta}^{(10)} + t_{\beta'\alpha}^{(10)}), \quad (4.108)$$

$$t_{\beta'\beta}^{(12,14)} = \frac{3}{4}t_{\alpha'\alpha}^{(10)} + \frac{1}{4}t_{\beta'\beta}^{(10)} \pm \frac{\sqrt{3}}{4}(t_{\alpha'\beta}^{(10)} + t_{\beta'\alpha}^{(10)}), \quad (4.109)$$

$$t_{\beta'\alpha}^{(12,14)} = \pm \frac{\sqrt{3}}{4}(t_{\alpha'\alpha}^{(10)} - t_{\beta'\beta}^{(10)}) + \frac{1}{4}t_{\beta'\alpha}^{(10)} - \frac{3}{4}t_{\alpha'\beta}^{(10)}, \quad (4.110)$$

$$t_{\alpha'\beta}^{(12,14)} = \pm \frac{\sqrt{3}}{4}(t_{\alpha'\alpha}^{(10)} - t_{\beta'\beta}^{(10)}) + \frac{1}{4}t_{\alpha'\beta}^{(10)} - \frac{3}{4}t_{\beta'\alpha}^{(10)}, \quad (4.111)$$

$$t_{\gamma'\alpha}^{(12,14)} = -\frac{1}{2}t_{\gamma'\alpha}^{(10)} \pm \frac{\sqrt{3}}{2}t_{\gamma'\beta}^{(10)}, \quad (4.112)$$

$$t_{\gamma'\beta}^{(12,14)} = \mp \frac{\sqrt{3}}{2}t_{\gamma'\alpha}^{(10)} - \frac{1}{2}t_{\gamma'\beta}^{(10)}, \quad (4.113)$$

$$t_{96}^{(12,14)} = t_{96}^{(10)}, \quad (4.114)$$

$$t_{106}^{(12,14)} = -\frac{1}{2}t_{106}^{(10)} \pm \frac{\sqrt{3}}{2}t_{116}^{(10)}, \quad (4.115)$$

$$t_{116}^{(12,14)} = \mp \frac{\sqrt{3}}{2} t_{106}^{(10)} - \frac{1}{2} t_{116}^{(10)} . \quad (4.116)$$

4.6 Spin-orbit coupling

There is one more important factor that needs to be considered: spin. TMDs exhibit strong spin-orbit coupling[1]. Even in the monolayer case, the electronic bandstructure shows strong spin-splitting, particularly at the high-symmetry points K and K' . Furthermore, as alluded to in Sec. 2.2.1, the spin-character of TMD bilayer bandstructures is strongly stacking dependent. The A and B peaks in the optical spectrum of monolayer TMDs are also a consequence of spin-splitting at the direct gaps at K and K'[161].

In this work, following Ref. [1], spin-orbit coupling is included in the tight-binding model as an on-site term,

$$\lambda_{M/X}^{\text{SOC}} \mathbf{L} \cdot \mathbf{S} . \quad (4.117)$$

where $\mathbf{L}$ is the orbital angular momentum, $\mathbf{S}$ is the spin angular momentum, and $\lambda_{M/X}^{\text{SOC}}$ is a material-specific constant. In [1], this term is calculated by computing the spin-splitting for a single atom within a large unit cell using a DFT calculation. They obtain:

$$\lambda_{\text{Mo}}^{\text{SOC}} = 0.0836 \text{ eV}/\hbar , \quad (4.118)$$

$$\lambda_{\text{W}}^{\text{SOC}} = 0.2874 \text{ eV}/\hbar , \quad (4.119)$$

$$\lambda_{\text{S}}^{\text{SOC}} = 0.0556 \text{ eV}/\hbar , \quad (4.120)$$

$$\lambda_{\text{Se}}^{\text{SOC}} = 0.2470 \text{ eV}/\hbar . \quad (4.121)$$

The impact of spin-orbit coupling on the electronic bandstructure of TMDs is strongly related to symmetry.

For time-reversal symmetric Hamiltonians (in practice, Hamiltonians without magnetic fields),

the energy dispersion is inversion-symmetric in the Brillouin zone, even if there is no inversion-symmetry in the real crystal[191]. That is, for every state at a given Brillouin zone point $\mathbf{k}$ with spin s , there is a state at $-\mathbf{k}$ with spin $-s$ with the same energy.

If, for a given $\mathbf{k}$, the transformation $\mathbf{k} \rightarrow -\mathbf{k}$ can be achieved from a different symmetry operation of the crystal which does not invert spin, then the corresponding energy $\epsilon_{\mathbf{k}}$ is spin-degenerate.

For TMDs, this means that any Brillouin zone vector orthogonal to the symmetry axis $\mathcal{M}_2$ has spin-degenerate energy dispersion. Both inversion and $\mathcal{M}_2$ map any point between Γ and M to the same point between Γ and $-M$. Therefore, the bandstructure is spin-degenerate along the line ΓM .

Note that the two high-symmetry points on this line, Γ and M , would have spin-degenerate dispersion even without $\mathcal{M}_2$ -symmetry, as Γ maps onto itself under inversion, and M and $-M$ are related through translation symmetry.

Finally, K and K' do not have spin-degenerate dispersion (in fact, they exhibit quite strong spin-splitting, particularly at the valence edge). However, they transform into one another through inversion symmetry and therefore form a pair. For every spin-up state at K , there is a spin-down state at K' with the same energy, and vice versa.

4.7 Conclusion

In this chapter, I extended the third-nearest neighbour tight-binding model for TMD monolayers originally presented by Fang et al.[1] to include up to sixth-nearest neighbour hopping. Following the approach from Fang et al., I derived symmetry-reduced analytical expressions for the Hamiltonian matrix elements. This results in a total of 97 free parameters, compared to 1275 with no symmetry considerations.

Note that, since we know the symmetry of the system, we could have calculated the Hamiltonian without any symmetry considerations for the irreducible Brillouin zone and enforced the symmetry on the whole Brillouin zone. This would result in the same symmetry precision, but would require using all 1275 parameters.

The main use of this enforced symmetry is as a numerical test. One of the consequences of the symmetry on the optical properties is that excitonic states come in degenerate sets, with exactly the same energy. The full sets have the full crystal symmetry, but there are often two or more excitons within a set. In particular, the lowest energy excitons in TMD monolayers are doubly degenerate[161]. This degeneracy is very easily broken if there are errors in the code. Enforcing the symmetry on the tight-binding Hamiltonian avoids numerical inaccuracies that may themselves break the degeneracies.

Chapter 5

Impact of longer-ranged hoppings on optoelectronic properties of MoS₂ monolayers

In this chapter, I will present the impacts of the longer ranged hopping described in Ch. 4 on the electronic bandstructures and optical spectra of MoS₂ monolayers. I will compare the electronic bandstructures to DFT calculations from which the tight-binding parameters were derived and which they are meant to approximate. I will also compare the resulting spectra to ab initio spectra obtained by Qiu et al.[6]. This will serve both to illustrate the impact of the longer ranged hopping, and help to highlight which of the features which will later be observed in bilayer systems are fundamentally monolayer/intralayer physics.

5.1 Impact of longer-ranged hoppings on MoS₂ monolayer band structure

The question is now what impact the longer-ranged hoppings that are included in our tight-binding model have on the optoelectronic properties of TMDs, focussing on MoS₂. The mono-

layer tight-binding parameters for MoS_2 are detailed in Table A.1 in Appendix A. As described in Sec. 3.4, we obtained the parameters by performing a DFT calculation first (see Sec. 3.10.1 for details) and then wannierizing the resulting Hamiltonian.

Let us first consider the electronic properties. Figure 5.1 shows the tight-binding band struc-

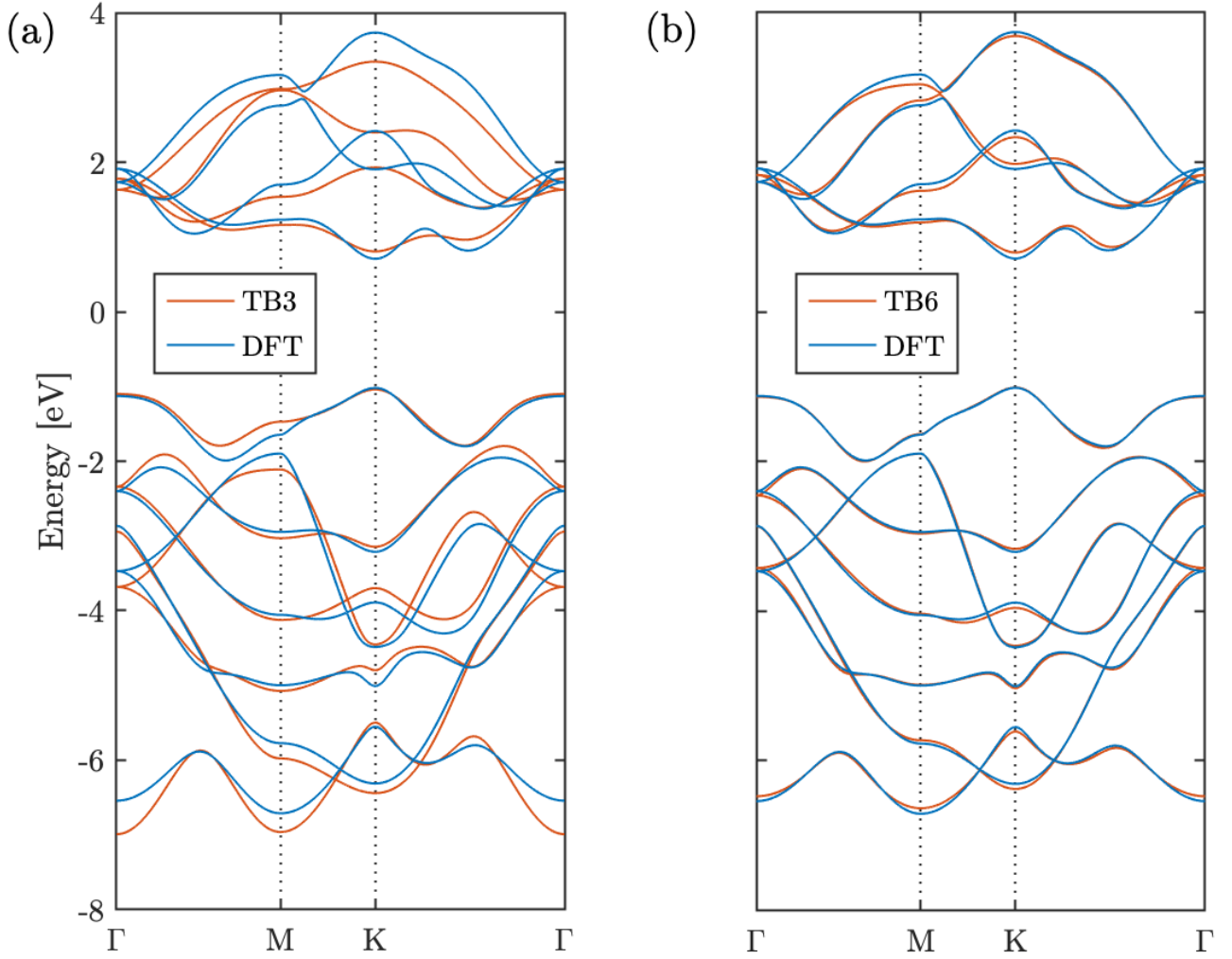


Figure 5.1: This figure compares the third (left) and sixth (right) nearest neighbour tight-binding bandstructures to the DFT bandstructure from which our parameters were derived. SOC is not included in this comparison, because the DFT calculation was performed without SOC.

tures for monolayer MoS_2 without spin-orbit coupling for both the third-nearest neighbour and the sixth-nearest neighbour case (shown in red), comparing it to the DFT calculation from which our parameters were derived (in blue). The third nearest neighbour model describes the valence manifold reasonably well, particularly at the valence band edge at K. However, some

of the conduction manifold features are not well reproduced at all.

Including the longer-ranged hopping shows marked improvement in the band structure overall. The valence manifold is nearly perfectly reproduced. The mean absolute difference of the top valence band energy between DFT and TB is 0.063 eV in the third-nearest neighbour model, down to 0.009 eV in the sixth-nearest neighbour model.

The conduction manifold is much improved as well. The mean absolute difference of the bottom conduction band energy between DFT and TB is 0.079 eV in the third-nearest neighbour model, and 0.032 eV in the sixth-nearest neighbour model. Particularly the band crossing of the two middle conduction bands near the K-point is completely absent in the third nearest neighbour model, but appears well reproduced in the sixth nearest neighbour case. The shape of the bands that are involved in this crossing does not qualitatively change. This apparent change from crossing to anticrossing behaviour is due to the the bands being at different energies relative to each other when comparing the third- to the sixth-nearest neighbour model. The location of the band crossing of the top two conduction bands near the M-point is located at the correct k-point once the longer ranged hoppings are included.

	direct gap	$v_{\Gamma}-v_K$	c_Q-c_K	m_e^*	m_h^*
TB3, wSOC	1.769	-0.130	0.134	0.93	-0.71
TB6, wSOC	1.727	-0.194	0.045	0.58	-0.58
TB3, noSOC	1.848	-0.061	0.160	0.99	-0.79
TB6, noSOC	1.805	-0.125	0.075	0.61	-0.62
DFT, noSOC	1.729	-0.109	0.111	0.50	-0.60

Table 5.1: Direct band gap (in eV), difference between valence and conduction band extrema (in eV), and electron and hole effective masses (in units of electron mass) in monolayer MoS₂, for third- and sixth-nearest neighbour tight-binding model and DFT calculations, both with and without spin-orbit coupling. The direct gap is located at K in all cases.

5.2 Electron and hole effective masses

For a more quantitative measure of the impact of the longer-ranged hopping on the electronic band structure it is useful to compute the electron and hole effective masses at the K-point.

Furthermore, the effective masses are a useful quantitative measure to compare our tight-binding model to other tight-binding models used in the literature. Lastly, we can estimate exciton binding energies from the effective masses within the Rydberg exciton model, see Sec. 3.5. This allows us to see which of the trends observed in the BSE binding energies may and may not be explained by this simpler model.

As discussed in Sec. 3.5, electron and hole effective masses can be calculated from the band curvature at the relevant conduction band minimum and valence band maximum according to Eq. (3.29). Generically, the effective masses will be direction dependent, in which case we would need to specify the direction in which the effective masses were calculated. In fact, this is the case in Refs. [192, 117, 193]. However, the effective masses of monolayer MoS₂ at the K-point are isotropic[35, 194], and therefore the apparent anisotropy shown in Table 5.2 is likely a result of a lack of convergence. We will be using the isotropy of the effective masses as a convergence criterion.

Computing effective masses is straightforward conceptually. However, it can be numerically tricky.

I will consider two ways of calculating the second derivative of a curve from a discrete set of data.

First, it is possible to directly compute the second derivative, by approximating

$$\frac{\partial^2 f}{\partial x^2} \approx \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{\Delta x^2} . \quad (5.1)$$

It is possible to use significantly more sophisticated finite difference methods for this calculation, but for our purposes this is sufficient.

Secondly, a second (or higher) order polynomial can be fitted to the data (or a small interval of data near the K point), and the second order term can be read off. This is more numerically stable. However, this method has three convergence parameters: the order of the polynomial, the k-point fineness, and the interval to which the data is fitted.

In this case, it turns out that a very dense k-grid needs to be employed in order to get results which fulfil the isotropy requirement. Figures 5.2 and 5.3 show the electron (right) and hole (left) effective masses from third (top) and sixth (bottom) nearest neighbour tight-binding calculations for MoS₂ monolayers as functions of the k-interval which is taken into account for the fitting. The band structure was calculated with up to 50,000 k-points between K and Γ , corresponding to about 50 k-points for the widest interval (whose length is approximately $1.5 \times 10^{-3} \text{\AA}^{-1}$ in MK direction (blue dotted lines), and $0.6 \times 10^{-3} \text{\AA}^{-1}$ in K Γ direction (red dotted lines)). Figure 5.2 uses second order polynomials, Figure 5.3 uses fourth order polynomials. In comparison, the dashed line shows the same effective mass computed with the finite difference method using only 500 k-point between K and Γ . This method is cruder, and does not perfectly align with the polynomial method. However, we do not require effective masses with a higher than $0.01 m_e$ precision, for three reasons. Firstly, the disagreement between literature values is much larger than that (see Table 5.2). Secondly, the difference in effective masses between third and sixth nearest neighbour calculations is larger than that (see Table 5.1). And thirdly, because the estimated Rydberg exciton binding energies do not depend very strongly on the effective masses.

For all these reasons, we have decided to work with the much simpler and quicker finite difference method to approximate effective masses for the remainder of this work.

Table 5.1 quantifies some of the differences between third and sixth nearest neighbour tight-

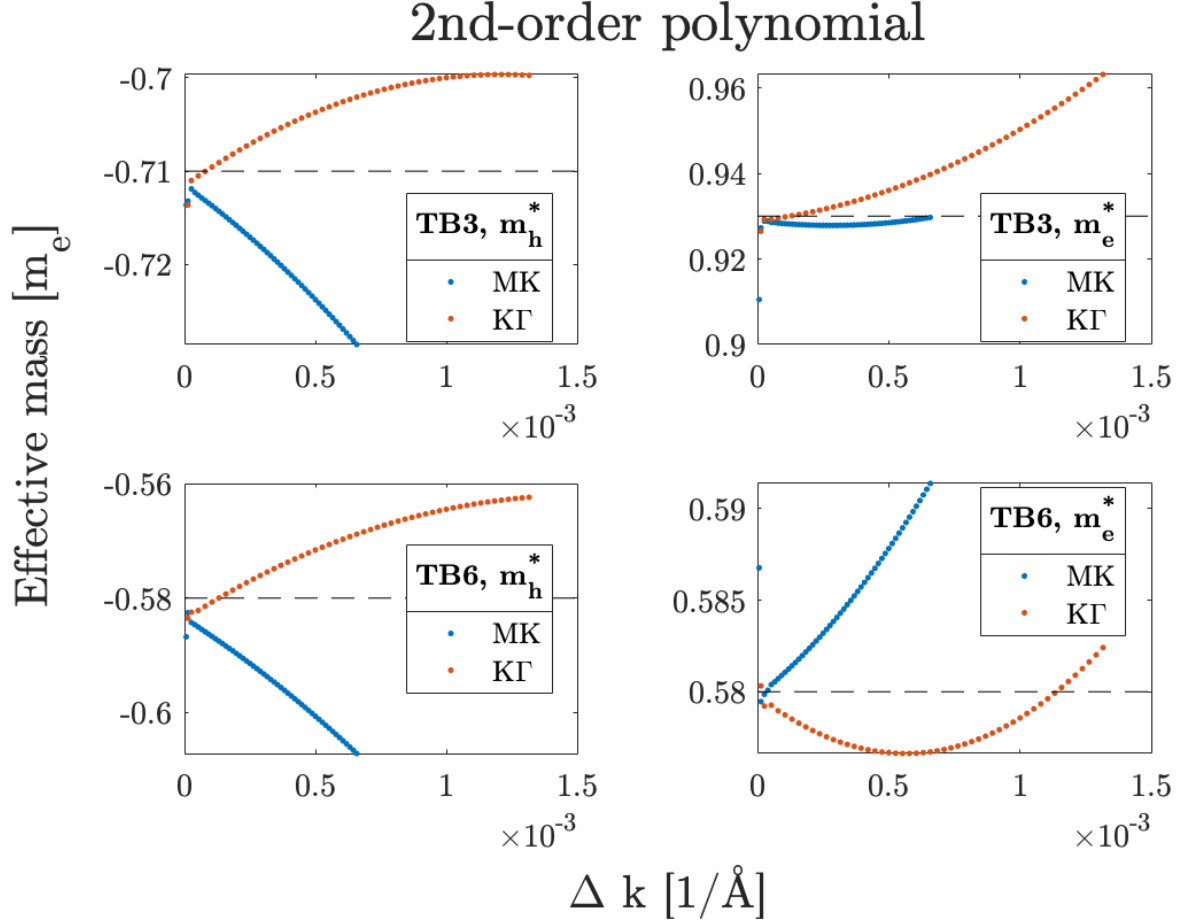


Figure 5.2: Comparison of 2nd-order polynomial and derivative methods for the calculation of electron and hole effective masses in third and sixth nearest neighbour models for monolayer MoS₂ including SOC. The red and blue dotted lines correspond to the polynomially computed effective masses in K Γ and MK direction, respectively, and the black dashed line corresponds to the effective masses calculated using the derivative.

binding model (with and without spin-orbit coupling) and DFT, including effective masses. All tight-binding calculations overestimate the electron effective mass (as is consistent with the too flat conduction band edges), but the sixth-nearest neighbour model shows a big improvement, from a difference of 100% to a difference of only 20%. The hole effective mass difference is reduced from 15% to about 3%. The band gaps without spin-orbit coupling are also large compared to DFT (without SOC) and improved in the sixth-nearest neighbour model.

The agreement between our calculations and previous calculations in literature (as detailed in Table 5.2 is decent, although it has to be noted that there is a large spread of values for both the band gap and the effective masses. Our electron effective masses are on the large side,

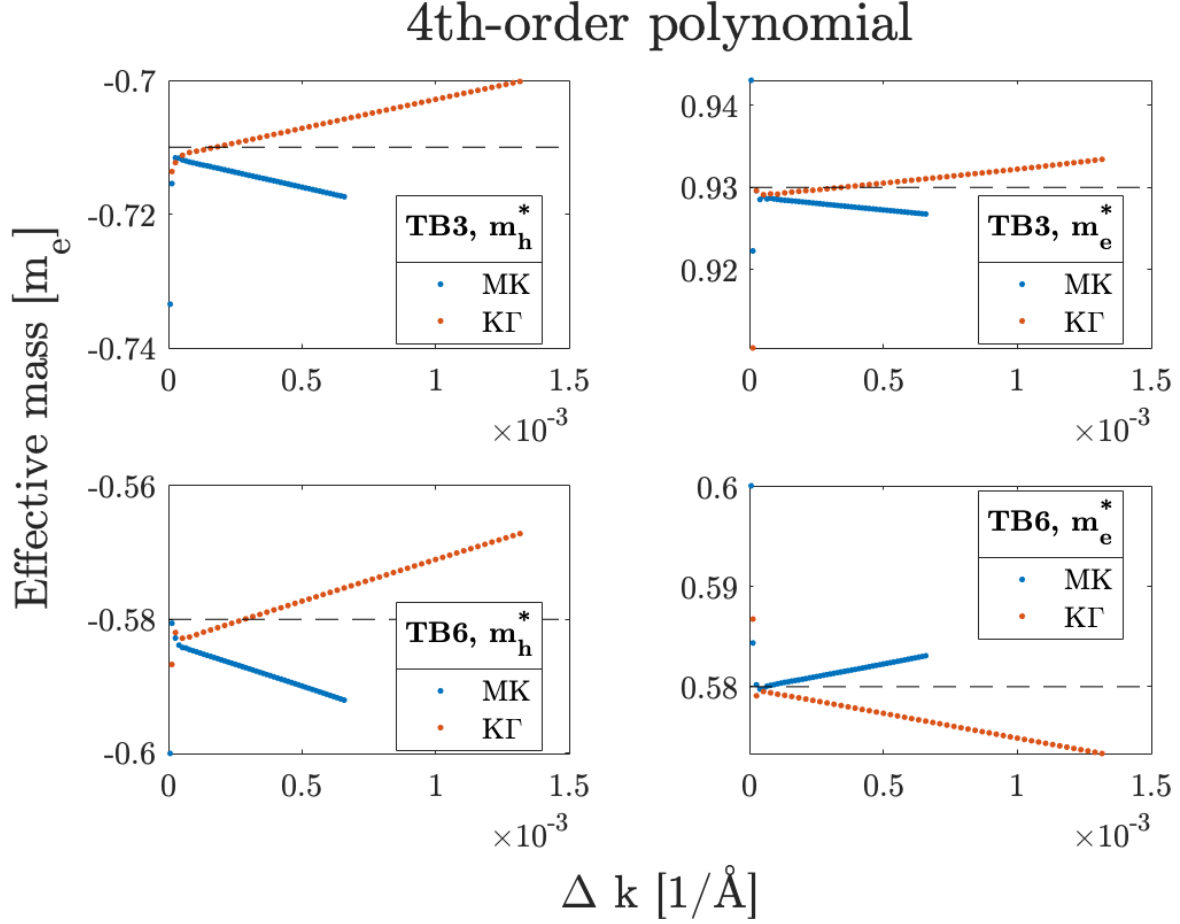


Figure 5.3: Comparison of 4th-order polynomial and derivative methods for the calculation of electron and hole effective masses in third and sixth nearest neighbour models for monolayer MoS₂ including SOC. The red and blue dotted lines correspond to the polynomially computed effective masses in K Γ and MK direction, respectively, and the black dashed line corresponds to the effective masses calculated using the derivative.

slightly larger than even the largest value of $0.54 m_e$ found in Kadantsev et al.[35]. Our hole effective masses seem somewhat closer to literature, which is also more internally consistent (with the exception of Phuc et al.[194]).

Next, we consider the impact of long-ranged hopping on the optical properties of MoS₂ monolayers. To that end, we perform BSE calculations based on the monolayer tight-binding model described in the previous sections, including spin-orbit coupling. We chose to simulate MoS₂ in vacuum, in order to compare our results with ab initio calculations in vacuum.

	gap	$m_e^*(m_e)$	$m_h^*(m_e)$
Fang et al.[4]	1.674	0.467	-0.573
Kadantsev et al.[35]	1.79	0.54	-0.44
Peelaers et al.[192], KT	2.16	0.37	-0.44
KM		0.38	-0.48
Phuc et al.[194]	1.72	0.45	-0.63
Zahid et al.[193], KT	1.805	0.407	-0.485
trans.		0.404	-0.480
Cheiwchanchamnangij et al.[117], KT	2.759	0.342	-0.455
trans.		0.350	-0.428

Table 5.2: Comparison of monolayer electron and hole effective masses at K/K' between the DFT calculation from which our tight-binding parameters were obtained, and the third- and sixth-nearest neighbour tight-binding models without spin-orbit coupling, as well as our tight-binding models with spin-orbit coupling, and some literature values. Values in both Refs. [193] and [117] are calculated in longitudinal direction (i.e. in KT direction) and in transverse direction (orthogonal to KT).

5.3 Convergence of monolayer optical properties with k-grid fineness and cutoff energy

In this section, I will discuss the convergence of both BSE eigenvalues and optical spectra with the cutoff energy described in Sec. 3.10.2 and k-grid, which are the two quantities which determine the size of the BSE matrix.

Figures 5.4 and 5.5 show the convergence of the first ten exciton eigenvalues with cutoff energy and k-grid, respectively. Due to the degeneracy between K and K', all of the eigenvalues are doubly degenerate, therefore only five curves appear in the figures. This degeneracy is a very useful test—it breaks very easily if there are errors in the code.

It is useful to remember that the band gaps of the third and sixth nearest neighbour models are not quite the same (1.727 eV vs. 1.769 eV), so a cutoff energy of 3.0 eV does not imply that the same number of transitions are included. The difference of these two gap energies is smaller than the cutoff difference between “adjacent” calculations in the convergence calculations, so it is not important here, but in general, it makes sense to think of the cutoff energy as being some amount of energy above the band gap. For instance, we find here that the lowest

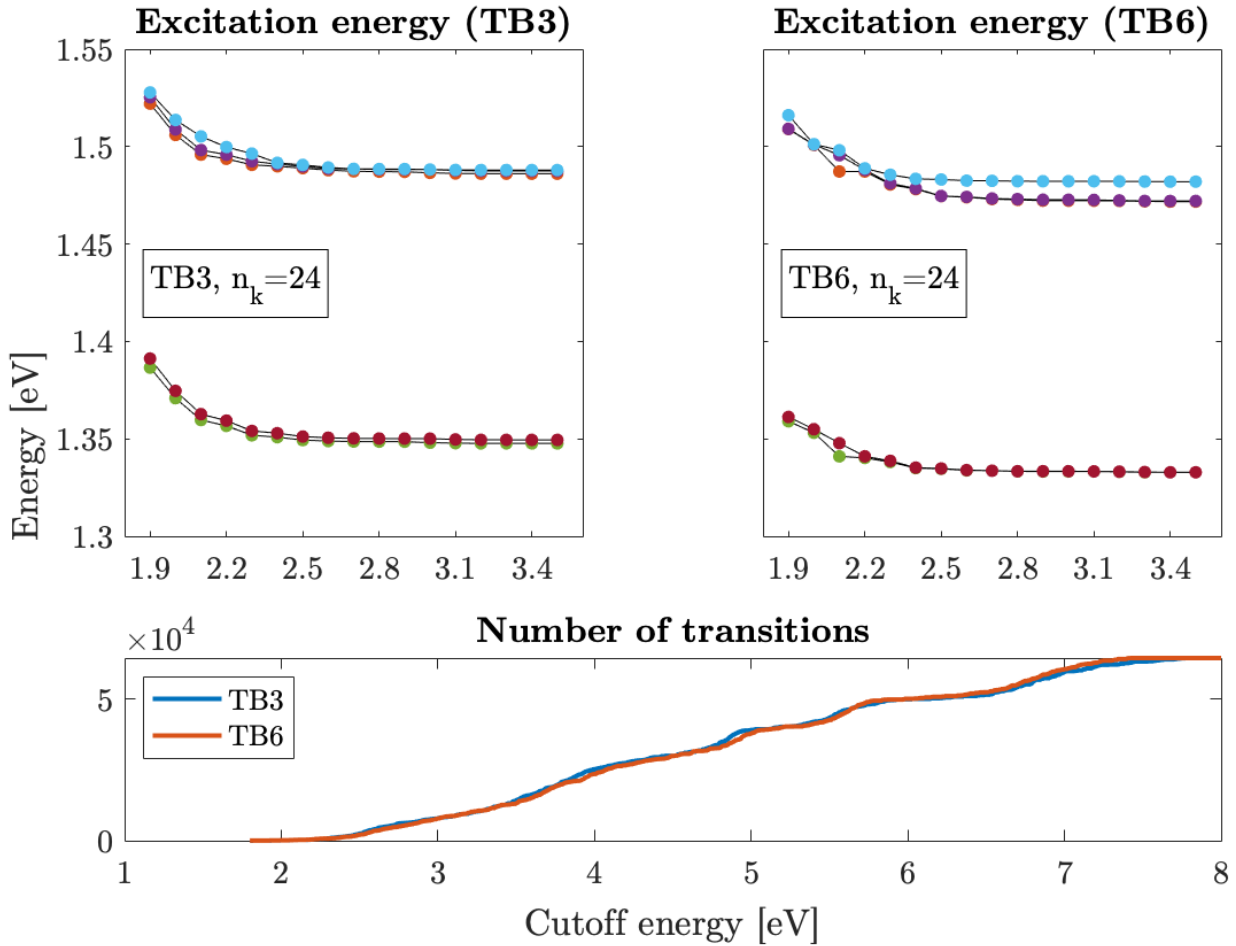


Figure 5.4: Convergence of third- and sixth-nearest neighbour exciton excitation energies in MoS₂ monolayers with cutoff energy, for a 24×24 k -grid. The bottom panel shows the number of transitions $|v\mathbf{k}\rangle \rightarrow |c\mathbf{k}\rangle$ included for a given cutoff energy, showing no artificial temporary levelling-off in the area of convergence, between 2.5 and 3.5 eV.

excitation energy appears well converged (up to 1 meV) at a cutoff of 2.5 eV for the sixth nearest neighbour model. This is equivalent to 0.7 eV above the band gap. We also find that at 0.3 eV above the band gap, the energy is converged up to 10 meV. This is slightly faster than for the third nearest neighbour case, in which 0.5 eV above the band gap are necessary to get convergence up to 10 meV, and 0.8 eV to get convergence up to 1 meV.

It is a priori possible that the excitations energies could appear converged, but that, in reality, no (or only few) additional transitions were included with increasing cutoff energy between the area of apparent convergence between 2.2 and 3.0 eV. The bottom panel of Fig. 5.4 shows the number of transitions for a given cutoff energy for both third and sixth nearest neighbour models (with a 24×24 k -grid). This shows that there is no flattening of the number of optical

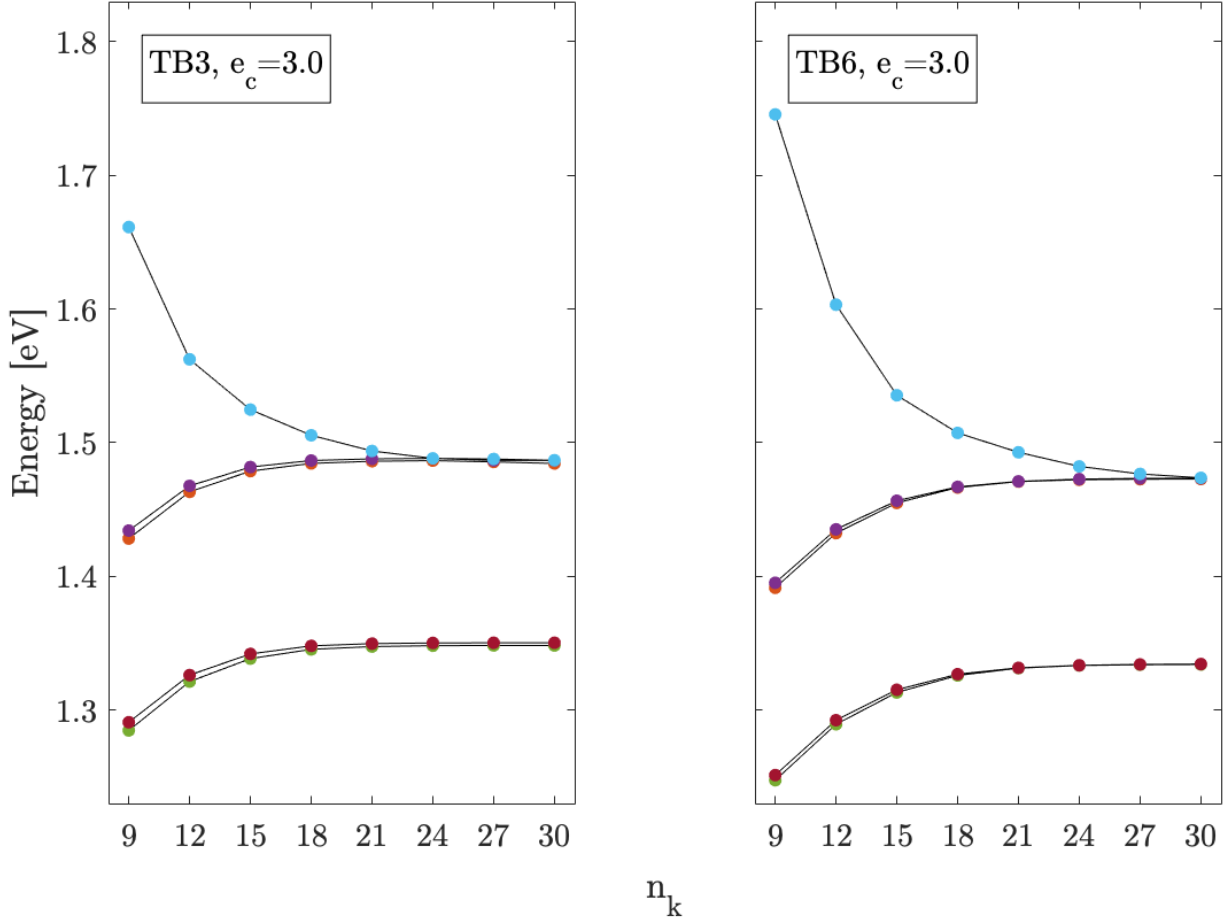


Figure 5.5: Convergence of third- and sixth-nearest neighbour exciton excitation energies in MoS_2 monolayers with k-grid fineness, for a cutoff energy of 3.0 eV.

transitions in the energy regime 2.2-3.0 eV. This supports the hypothesis that the excitation energies are truly converged.

For the k-grid density, we find that for a 3.0 eV cutoff, for the third-nearest neighbour model, the lowest excitation energies appear converged up to 1 meV for a 21×21 k-grid, and converged up to 10 meV for a 15×15 k-grid. For the sixth nearest neighbour model, the lowest excitation energies appear converged up to 1 meV for a 24×24 k-grid, and converged up to 10 meV for a 18×18 k-grid.

Figures 5.6 and 5.7 show the convergence of the optical spectra with cutoff energy and k-grid density, respectively. The low-energy spectrum converges more quickly than the high-energy spectrum, not just with cutoff energy (as is to be expected) but also with k-grid density. This

is likely because, as we will see in Sec. 6.6, the low-energy excitons are well localized at K and K'. High-energy excitons, on the other hand, tend to be more spread out in k -space, so their precise description requires a higher resolution in reciprocal space.

The low-energy spectrum, below about 1.5 eV in excitation energy, appears reasonably well converged for the same cutoff energy and k -grid fineness as the bare exciton binding energies, at 3.0 eV and a 24×24 k -grid.

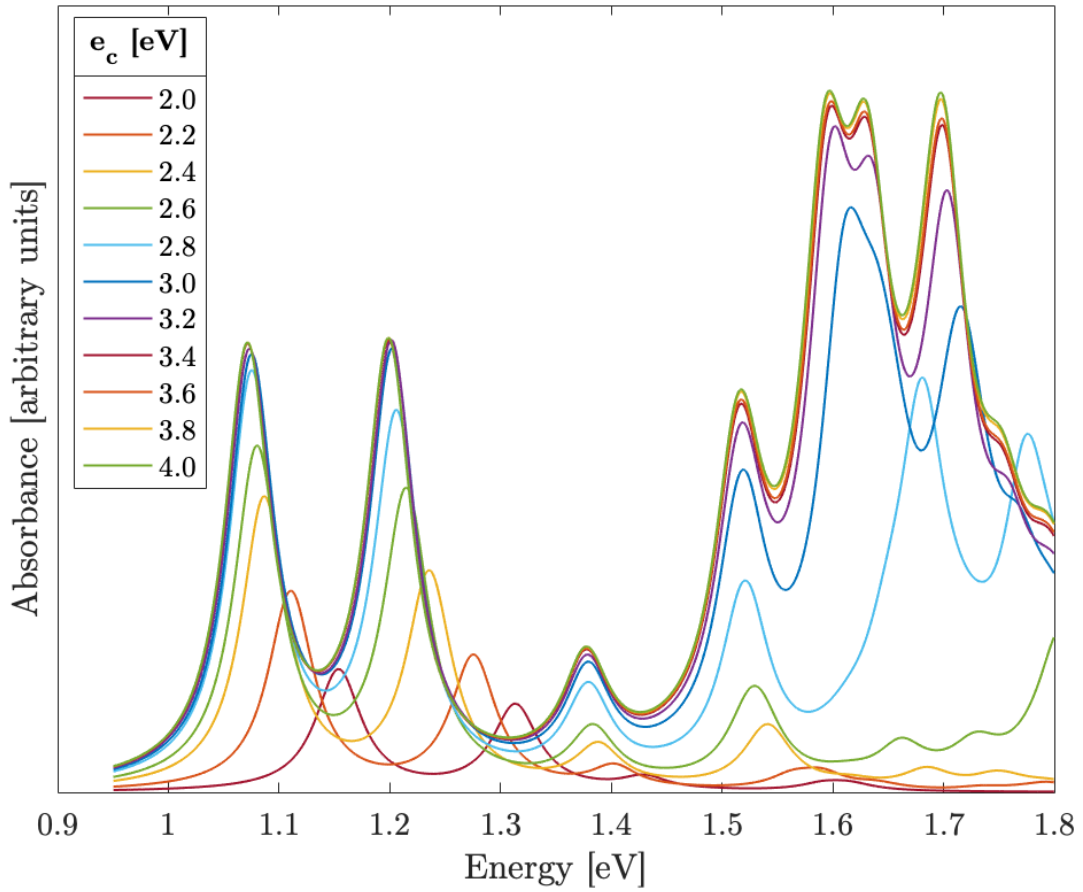


Figure 5.6: Convergence of sixth-nearest neighbour optical spectra of MoS₂ monolayers with cutoff energy, for a 24×24 k -grid.

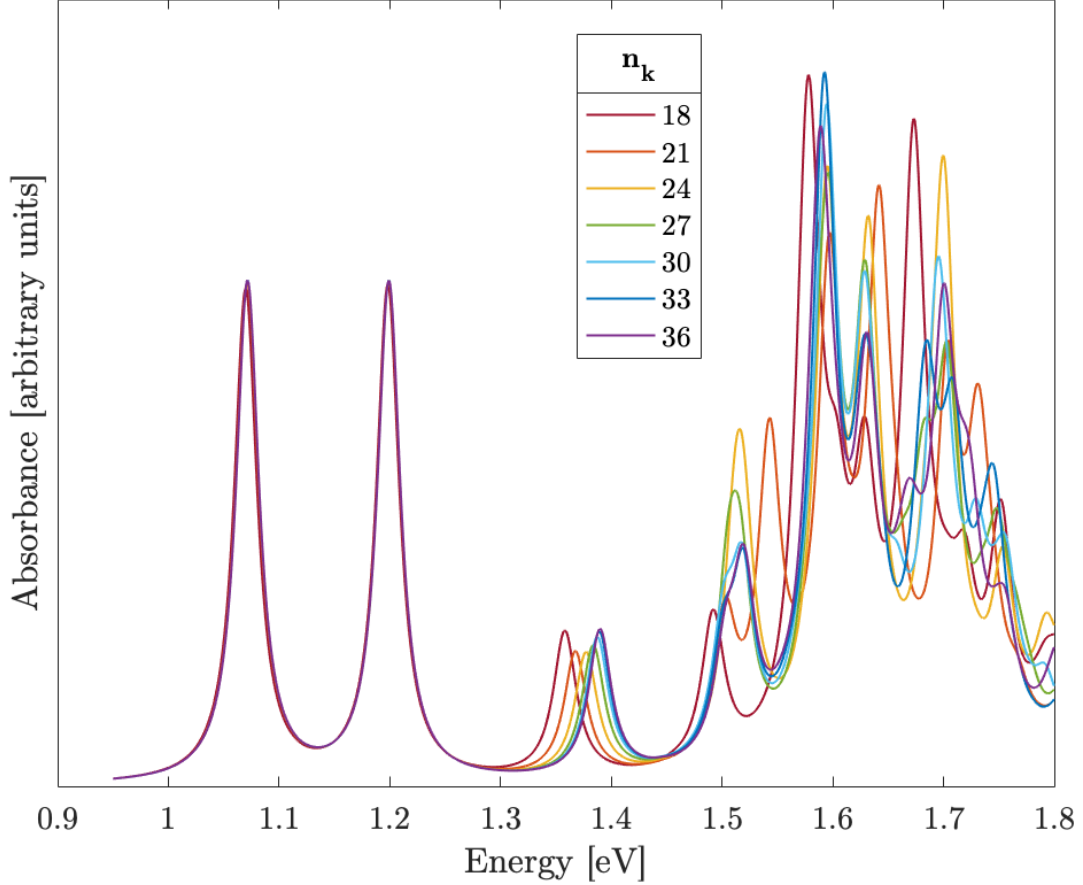


Figure 5.7: Convergence of sixth-nearest neighbour optical spectra of MoS_2 monolayers with k-grid fineness, for a cutoff of 3.5 eV.

5.4 Impact of longer-ranged hoppings on monolayer optical properties

Finally, we calculate the optical spectra for the MoS_2 monolayer in both the third and sixth-nearest neighbour models including SOC, and compare them to spectra calculated from ab initio GW-BSE calculations performed by Qiu et al.[6]. The results are shown in Fig. 5.8.

Since the GW bandgap is significantly larger than the DFT one, we implement a scissor shift in order to compare the optical spectra, shifting the conduction band energies rigidly so that the gaps of the two calculations align, while leaving the valence band energies and tight-binding wavefunctions unchanged. The BSE, Eq. (3.57), consists of a diagonal term which

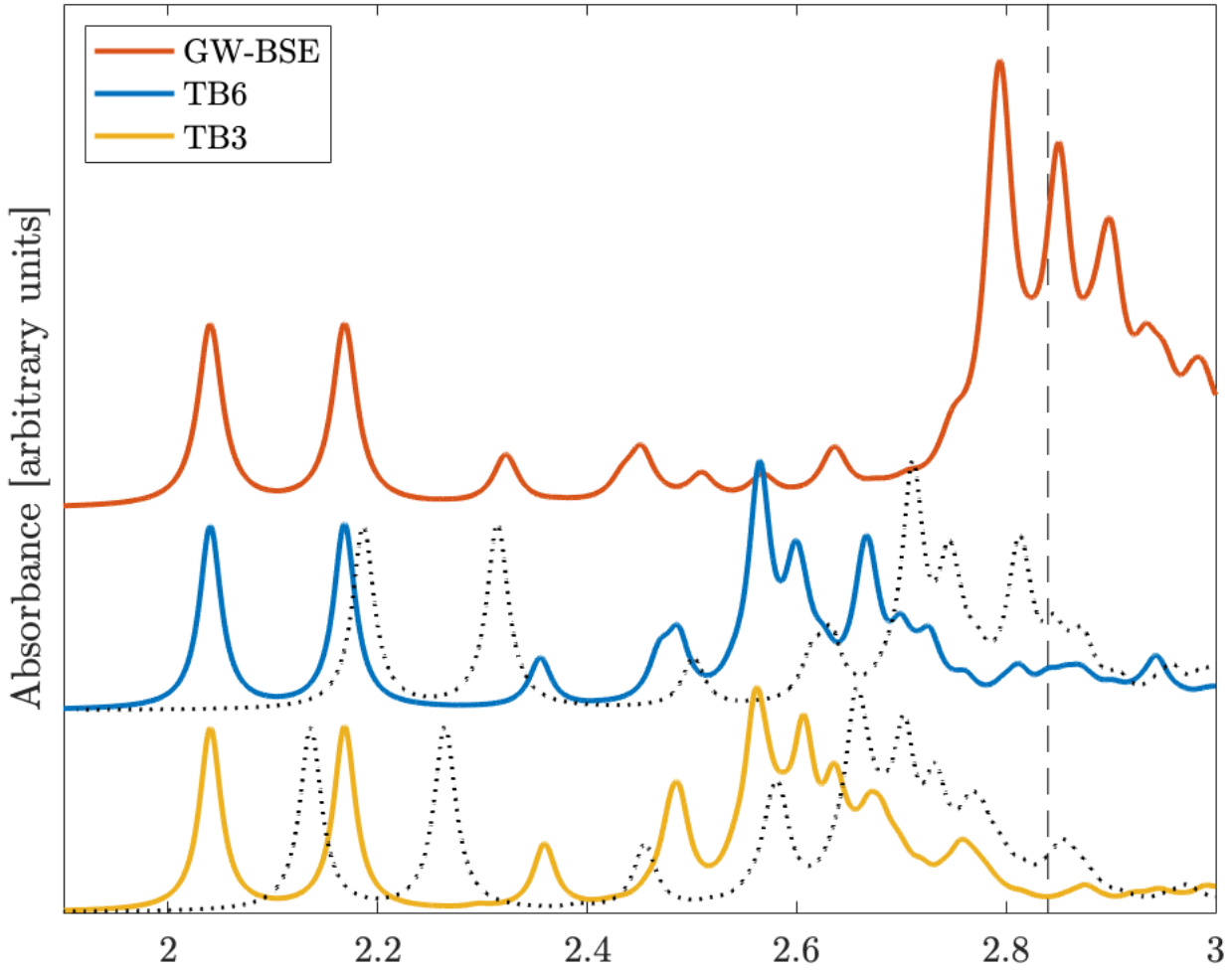


Figure 5.8: Absorption of MoS₂ monolayers in vacuum for the BSE calculation in the tight-binding basis compared to an ab initio spectrum from Qiu et al[6] (red line). The yellow line shows the third-nearest neighbour model, the blue line the sixth-nearest neighbour model. We use a 30x30 k-grid for our calculations, and a cutoff energy of 3.2 eV. The dotted grey lines represent the spectrum when the band gaps are aligned to the ab initio band gap (indicated by the dashed grey line), whereas the yellow and blue lines are shifted so that the tight-binding A peaks coincide with the ab initio result.

depends on the difference between conduction and valence band energies, and an off-diagonal interaction term which does not depend on the tight-binding energies (since we use static—i.e., energy-independent—electronic screening). Implementing a scissor shift is therefore equivalent to adding the shift energy times a unit matrix to the Bethe–Salpeter Hamiltonian, which leaves the exciton wavefunctions unchanged and shifts the excitation energies by the shift energy. This is to say, implementing a scissor shift requires no change in the code. Instead, it is sufficient to shift the optical spectrum by the shift energy (chosen to align the band gaps)

	E^{exc} (eV)	E^{bind} (eV)	E^{Ryd} (eV)
TB3	1.065	0.704	0.96
TB6	1.069	0.658	0.92

Table 5.3: Excitation and binding energies of lowest-energy exciton states and binding energy of corresponding Rydberg exciton for third- and sixth-nearest neighbour based calculations of MoS₂ monolayers in vacuum, using a 30×30 k-grid and a cutoff energy of 3.0 eV.

during postprocessing. The resulting spectrum is drawn as grey dotted lines in Fig. 5.8. As an alternative means of comparison, we have also plotted the optical spectrum with the first peaks aligned as solid lines, so the relative alignment of the subsequent peaks is more visually evident.

We find good agreement in both third and sixth-nearest neighbour model (denoted TB3 and TB6) for the first two peaks, both in terms of relative height and energy separation. There is improvement in the description of the next two peaks, both in terms of position and height.

The exciton binding energies, on the other hand, actually seem to get worse when compared to the ab initio results when long-ranged hoppings are included, as indicated by the position of the grey dotted peaks in Fig. 5.8. We believe this is due to our choice of DFT calculation, since the reduction of binding energy is also present in the simple hydrogenic model, see Table 5.3. That is, our DFT calculations do not agree sufficiently with the GW spectra, and the third-nearest neighbour calculations coincidentally result in exciton binding energies closer to the ab initio results.

Specifically, we saw in Sec. 5.2 that the effective masses in the sixth nearest neighbour model were closer to results from literature than the third nearest neighbour model, see Tabs. 5.1 and 5.2. The Rydberg energy, as given in Tab. 5.3, correspondingly decreases by 40 meV with the addition of the longer-ranged hoppings. The BSE binding energies change by almost the same amount, in the same direction (from 0.704 eV to 0.658 eV). Therefore, given our DFT calculation, the BSE calculation also likely showed an improvement in the description of binding energies and optical spectra, even though the comparison to the GW spectrum appears to be unfavourable.

5.5 Conclusion

We find overall that the longer-ranged hoppings have a significant impact on the monolayer band structures and a modest impact on the optical properties. Unfortunately, the impact on the optical spectra is mostly apparent in the high-energy parts. This can at least heuristically be understood by identifying hopping with kinetic energy. Longer-ranged hoppings require more energy, and therefore including longer-ranged hoppings is a high-energy correction. Comparing Figs. 5.7 and 5.8, the differences of the optical spectra of third- and sixth-nearest neighbour model are small in energy regimes that are well converged with k-point density.

Furthermore, we find that we can reproduce several features of the low-energy optical spectrum of monolayer MoS₂ when compared to ab initio calculations, which is very encouraging, particularly considering how much more computationally expensive the ab initio calculation is. In particular, we can reproduce the characteristic A and B peaks observed in both prior theoretical work (e.g. Ref. [124]) and experiment (e.g. Ref. [50]), with the same peak height ratio and energy separation as the GW-BSE spectrum calculated by Qiu et al.[6].

Chapter 6

Impact of long-ranged hoppings on the optoelectronic properties of untwisted MoS₂ homobilayers

In this chapter, I will explain the generalization of the monolayer tight-binding model described in Ch. 4 to TMD bilayers, and calculate electronic and optical spectra for the high-symmetry stacking configurations of bilayer MoS₂.

I will discuss the high-symmetry stacking geometries in Sec. 6.1. In Sec. 6.2, I will explain how interlayer hoppings are modelled in the tight-binding model. In Sec. 6.3, I will compute the relaxed atomic structures of the high-symmetry stackings using DFT, and motivate why this is an important step. Finally, in Secs. 6.4, 6.5, and 6.6, I will show the impact of longer-ranged hoppings on electronic bandstructures, discuss the impact of the stacking geometry on optical spectra, and analyze the layer character of different excitons in different stackings, which account for many of the stacking dependent differences of the optical spectra.

6.1 High-symmetry bilayer stackings of semiconducting transition metal dichalcogenides

There are infinitely many distinct ways in which two rigid monolayer crystals can be stacked on top of each other to form a bilayer. We can broadly separate the resulting bilayers into two categories, according to their periodicity: systems with the same periodicity as the monolayer, and moiré systems with lattice vectors that are an integer multiple of the lattice vectors of the monolayer.

In this chapter, we consider bilayers with minimal unit cells composed of one unit cell from the top layer and one unit cell from the bottom layer—in these systems, the full bilayer inherits the translational symmetry from the monolayer. The other option, which we will explore in Chapter 7, is systems in which the periodicity of the bilayer is a subset of the periodicity of the monolayers, i.e., the unit cell contains a top layer supercell and a bottom layer supercell.

The conceptually simplest bilayer stacking is AA stacking, consisting of two monolayers which are directly stacked on top of each other, with metal atoms of the top layer directly on top of metal atoms of the bottom layer, and chalcogen atom pairs of the top layer directly on top of chalcogen atom pairs of the bottom layer. This is illustrated in the top left plot in Fig. 6.1. From this starting point, other stackings can be created by rigidly shifting the layers relative to each other.

The resulting systems have the same unit cell size as AA stacked systems, and we calculate the DFT band structures for incrementally shifted systems in order to obtain Slater–Koster parameters for the interlayer hopping, cf. Sec. 6.2.

For some shift vectors, this results in another high-symmetry stacking which retains $\mathcal{R}_3$ symmetry (which is broken for most arbitrary shifts). Depending on whether a top layer metal atom is now on top of a bottom layer chalcogen atom pair, or whether a top layer chalcogen

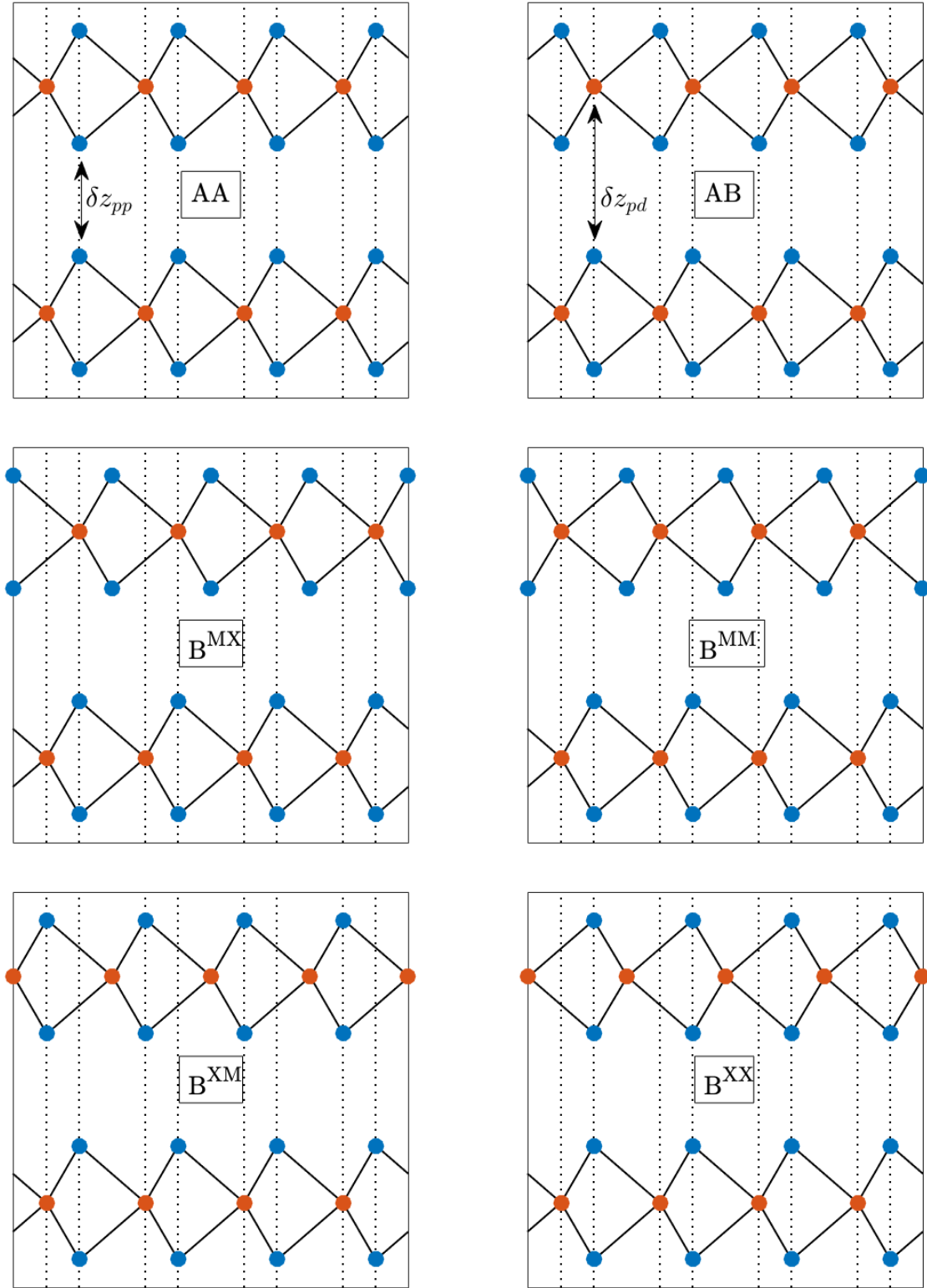


Figure 6.1: Illustration of the basic stacking configurations of TMD bilayers, and the notation used here to describe them, following Ref. [195]. Metal atoms are drawn in red, chalcogen atoms in blue.

atom pair is on top of a bottom layer metal atom, this is labelled here as B^{MX} or B^{XM} stacking, following Ref. [195], and illustrated in the middle and bottom lefthand figures in Fig. 6.1. (B stands for Bernal stacking, which is what this geometry is called for graphene[196].)

Note that TMD monolayers that we consider here do not have inversion symmetry. This is relevant in two ways. Firstly, the B^{MX} and B^{XM} stackings described above are related to each other by inversion symmetry, which means they have the same band structures and optical spectra. We will present results for both stackings, to show that our model correctly produces this equivalence.

Secondly, another class of high-symmetry stackings, not equivalent to the previously presented stackings, can be obtained by flipping one of the composite monolayers (that is, rotate around e.g. the x -axis by 180°) but not the other, then stacking them. Again, it is possible to obtain several high symmetry stackings, illustrated on the righthand side of Fig. 6.1.

The stacking in which a top layer metal atom is located on top of a bottom layer chalcogen atom pair, and a top layer chalcogen atom pair on top of a bottom layer metal atom is labelled as AB-stacking (shown top right). The stacking in which metal atoms are located directly on top of each other is labelled B^{MM} , and the stacking in which chalcogen atom pairs are located directly on top of each other is labelled B^{XX} .

It is somewhat combinatorically intuitive that there should be six high-symmetry stackings. Considering a monolayer unit cell as consisting of a metal site, a chalcogen site, and an empty site, there are $3!=6$ ways of stacking one of the three top layer sites directly on top of one of the three bottom layer sites.

Finally, note that, while the terminology “AA stacking” for two monolayers stacked directly on top of each other is widely agreed upon, the stacking here called AB is also often called AA’ stacking (e.g. Ref. [197]), while AB stacking is sometimes used to refer to what we call B^{MX} ,

e.g. Ref. [197]. Some papers use different notations altogether, e.g. Ref. [198].

6.2 Interlayer interaction in the tight-binding model

In order to generalize the monolayer tight-binding model described in Chapter 4 to bilayer systems, we need to include interlayer hopping (by using Slater–Koster parameters, in this case), and we need to take into account atomic relaxation. This mostly affects the vertical position of the atoms, the horizontal position remains relatively unchanged[5] (at least for the case of homobilayers). Therefore, we will keep the monolayer model as described above to describe intralayer hoppings, with the assumption of constant atomic distances, even in the relaxed case.

For the interlayer hoppings, we take into account only selected pairs of orbitals. Firstly, we include hoppings between p -orbitals on adjacent (that is, inner) chalcogen layers. Secondly, we include hoppings between p_z -orbitals on inner chalcogen layers and d_{z^2} -orbitals located on the metal atoms on the opposite layer. These two types of orbitals are oriented orthogonally to the layers and therefore have some overlap despite not being on immediately adjacent layers. This was confirmed in Vitale et al.[5] to be the second-most important interlayer hopping after the $p-p$ -hoppings. This was done by including other types of interlayer hopping and testing their impact on the electronic bandstructure.

Both types of hoppings are expressed in terms of Slater–Koster parameters, as described in Chapter 3.3. An approximate functional form of their distance-dependence is given in Eqs. (6.2) and (6.4). Additionally, the fitting parameters are themselves dependent on the vertical layer distance to incorporate the effect of atomic relaxation.

Fang et al.[1] computed the horizontal distance dependence by fitting to ab initio calculations of TMD bilayers that were shifted relative to each other (keeping the size of the unit cell, and therefore the computational effort, the same as in the AA-stacked case) and extracting the hopping parameters from the results. Vitale et al.[5] then repeated the same procedure, varying

also the vertical distance between the monolayers in order to find the vertical distance dependence, computing different fitting parameters for a discrete number of interlayer distances. For any other vertical distances, the resulting Slater–Koster parameters are linearly interpolated.

The general Slater–Koster form for $p - p$ -hoppings is given by[1]

$$t_{p'_i, p_j}(\mathbf{r}) = (V_{pp\sigma}(r) - V_{pp\pi}(r)) \frac{r_i r_j}{r^2} + V_{pp\pi}(r) \delta_{ij} , \quad (6.1)$$

where $\mathbf{r} = (r_x, r_y, r_z)$ and $r = |\mathbf{r}|$. The Slater–Koster parameters can then be approximated by using a fitting function to fit the Wannier parameters[1]

$$V_{ppb} = \nu_b \exp \left(- \left(\frac{r}{R_b} \right)^{\eta_b} \right) , \quad (6.2)$$

with $b \in \{\sigma, \pi\}$. The interlayer hopping in this system does not strongly depend on the absolute location nor the absolute or relative orientations of the composite orbitals. Therefore, the fitting function neglects these contributions and only depends on the relative scalar distance between the orbitals.

The Slater–Koster form of the $p_x - d_{x^2}$ -hoppings is given by[5]

$$\begin{aligned} t_{p'_x, d_{x^2}}(\mathbf{r}) = & n \left(n^2 - \frac{1}{2} (l^2 + m^2) \right) V_{pd\sigma}(\mathbf{r}) \\ & + \sqrt{3} n (l^2 + m^2) V_{pd\pi}(\mathbf{r}) , \end{aligned} \quad (6.3)$$

where the direction cosines are given by $l = \frac{r_x}{r}$, $m = \frac{r_y}{r}$, $n = \frac{r_z}{r}$, and the parameters can be approximated by[5]

$$V_{pdb}(\mathbf{r}) = V_b \left(\frac{r}{d} \right)^{\alpha_b} \cos \left(\beta_b \frac{r}{d} + \gamma_b \right) . \quad (6.4)$$

Here, $d = 3.5 \text{ \AA}$ is the average interlayer distance. The material dependence of the actual average interlayer distance is included in the fitting parameters.

The fitting parameters are given in the supplementary material of Vitale et al.[5], and reproduced here for the case of MoS₂-MoS₂ bilayers in Tables A.2 and A.3. Different interlayer distances result in different sets of fitting parameters, and parameter sets are given for the average distance between the relevant orbitals $\delta z \pm n \cdot 0.1 \text{Å}$, $n \in \{-4 \dots 4\}$. The average distance, as well as the necessary span, have been calculated from twisted bilayer atomic relaxations. cf. Sec. 7.2.

6.3 DFT calculations of relaxed structures of high-symmetry stackings

I start by determining the relaxed atomic structures of the different high-symmetry stackings. Since the unit cell sizes are still very modest, I do this using DFT calculations with Quantum Espresso[186], as detailed in Sec. 3.10.1. The basic idea of these calculations is to minimize the total energy with respect to atomic structure. A potential pitfall of this type of calculation is to start with a structure sufficiently far away from the equilibrium structure that the resulting relaxed structure is at only a local total energy minimum instead of the global minimum. To avoid this, I try and start with a sensible guess (as detailed in the right-most column of Tab. 6.1), and compare my results to previous theoretical results obtained by Liu et al.[55].

Table 6.1 shows the z-components of the atomic positions in the unit cell for the different high-symmetry stackings, as well as the distance between the Mo layers (i.e. the difference between the z-components of the Mo atoms in different layers, as opposed to the total distance between Mo atoms).

Broadly, the stackings fall into two groups: AA and B^{xx} stacking, with an Mo-Mo distance of $\approx 6.8 \text{Å}$, and everything else, with an Mo-Mo distance of $6.2 - 6.3 \text{Å}$ in my calculations, and $6.1 - 6.2 \text{Å}$ in Liu et al.[55]. For this second group, my calculations result in slightly higher

	AA	AB	B^{MM}	B^{MX}	B^{XM}	B^{XX}	initial guess
S	1.0422	1.3194	1.2896	1.3291	1.3290	1.0551	1.4564
Mo	2.6040	2.8822	2.8526	2.8912	2.8916	2.6168	3.0078
S	4.1641	4.4430	4.4126	4.4512	4.4511	4.1767	4.5568
S	7.8641	7.5851	7.6155	7.5770	7.5768	7.8516	7.4695
Mo	9.4240	9.1458	9.1755	9.1365	9.1367	9.4111	9.0210
S	10.9856	10.7084	10.7382	10.6989	10.6987	10.9726	10.5725
Δz_{MM} (DFT)	6.8200	6.2636	6.3229	6.2453	6.2451	6.7943	6.0132
Δz_{MM} (Lit. [55])	6.8	6.1	6.2	6.1	6.1	6.8	

Table 6.1: Cartesian z-coordinate of atoms in relaxed unit cell of different stackings, all given in Å. Details of the relaxation are described in Sec. 6.3, the stackings are schematically illustrated in Fig. 6.1.

interlayer separation compared to Liu et al. However, the general trends are similar, with AB and $\text{B}^{\text{MX}}/\text{B}^{\text{XM}}$ having the same interlayer separation within $\mathcal{O}(0.01\text{Å})$, and B^{MM} having a slightly higher interlayer separation.

The difference in interlayer separation between the different types of stacking can be understood by looking at the stacking geometries as illustrated in Fig. 6.1. In the two systems in which the chalcogen pairs of the two layers are located directly on top of each other, the interlayer separation is significantly larger than in all the other stackings due to steric repulsion[55]. It turns out that the parameter range for the interlayer hoppings presented by Vitale et al.[5] has to be extended to include these large separations, since the twisted systems treated in that work (and in Chapter 7) all have interlayer separations more similar to e.g. AB stacking. The extended parameter tables for MoS_2 are presented in Appendix A.

6.4 Impact of long-ranged hoppings on electronic band structure of untwisted MoS_2 homobilayers

Finally, I compute bandstructures for all six high-symmetry stackings with the atomic positions obtained in the previous sections. Similar to the monolayer case, I calculate DFT bandstructures, and TB bandstructures with third- and sixth-nearest neighbours with and without spin-orbit coupling. Table 6.2 shows direct and indirect gaps, differences between the first two

conduction and valence band extrema, and electron and hole effective masses of all six stackings.

Figures 6.2-6.13 show the comparison of the DFT and TB calculations without

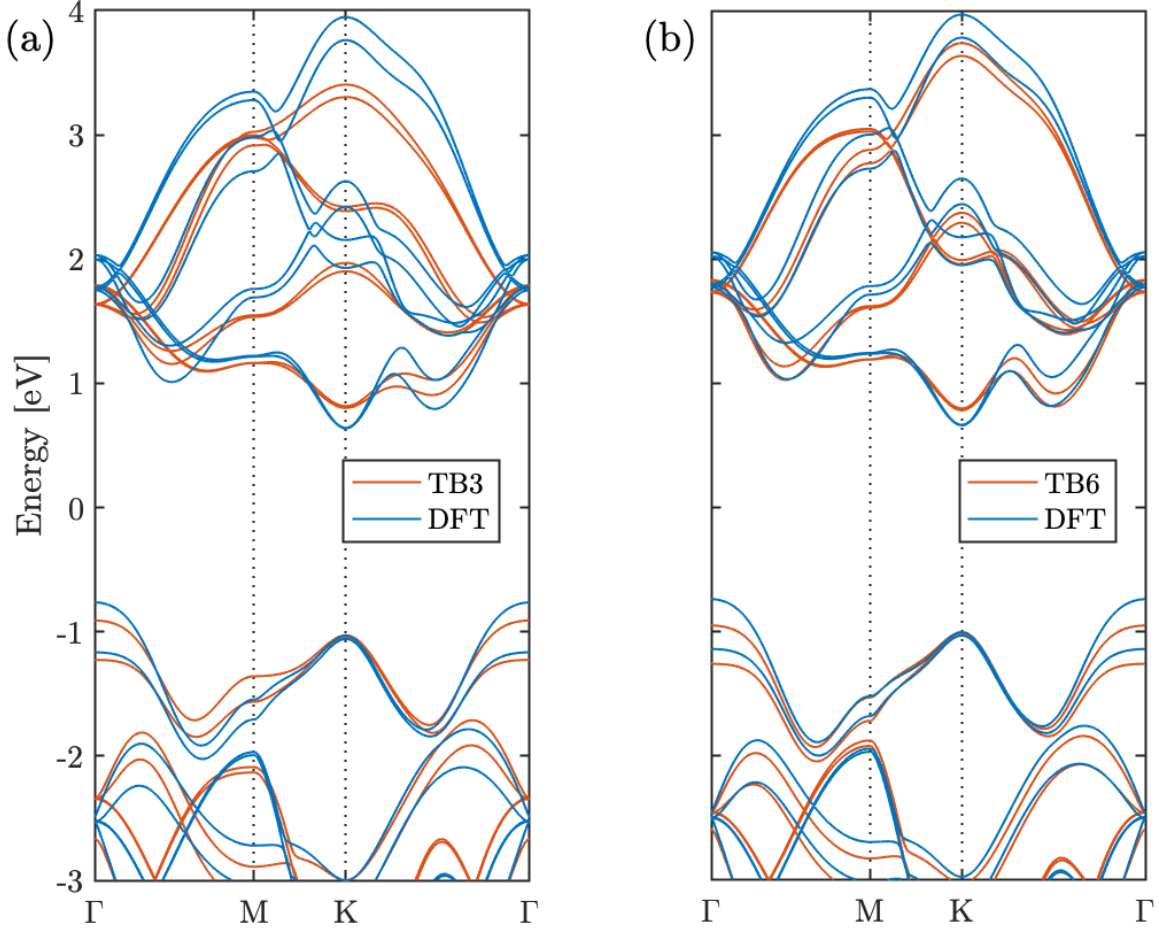


Figure 6.2: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for AA stacked MoS_2 homobilayers.

SOC. Figure 6.2 shows the bandstructures along the $\Gamma\text{MK}\Gamma$ Brillouin zone path, and Figure 6.3 shows a more detailed view of the band edges near K.

Let us first consider the direct and indirect bandgaps. Liu et al.[55] find that the dependence of both direct and indirect gaps on stacking configuration is due to the difference in interlayer separation, with a much stronger variation in the indirect gap. In general, they find the larger the interlayer separation, the larger the bandgap. The bottom panel of Fig. 6.14 shows a similar trend for the indirect bandgap. The tight-binding calculations overestimate the indirect bandgap by ~ 250 meV. The difference between the different tight-binding calculations

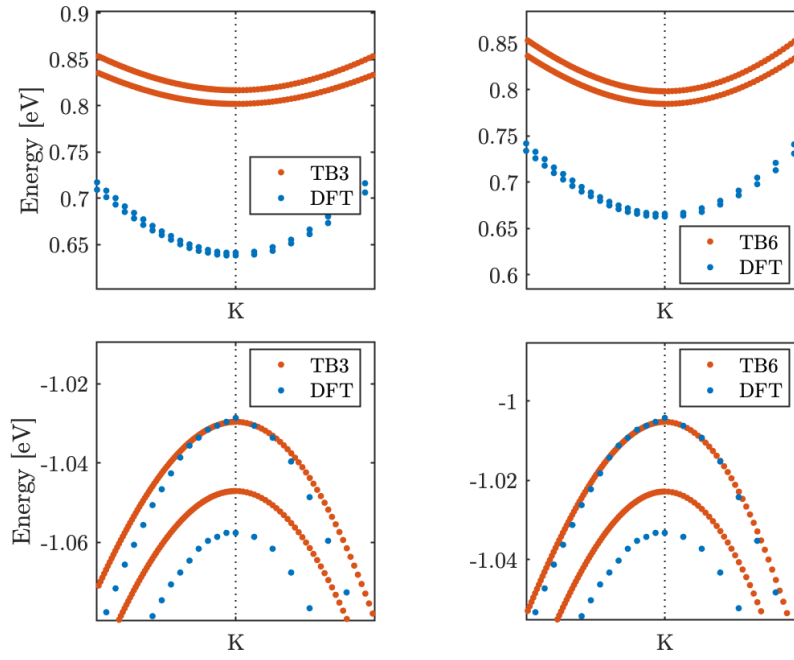


Figure 6.3: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for AA stacked MoS_2 homobilayers.

are, in comparison, very small. This can be understood by considering two facts. Firstly, monolayer MoS_2 is a direct bandgap semiconductor, and multilayer MoS_2 has an indirect bandgap. This means that the indirect bandgap is caused by the interlayer hoppings and is therefore not strongly influenced by an improvement in the intralayer hoppings. Secondly, the indirect gap is located at the valence band maximum at Γ (which is spin-degenerate) and the conduction band minimum at K, which is only weakly spin-split. Therefore spin-orbit coupling only weakly affects the indirect gap.

The direct bandgap has a weaker dependence on the interlayer distance, as shown in the top panel of Fig. 6.14. It also has a stronger dependence on the range of intralayer hoppings. Both of these facts can again be understood from the fact that the gap at K is inherited from the monolayer system—as can be seen from the effective masses, which tend to be similar to the monolayer case. Both monolayer and bilayer calculations result in a direct bandgap about 40 meV smaller in the sixth-nearest neighbour calculations compared to the third-nearest neighbour calculations.

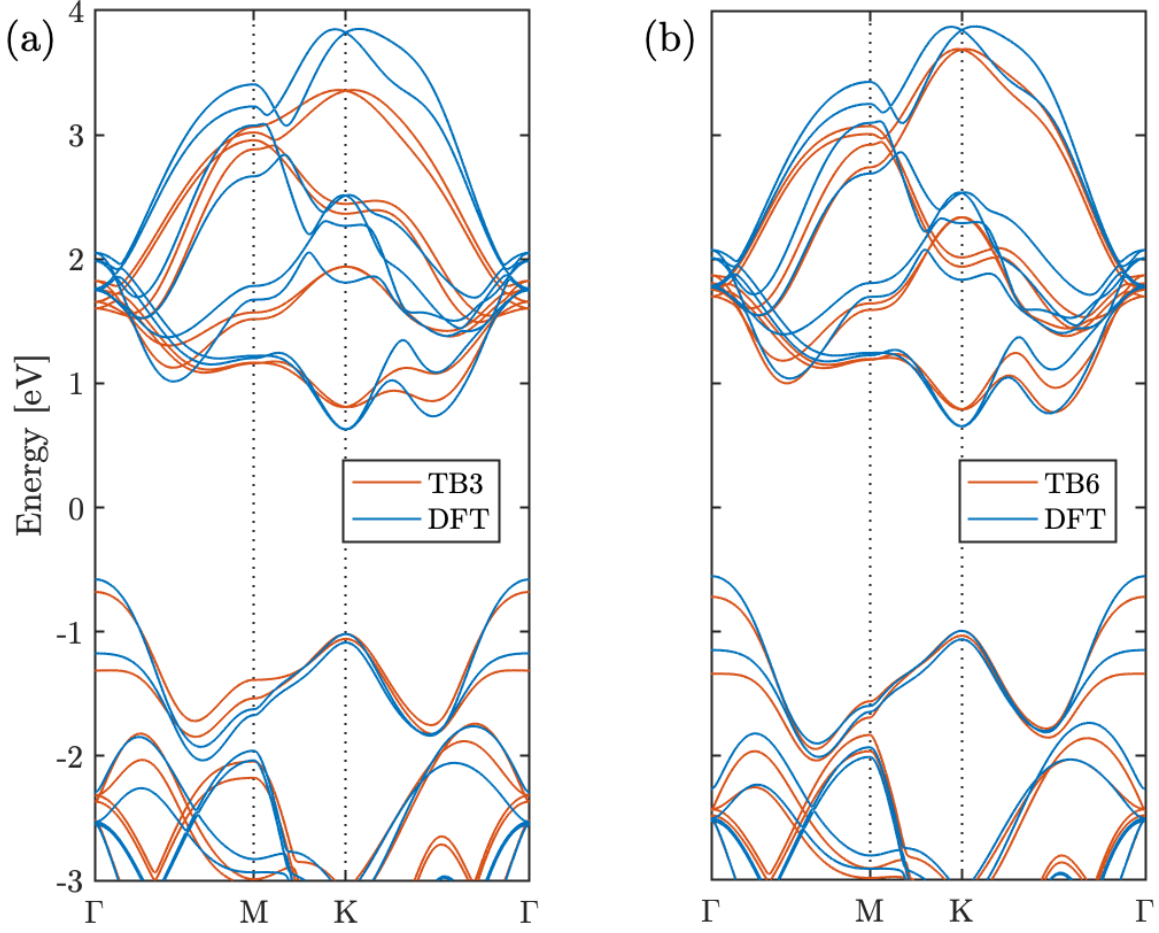


Figure 6.4: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for AB stacked MoS_2 homobilayers.

The direct bandgap is also more strongly influenced by spin-orbit coupling, due to the fact that the spin-splitting at the K valence band edge is much stronger than at the conduction band edge, resulting in the gaps being smaller by about ~ 80 meV compared to the calculations without spin-orbit coupling.

The agreement between the DFT bandstructures and the sixth-nearest neighbour calculations is generally good. However, the difference between the different band extrema in both the lowest conduction band and the highest valence band is underestimated in all systems. The two lowest-energy conduction band minima are at K and Q (halfway between Γ and K), and the two highest-energy valence band maxima are at Γ and K. In the DFT calculations, for all six systems, the Γ valence band maximum is at least 265 meV higher than the K maximum, and the K conduction band minimum is at least 106 meV lower than the Q conduction band

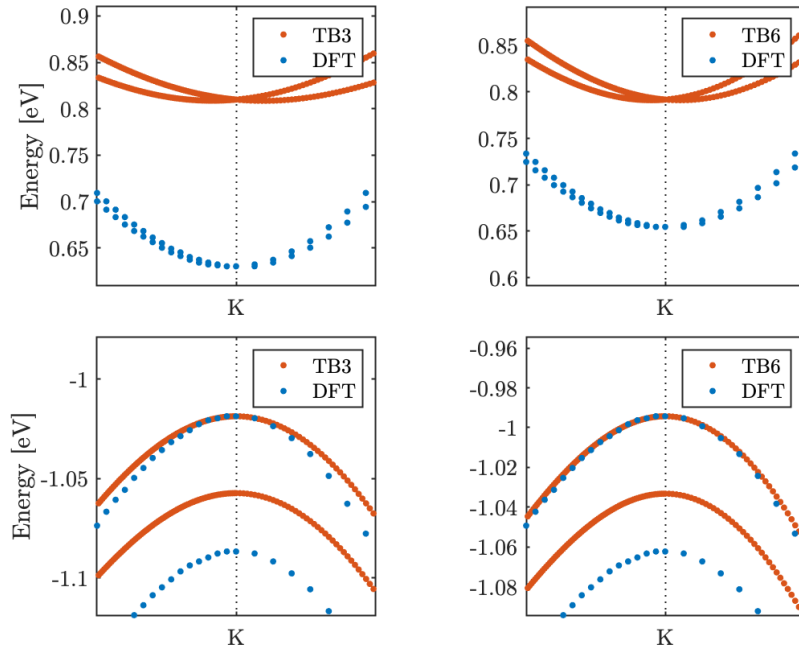


Figure 6.5: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for AB stacked MoS_2 homobilayers.

minimum, with these differences being the smallest in the AA stacked system.

The tight-binding model correctly reproduces the location of the valence band maximum in the calculations without spin-orbit coupling. However, it underestimates the difference by over 100 meV in the third-nearest neighbour case, and even more in the sixth-nearest neighbour case. For both AA and B^{XX} stackings, which have the largest interlayer separations, and therefore the weakest interlayer interactions, the energetic ordering of the valence band maxima is swapped in the sixth-nearest neighbour case when SOC is taken into account. This probably means that we are underestimating interlayer hopping.

Similar shortcomings are found in the lowest conduction band. Interestingly, the conduction band minima also change their energetic ordering in the sixth-nearest neighbour calculation, but only for the stackings with smaller interlayer separation, that is, AB, B^{MM} , and $\text{B}^{\text{MX}}/\text{B}^{\text{XM}}$. The conduction band minima also swap in the AA stacking case for sixth-nearest neighbour calculations with SOC, but only barely, with a difference of less than 1 meV.

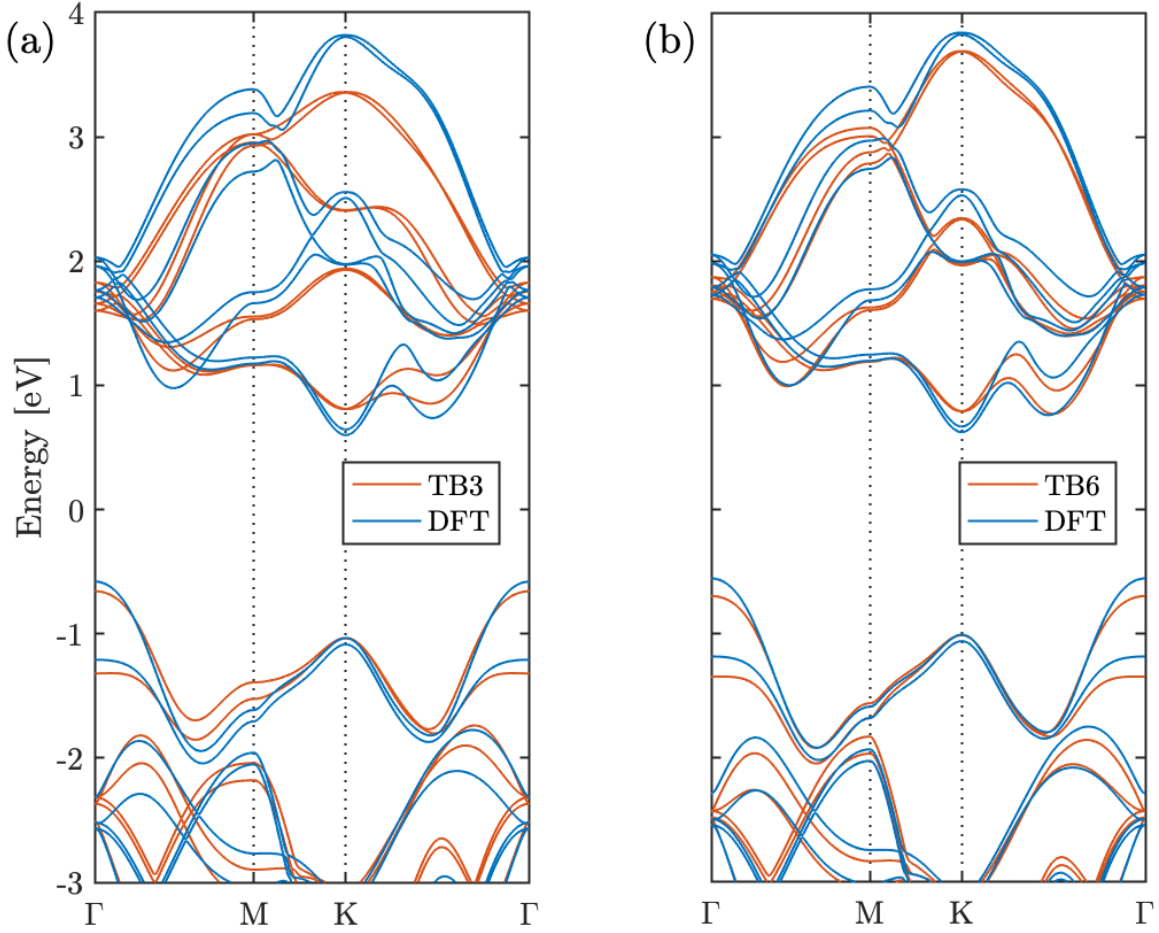


Figure 6.6: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{MX} stacked MoS₂ homobilayers.

It is an interesting future question why the longer-ranged hoppings seems to change the order of the band extrema. However, here, I only note this as a shortcoming of the model and proceed, since the direct bandgap is still located at K in all cases, and since I am only taking into account direct optical transitions in this work.

Next, let us consider the effective masses at the K band edges. For AA stacking, the electron and hole effective masses are very similar to the monolayer case, as expected. However, for all other stackings, some more interesting things happen: for AB, $B^{\text{MX}}/B^{\text{XM}}$, and B^{XX} stackings, in tight-binding calculations without SOC, the conduction band edge is not parabolic, but instead features a band crossing, as can be seen in the top panels of Figs. 6.5, 6.7, 6.9, and 6.13. This is not featured in the DFT calculations, except possibly in the AB stacked case, where the bottom two conduction bands are degenerate at K, but it is difficult to tell whether

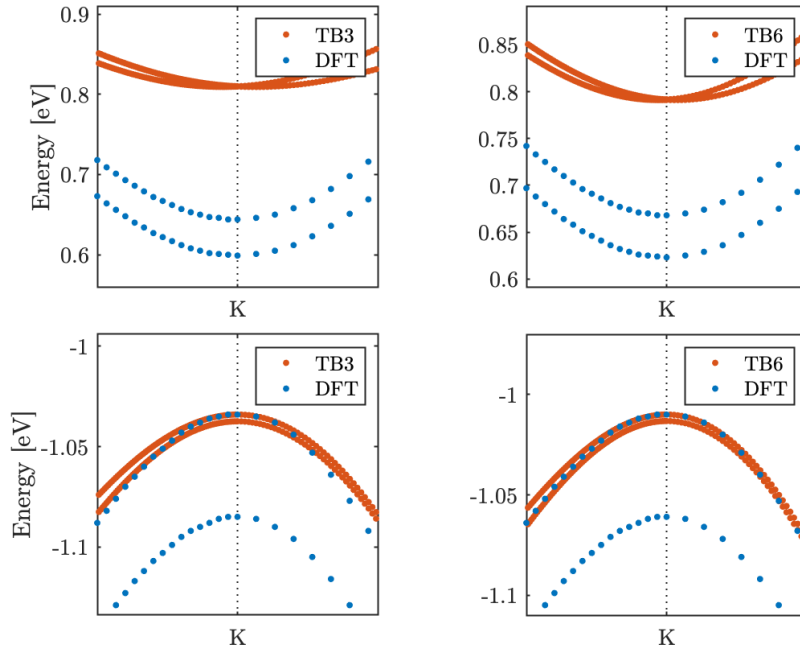


Figure 6.7: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{MX} stacked MoS₂ homobilayers.

this is a band crossing, or instead two parabolas that share a minimum. One indication that it might be a band crossing is the fact that the corresponding effective mass is very large. When spin-orbit coupling is taken into account, the degeneracy at the crossing point is lifted in all tight-binding calculations, resulting in very flat band edges and correspondingly large effective masses, particularly in the $B^{\text{MX}}/B^{\text{XM}}$ case. For all systems, the sixth-nearest neighbour model results in less flat bands.

The hole effective masses are generally much closer to DFT, as is the case for the monolayer. However, in both B^{MM} and B^{XX} , there is a band crossing at the valence band edge (see Figs. 6.11 and 6.13). For B^{MM} , this is particularly striking and also present in the DFT calculation. For B^{XX} , the bands are much closer together, and again the DFT bands are degenerate at K. These degeneracies are lifted when SOC is taken into account, and the resulting effective masses are very close to the monolayer case and do not appear particularly flat. This may be due to the fact that the valence band spin splitting at K is so much stronger than the conduction band spin splitting.

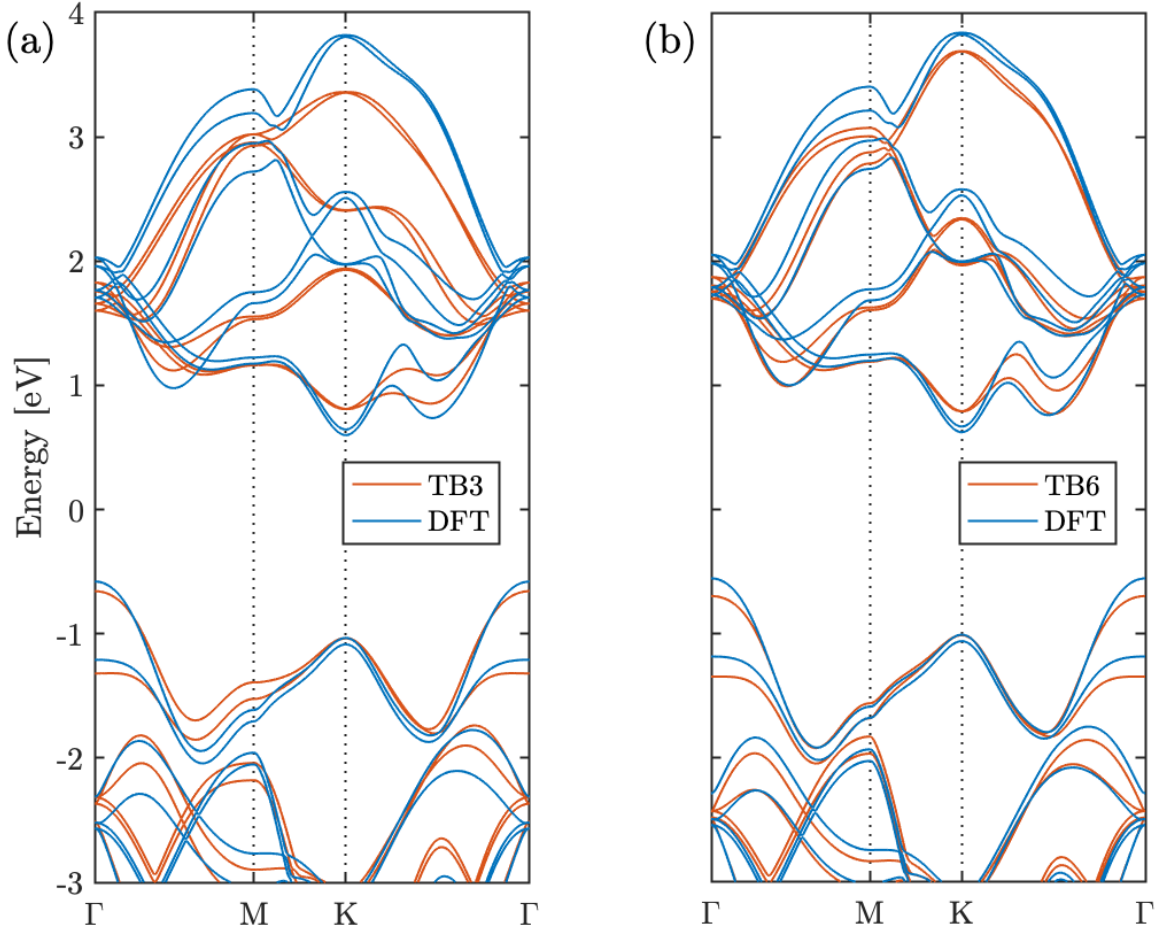


Figure 6.8: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{XM} stacked MoS₂ homobilayers.

Again, I note this as a potentially incorrect feature of this model and proceed anyway. It is possible that the large electron effective masses may be an issue for the optical calculations, however, this may not be an issue for two reasons. First, using Eq. (3.34) to estimate the exciton binding energy, we do not expect the energy to depend very strongly on the reduced effective mass. Secondly, the band flattening due to the lifted degeneracy is a very local effect. For the k-grid resolution used in the BSE calculations, the effective masses are reduced even further. Despite the shortcomings for the effective masses, however, I am still able to get qualitatively good optical spectra.

Overall, I find that including longer-ranged hopping has a significant qualitative and quantitative impact on the bandstructures of MoS₂ homobilayers.

		direct	indirect	$v_{\Gamma} - v_K$	$c_Q - c_K$	m_e^*	m_h^*
AA							
	DFT	1.667	1.402	0.265	0.155	0.46	-0.56
	TB3, no SOC	1.832	1.711	0.120	0.108	1.06	-0.77
	TB6, no SOC	1.790	1.736	0.054	0.029	0.64	-0.63
	TB3, wSOC	1.754	1.703	0.051	0.085	0.99	-0.72
	TB6, wSOC	1.712	1.712	-0.016	-0.0002	0.60	-0.59
AB							
	DFT	1.649	1.208	0.441	0.106	1	-0.56
	TB3, no SOC	1.828	1.488	0.339	0.053	n/a	-0.75
	TB6, no SOC	1.786	1.488	0.274	-0.024	n/a	-0.61
	TB3, wSOC	1.767	1.481	0.286	0.053	2.9	-0.71
	TB6, wSOC	1.725	1.479	0.221	-0.026	1.25	-0.58
B ^{MM}							
	DFT	1.675	1.236	0.439	0.139	0.48	n/a
	TB3, no SOC	1.829	1.501	0.329	0.071	1.11	n/a
	TB6, no SOC	1.788	1.520	0.264	-0.004	0.66	n/a
	TB3, wSOC	1.754	1.495	0.259	0.068	1.09	-0.72
	TB6, wSOC	1.713	1.511	0.194	-0.008	0.65	-0.59
B ^{MX}							
	DFT	1.633	1.179	0.454	0.141	0.45	-0.57
	TB3, no SOC	1.843	1.466	0.377	0.052	n/a	-0.77
	TB6, no SOC	1.801	1.468	0.312	-0.020	n/a	-0.63
	TB3, wSOC	1.763	1.457	0.306	0.034	8	-0.72
	TB6, wSOC	1.721	1.435	0.242	-0.044	0.95	-0.59
B ^{XM}							
	DFT	1.632	1.178	0.454	0.141	0.45	-0.57
	TB3, no SOC	1.843	1.466	0.377	0.052	n/a	-0.77
	TB6, no SOC	1.801	1.468	0.312	-0.020	n/a	-0.63
	TB3, wSOC	1.763	1.457	0.306	0.034	8	-0.72
	TB6, wSOC	1.721	1.435	0.242	-0.044	0.94	-0.59
B ^{XX}							
	DFT	1.681	1.393	0.288	0.161	0.46	-0.63
	TB3, no SOC	1.848	1.713	0.135	0.100	n/a	n/a
	TB6, no SOC	1.805	1.737	0.068	0.023	n/a	n/a
	TB3, wSOC	1.769	1.704	0.065	0.097	1.2	-0.71
	TB6, wSOC	1.727	1.727	-0.002	0.016	0.7	-0.58

Table 6.2: Band structure properties of high symmetry stackings of MoS₂ homobilayers: direct and indirect gap energies in eV; the difference between valence band maxima at Γ and K and conduction band minima at Q and K (also in eV) - noting that the sign indicates the location of the global band extrema, and noting also that the sixth nearest neighbour tight-binding model has the tendency to swap the order of band extrema, particularly for the conduction band minima; and effective electron and hole effective masses at K (where all the direct gaps are located), given in units of electron mass.

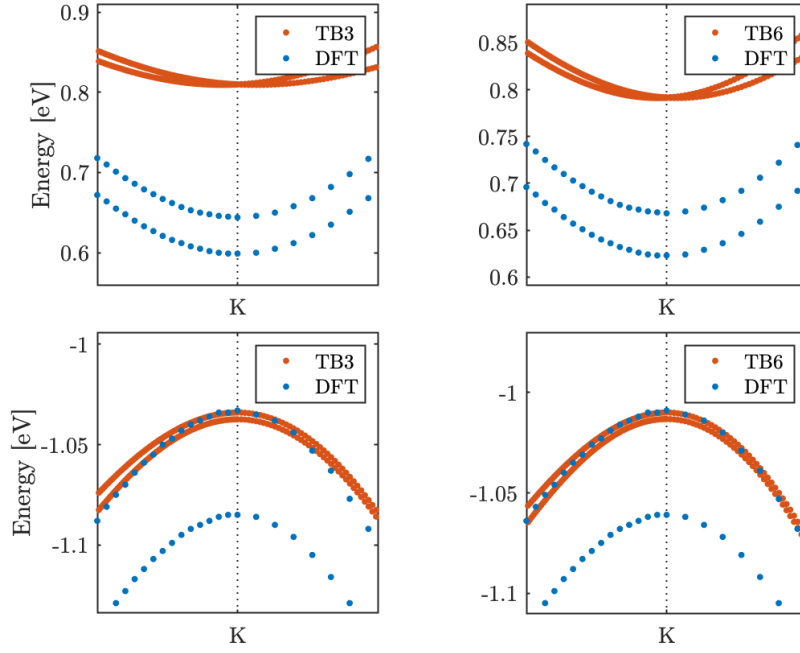


Figure 6.9: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{XM} stacked MoS₂ homobilayers.

	E ^{exc}	E ^{bind}	E ^{Ryd}		E ^{exc}	E ^{bind}	E ^{Ryd}
AA, TB3	1.343	0.411	0.512	AB, TB3	1.346	0.421	0.524
TB6	1.329	0.383	0.497	TB6	1.332	0.393	0.510
B ^{MX} , TB3	1.344	0.419	0.529	B ^{MM} , TB3	1.340	0.414	0.514
TB6	1.330	0.391	0.506	TB6	1.326	0.387	0.499
B ^{XM} , TB3	1.344	0.419	0.529	B ^{XX} , TB3	1.348	0.421	0.515
TB6	1.330	0.391	0.506	TB6	1.334	0.393	0.500

Table 6.3: Stacking dependence of the lowest exciton excitation energy (and corresponding binding energy) of MoS₂ homobilayers in vacuum in eV, using a 30×30 k-grid and a cutoff energy of 3.0 eV.

6.5 Impact of long-ranged hoppings on optical properties of untwisted MoS₂ homobilayers

Now, let us look at the impact of long-ranged hopping on the optical properties of MoS₂ homobilayers, as well as the dependence of the optical properties on the stacking configurations. Similar to Chapter 4, I model MoS₂ in vacuum, without a substrate.

Table 6.3 shows the lowest excitonic excitation energy and corresponding excitonic binding

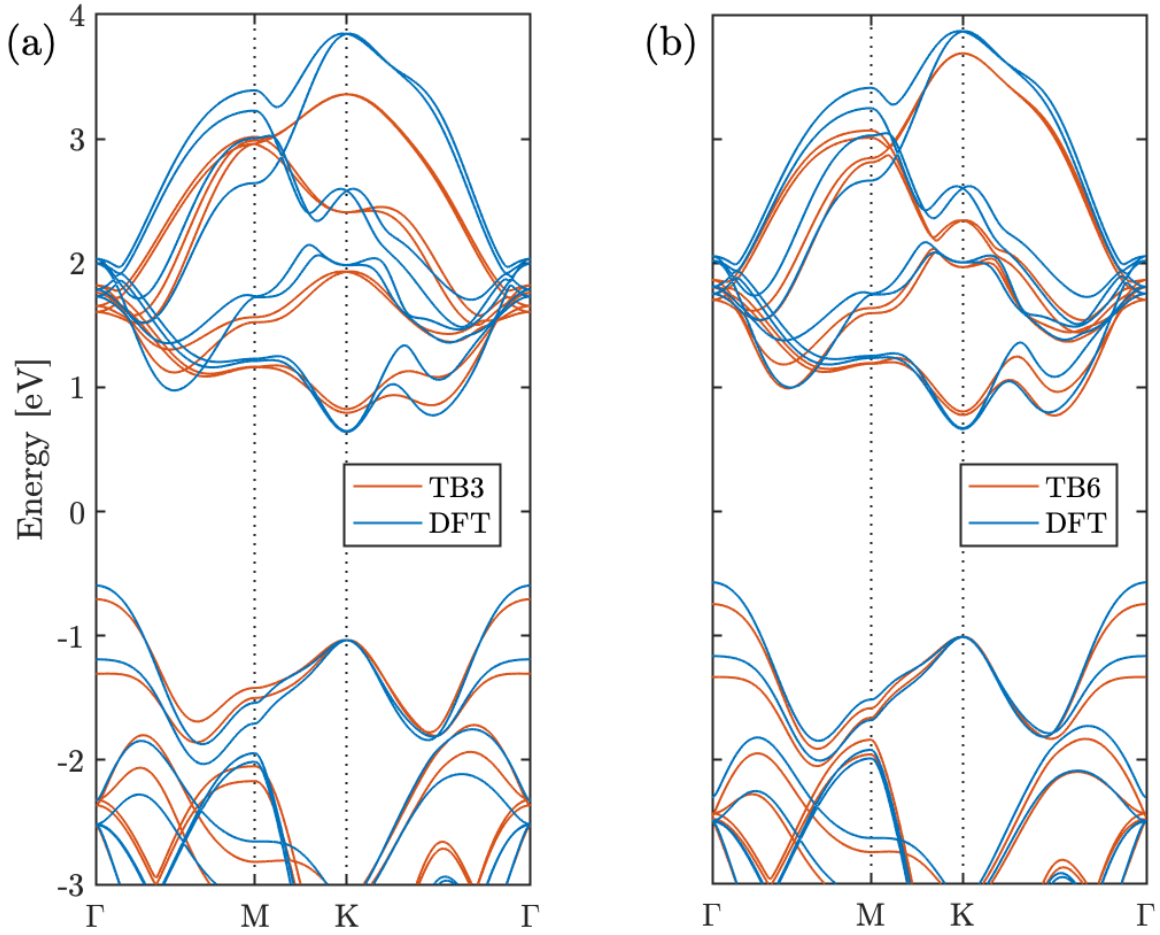


Figure 6.10: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{MM} stacked MoS₂ homobilayers.

energy for all six high-symmetry stackings. For all systems, the inclusion of longer-ranged hoppings decreases the binding energy by about 30 meV. This decrease is qualitatively still present in the simple Rydberg model, although it is less pronounced, so this effect can be at least in part understood from the effective masses.

The difference in binding energy between different types of stackings is very small, with a variation of up to 10 meV for both the third- and sixth-nearest neighbour calculations.

Correspondingly, the difference between the low-energy parts of third- and sixth-nearest neighbour optical spectra are small (Figs. 6.15a-6.15d). There seems to be a tendency for adjacent peaks to move closer together in the sixth-nearest neighbour case—all of the B peaks have a "shoulder" (not present in the monolayer spectra), which is more distinct in the third-nearest

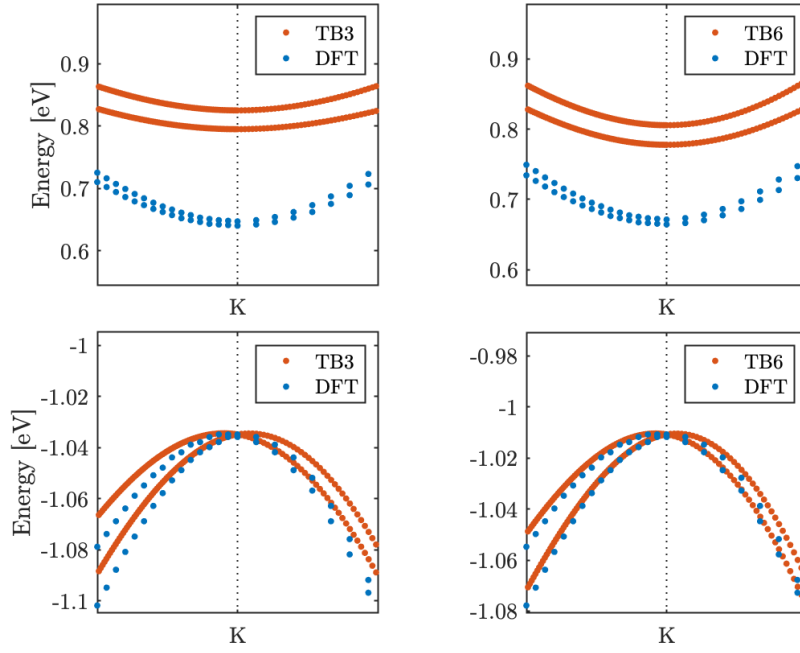


Figure 6.11: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{MM} stacked MoS₂ homobilayers.

neighbour case. Somewhat similarly, the small peak inbetween the first two large peaks present in both AB and B^{MM} stacking is more distinct in the third-nearest neighbour case.

Comparing the sixth-nearest neighbour spectra of different stacking configurations directly (Fig. 6.16), some of the features are very similar; namely the two large peaks near 1.3 eV and 1.5 eV, the second of which has a shoulder to its right, as well as two sets of double peaks near 1.6 eV and 1.75 eV. The inversion symmetric stackings AB, B^{MM} , and B^{XX} have smaller peaks by about a third compared to the non inversion symmetric stackings AA, B^{MX} , and B^{XM} . Both AB and B^{MM} have a small interlayer peak in between the first two large peaks, but it is much more distinct in the B^{MM} case. B^{MM} is also the only stacking in which the first peak is taller than the second large peak. It is interesting to see that B^{XX} does not have a small interlayer peak. This may be due to the fact that the interlayer distance in this case is too large for a low-energy interlayer transition.

Figure 6.17 shows optical spectra as calculated by Gerber et al.[52]. Note that the notation used in that work is different from ours. The stacking labelled *AB* in the top panel corresponds

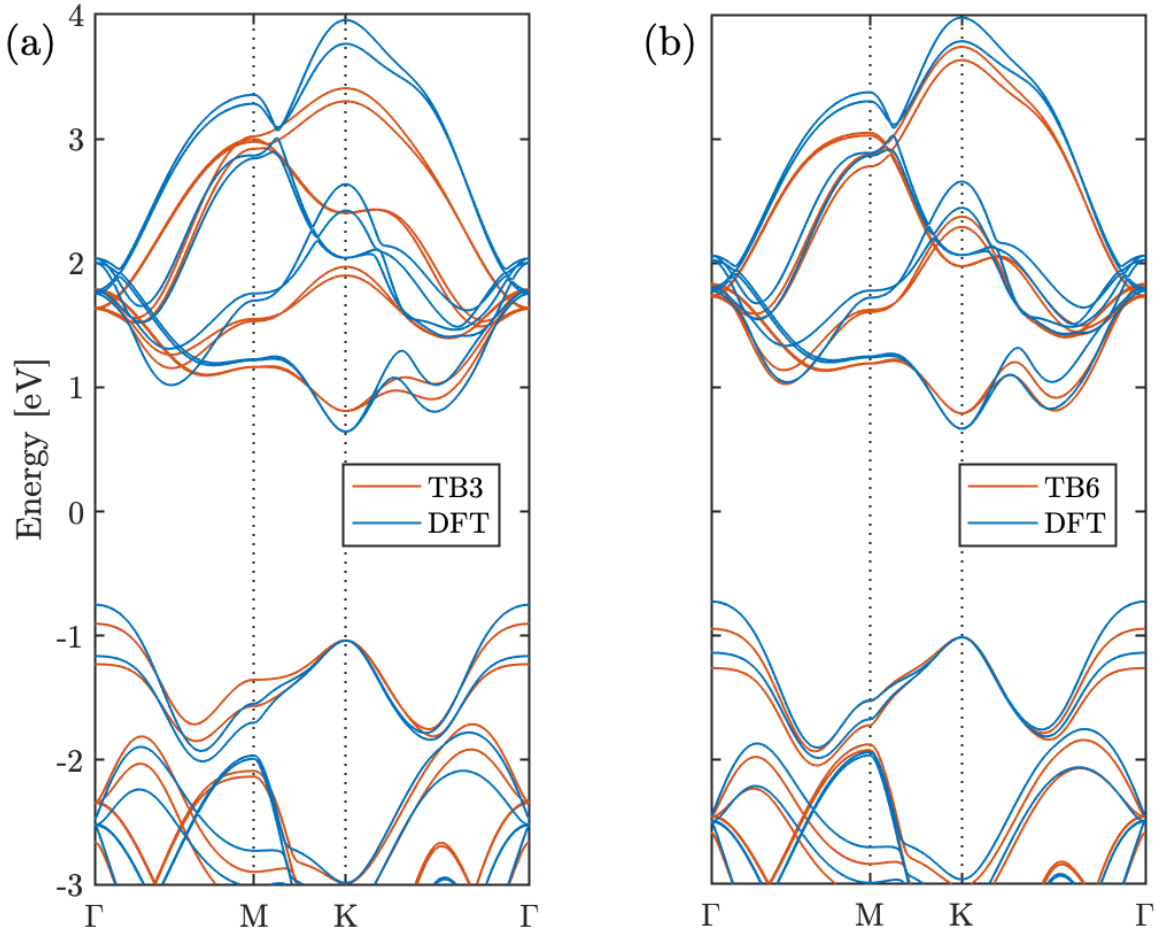


Figure 6.12: Comparison of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{XX} stacked MoS₂ homobilayers.

to what I call B^{MX} stacking and AA' in the middle panel corresponds to AB stacking. (To avoid confusion, I will continue to use my previous notation when referring to the different stacking configurations.) Gerber et al.[52] performed GW-BSE calculations to simulate these three MoS₂ homobilayer stackings in vacuum, and compare their calculations to measurements performed on AB stacked bilayers on a hBN substrate. The middle panel of Fig. 6.17 shows two peaks not present in AA and B^{MX} stacking, which is qualitatively similar to what we find in B^{MM} stacking, and the general structure of having the two large peaks similar to the monolayer spectrum in all cases, with the second peak slightly higher than the first peak, is also present. In my calculations, AB stacking also displays extra peaks compared to the non-inversion symmetric stackings, but they are much more subtle. The first is very small and nearly merged into the A peak, and the second is much higher in energy, visible as a third peak in what is otherwise a double peak feature near 1.6 eV.

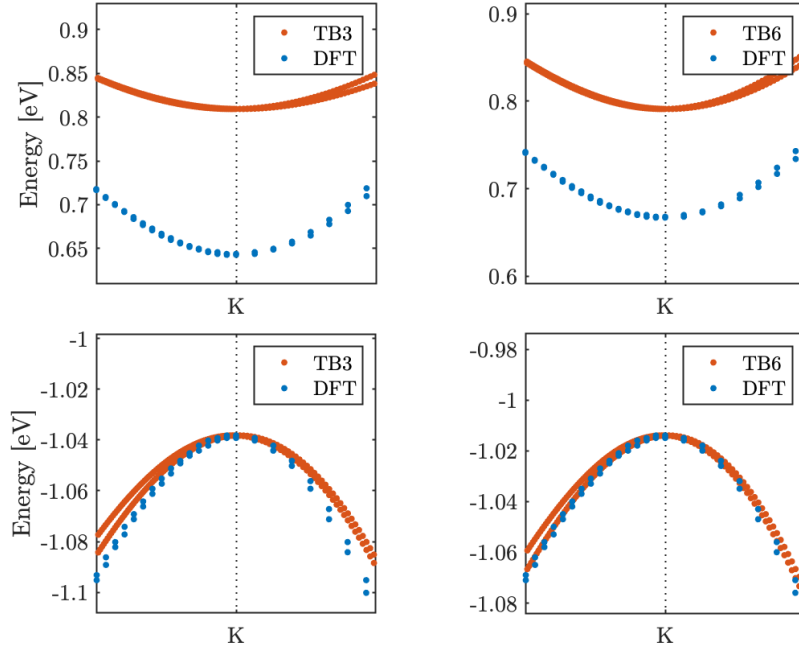


Figure 6.13: Close up of valence and conduction band edges near the K point of third- and sixth-nearest neighbour tight-binding bandstructures without SOC to corresponding DFT bandstructure for B^{XX} stacked MoS_2 homobilayers.

There are some notable differences between our spectra and the ones given in Gerber et al.[52]. Particularly, the A and B peaks are closer together in our work, and we do not have a third large peak (labelled A:2s in the bottom panel of Fig. 6.17). This may be at least partly due to a convergence issue on the part of Gerber et al., who use a 15×15 k-grid for their optical calculations, which is not sufficient for the description of the higher-energy features in GW-BSE[199] (as they acknowledge).

Overall, the impact of longer ranged hopping on the optical properties is much smaller than the impact on the electronic structure. The stacking configuration does have an impact, as we will see in the next section, mainly due to the interlayer separation and the presence or absence of inversion symmetry.

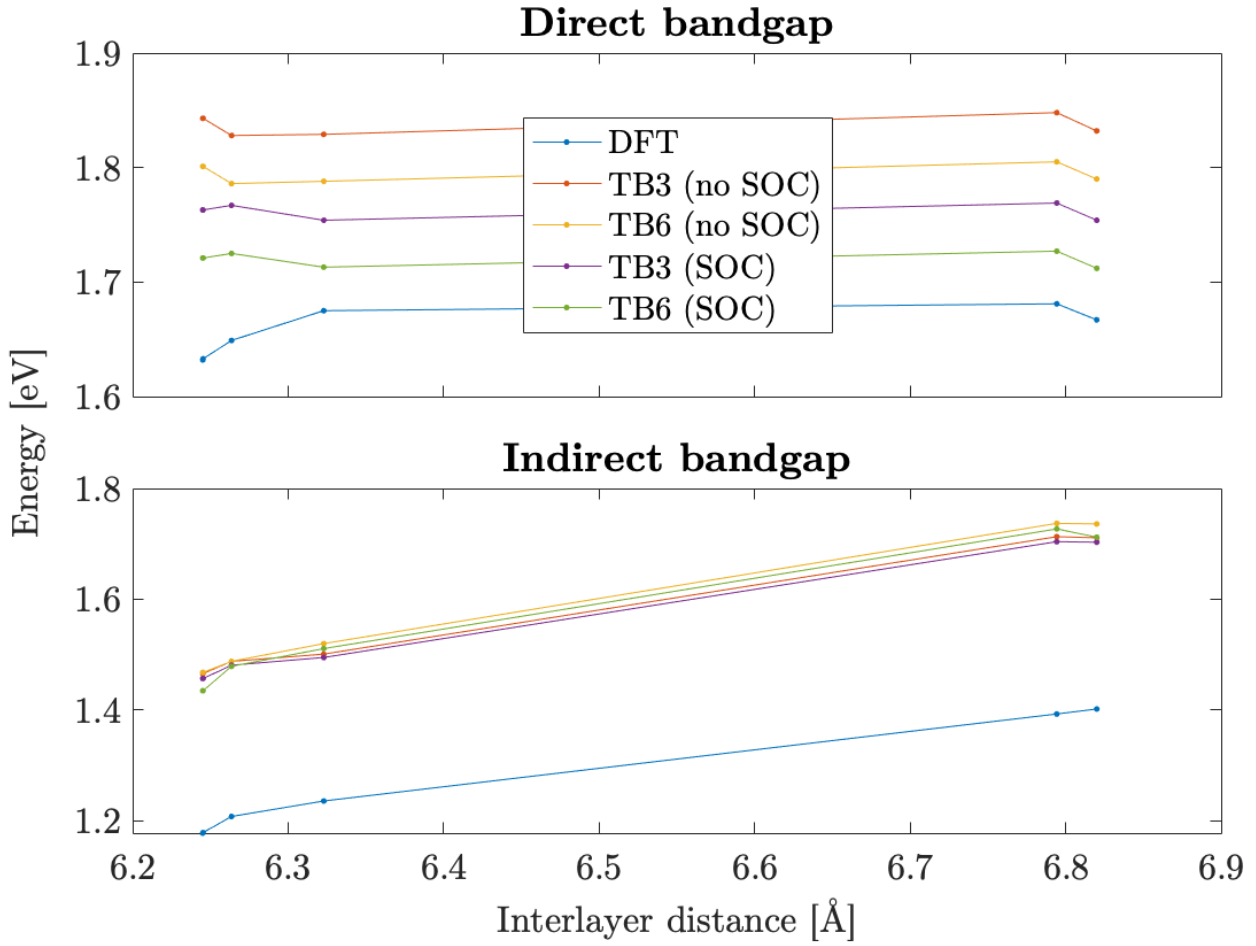
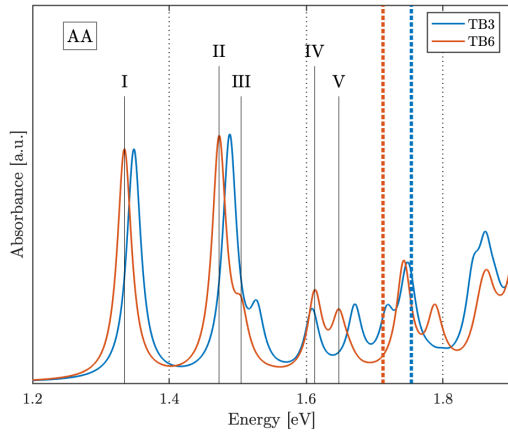


Figure 6.14: Direct and indirect gap vs. interlayer separation in DFT and TB calculations for high-symmetry stacked MoS₂ homobilayers. Note that the indirect bandgap is interlayer distance dependent, but the direct bandgap is not.

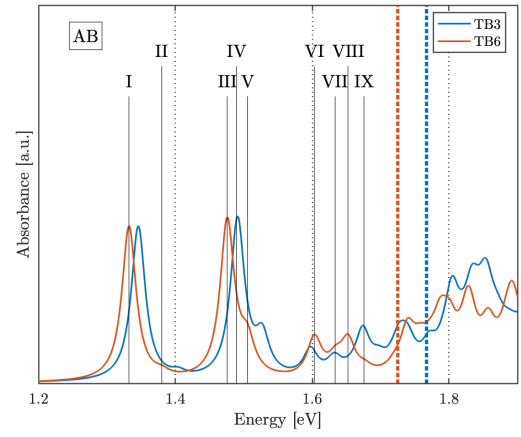
6.6 Impact of stacking geometry on layer character of excitons in untwisted MoS₂ homobilayers

Finally, I am interested in the layer character of the optically active excitons in different stacking configurations of untwisted MoS₂ homobilayers.

The first step in this analysis is to determine which excitons are optically active. This can be done by sorting the excitons by the magnitude of their optical matrix elements, and then matching the corresponding excitation energies to the peaks in the optical spectra. The results of this for the untwisted MoS₂ bilayers is detailed in Appendix C. For the remainder of this chapter I will focus on results from the sixth nearest neighbour tight-binding model.



(a) AA stacking



(b) AB stacking

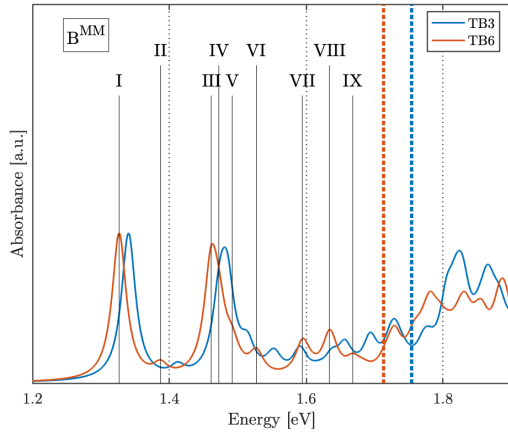
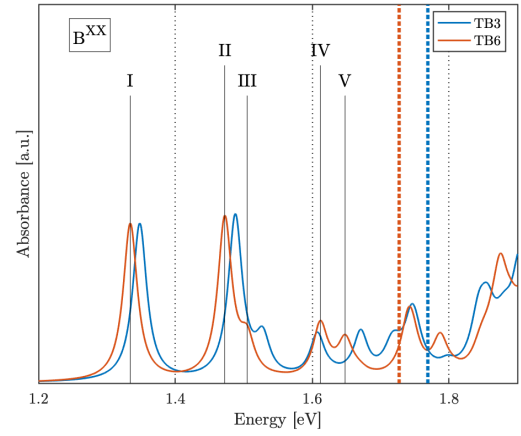
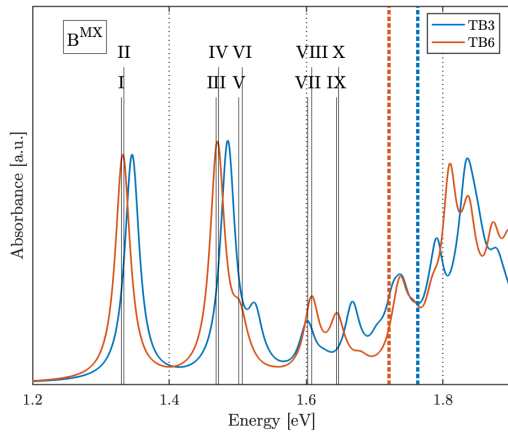
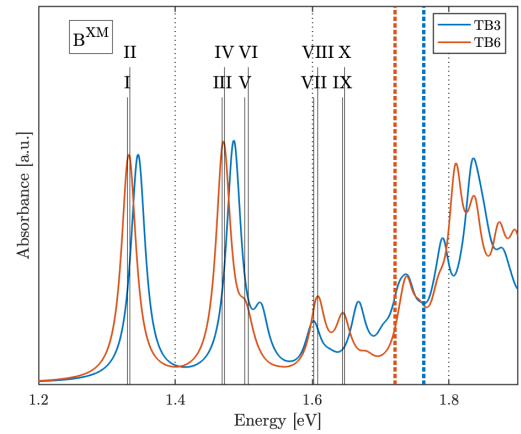
(c) B^{MM} stacking(d) B^{XX} stacking(e) B^{MX} stacking(f) B^{XM} stacking

Figure 6.15: Optical spectra of different stacking geometries of MoS_2 homobilayers in vacuum in third-nearest neighbour (blue) vs. sixth-nearest neighbour (red) tight-binding model. The bandgaps are indicated with vertical dashed lines of the same colour.

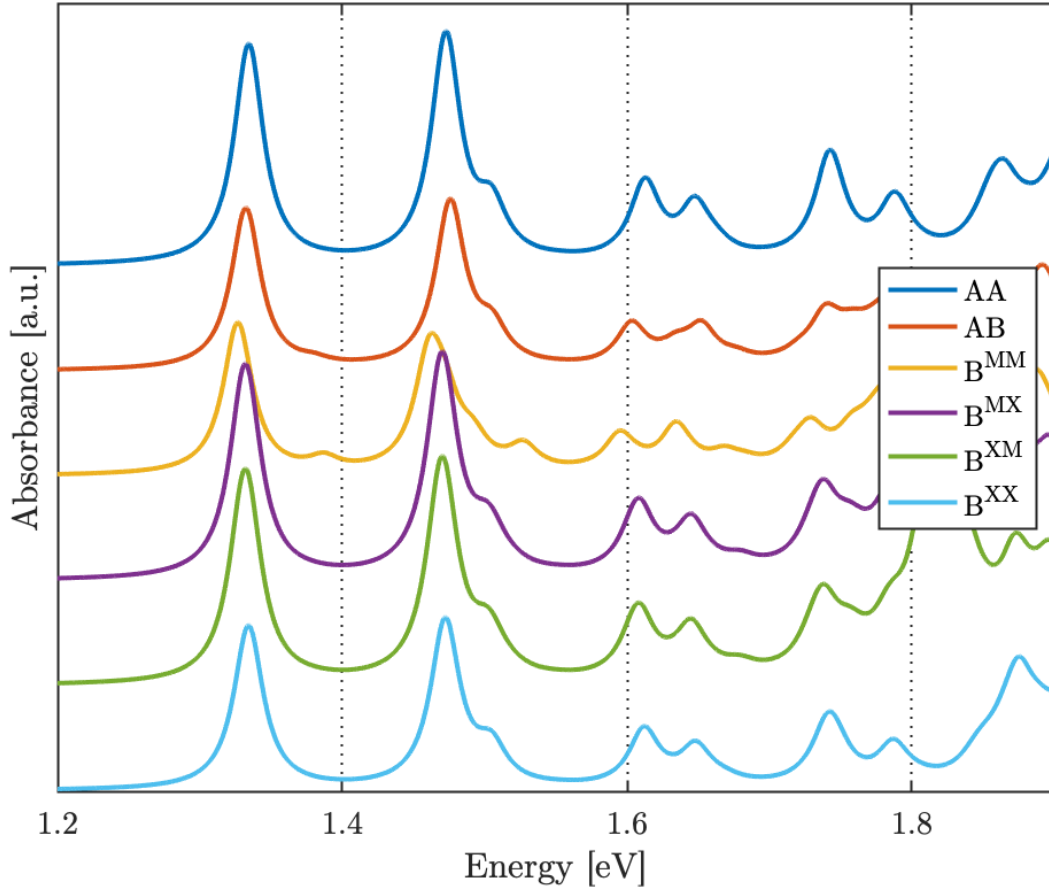


Figure 6.16: Comparison of optical spectra of different high-symmetry stackings of MoS₂ homobilayers in vacuum from sixth-nearest neighbour calculations.

AB stacking

There are nine distinct subbandgap peaks in the optical spectrum of AB stacked bilayers in our model, as shown and labelled in Fig. 6.15b. The excitons corresponding to those peaks can be doubly or quadruply (or not at all) degenerate. This is due to the spin and valley symmetries.

Peak I at 1.332 eV is quadruply degenerate and consists of transitions from the top two (degenerate) valence bands to the bottom two (degenerate) conduction bands at the K and K' points (see Table D.1.

Peak II at 1.380 eV is a nondegenerate exciton consisting of transitions from the top two (degenerate) valence band to the third and fourth (degenerate) conduction bands at K and

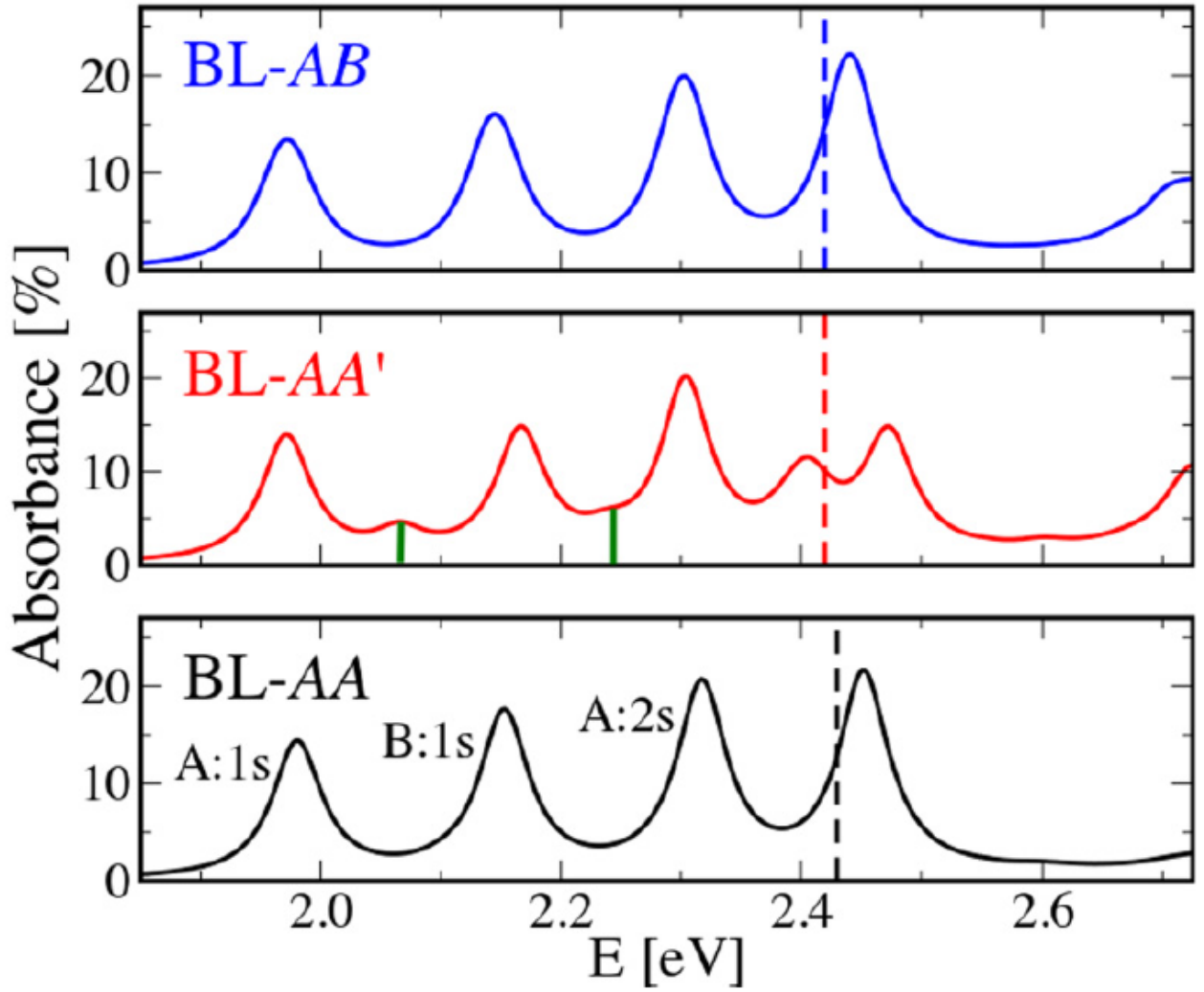


Figure 6.17: Optical spectra of different stackings of MoS₂ homobilayers in vacuum, calculated with GW-BSE. *AB* in this notation corresponds to B^{MX} stacking in our notation, *AA'* to *AB*, and *AA* to *AA* stacking. Reproduced from Ref. [52] with permission from the American Physical Society.

K' (see Table D.2. Looking at the orbital characters of the bands involved in the transitions, we can see that all the main transitions involved in this exciton are purely interlayer excitons. So even without looking at the realspace wavefunction, this is clearly an interlayer exciton, in agreement with the literature. So while the peak is less distinct than the corresponding experimental peak in Fig. 6.17, the interlayer peak can at least qualitatively be well reproduced. However, most of the bands have mixed-layer orbital character, reflecting the fact that flipping the whole system upside down would have no effect on the band structure. The fact that one of a pair of degenerate states is purely localized in one layer and the other in the other is an artifact of the layer localized atomic basis rather than a physical property of the system.

Peak III at 1.476 eV is again quadruply degenerate and consists of transitions exactly at K and K'. However, rather than transitions between the top valence and bottom conduction bands, this consists of transitions between the third and fourth (degenerate) valence bands and the third and fourth (degenerate) conduction bands (see Table D.3).

Peak IV at 1.489 eV is another nondegenerate exciton. This exciton is spread out in reciprocal space rather than being strictly localized at K and K' and consists of transitions between top valence band and bottom conduction band (see Table D.4).

Peak V at 1.505 eV is another quadruply degenerate exciton localized at K and K' and consisting of transitions between top valence band and bottom conduction band (see Table D.5).

Peak VI at 1.603 eV is more spread out in reciprocal space, but otherwise similar in character to peak V (see Table D.6).

Peak VII actually consists of two excitons. The first is a doubly degenerate exciton at 1.633 eV, spread out in reciprocal space and consisting of transitions between the top two valence bands and the third and fourth conduction bands. The second is a nondegenerate exciton at 1.635 eV, similarly spread out in reciprocal space, but consisting of transitions between the third and fourth valence bands and the bottom two conduction bands (see Table D.7).

Peak VIII at 1.652 eV is a strongly localized quadruply degenerate exciton consisting of transitions between the third and fourth valence bands and the third and fourth conduction bands (see Table D.8).

Peak IX at 1.676 eV is nondegenerate, spread out, and consists of the same type of transitions as peak VIII.

Figure 6.18 illustrates the real space distribution and therefore the layer character of the optically active excitons in AB stacked MoS₂ bilayers. More specifically, it shows the real space probability distribution of the optically active excitons, or the sum of probability distributions in the case of degenerate excitons, normalized to one. The real space wavefunction is calculated according to Eq. (3.70). Since the real-space wavefunction is a function of two coordinates, it is difficult to visualize. Often, in illustrations, the hole location is fixed and the corresponding electron location is shown. In this case, this would not be very informative. Firstly, there are only six locations in the untwisted bilayer unit cell, and secondly, fixing the hole would miss information about the hole wavefunction. Figure 6.18 therefore shows the probability distribution matrix elements corresponding to the electron being localized on one atom and the hole on the other. The first half of the atoms are located on one layer, the second on the other. The first atom in each layer is a Mo atom, the other two are the S atoms. So for example, the top left corner of Fig. 6.18 shows the probability of both an electron and a hole being located on the same atom, in this case a top layer Mo atom.

This means that probability distributions which are roughly block-diagonal correspond to intralayer excitons. Distributions which are block-off-diagonal correspond to interlayer excitons. And distributions which are neither block-diagonal nor block-off-diagonal correspond to hybrid excitons.

In the case of AB stacking, peak II is clearly an interlayer exciton, as is expected from qualitatively similar optical peaks in experiment. Peak VII consists of one mostly interlayer exciton and one mostly intralayer exciton. All other peaks appear to be intralayer excitons, although peak IV comes closest to also being a hybrid exciton.

In both AB stacking as well as B^{MM} stacking, which both exhibit interlayer excitons, the oscillator strength of the interlayer excitons is much smaller than those of the intralayer excitons, resulting in much smaller peaks. This is mainly due to the reduced wavefunction overlap between the more spatially separated interlayer excitons[200].

AA stacking

There are five distinct subbandgap peaks in the optical spectrum of AA stacked bilayers in our model, as shown and labelled in Fig. 6.15a. The excitons corresponding to those peaks can only be doubly (or not at all) degenerate, as there is spin splitting at K and K'.

Peak I at 1.334 eV is a doubly degenerate exciton at K and K' consisting of transitions between the third and fourth valence bands and the first and third conduction band (see Table D.10). Transitions to the second and fourth conduction band do not conserve spin (see Table B.2).

Peak II consists of two doubly degenerate excitons, one pair at 1.4726 eV and one at 1.4732 eV (see Table D.11). The first is localized at K and K' and consists of transitions from the third and fourth valence bands to the second and fourth conduction bands, the second is spread out near K and K' and consists of transitions between the top valence band and second conduction band.

Peak III is a doubly degenerate exciton at 1.505 eV, well localized at K, and consisting of transitions between the top two valence bands and the first and third conduction bands (see Table D.12).

Peak IV at 1.613 eV is spread out near K and K' and consists of transitions between the top two valence bands and the second and fourth conduction bands, similar to peak I (see Table D.13).

Peak V at 1.648 eV is a doubly degenerate exciton strongly localized at K and K', consisting of transitions between the third valence band and fourth conduction band, and the fourth valence band and second conduction band.

Figure 6.19 shows that all six peaks are intralayer peaks, with only very weak interlayer contributions.

B^{MX} stacking

There are five distinct subbandgap peaks in the optical spectrum of B^{MX} stacked bilayers in our model, as shown and labelled in Fig. 6.15e. However, each peak consists of two separate excitons with a large enough split in energy (corresponding to the valence spin splitting at K and K') that this is visible in the spectrum, so I am considering them as ten separate peaks. The excitons corresponding to those peaks can only be doubly (or not at all) degenerate, as there is there is (valence) spin splitting at K and K'. Most of the excitons in this stacking are well described by only a few transitions each.

Peak I at 1.330 eV is a doubly degenerate exciton consisting of transitions between the top valence band and bottom conduction band at K and K' (see Table D.15). Note that this is the only stacking in which the lowest energy exciton is optically active.

Peak II at 1.334 eV is a doubly degenerate exciton consisting of transitions between the second valence band and second conduction band at K and K' (see Table D.16).

Peak III at 1.468 eV is a doubly degenerate exciton consisting of transitions between the third valence band and third conduction band at K and K' (see Table D.17).

Peak IV at 1.472 eV is a doubly degenerate exciton consisting mainly of transitions between the fourth valence band and fourth conduction band at K and K', but also including transitions between the fourth valence band and bottom conduction band at K and K' (see Table D.17).

Peak V at 1.501 eV is a doubly degenerate exciton consisting of transitions between the top valence band and bottom conduction band at K and K', the same as peak I (see Table D.19).

Similarly, peak VI at 1.507 eV has the same character as peak II (see Table D.20).

Peak VII at 1.602 eV is a doubly degenerate exciton spread out near K and K' in recipro-

cal space and consists of transitions between the top valence band and bottom conduction band (see Table D.21).

Peak VIII actually consists of three doubly degenerate excitons very close in energy, at 1.8060 eV, 1.6083 eV, and 1.6092 eV. All three are spread out in reciprocal space near K and K' and consist of transitions between the top two valence bands and bottom two conduction bands (see Table D.22).

Peak IX is again a doubly degenerate exciton at 1.644 eV, consisting of transitions between the third valence band and the third conduction band at K and K' (see Table D.23).

Peak X is again a doubly degenerate exciton at 1.647 eV, consisting of transitions between the fourth valence band and the first, second, and fourth conduction bands at K and K' (see Table D.24)

Figure 6.20 illustrates the origin of the peak pairing in B^{MX} stacked MoS_2 bilayers. B^{MX} stacking is not inversely symmetric, instead it transforms into B^{XM} stacking when inversed. One consequence of this is that there is an energy splitting between excitons being in the top and bottom layers. All peaks are intralayer peaks, and the left column of Figure 6.20 shows all the (slightly lower energy) peaks located in the bottom layer, whereas the right column shows all the (slightly higher energy) peaks located in the top layer. For B^{XM} stacking, this is exactly reversed due to the inversion-symmetry relation between the two stackings.

B^{MM} stacking

There are nine distinct subbandgap peaks in the optical spectrum of B^{MM} stacked bilayers in our model, as shown and labelled in Fig. 6.15c. They can be doubly, quadruply, or not at all degenerate. However, not all excitons with degenerate eigenvalues couple equally strongly to light, which accounts for sometimes only three of them appearing in the tables of most optically active excitons.

Peak I at 1.327 eV is a quadruply degenerate exciton localized at K and K' and consisting of transitions from the top two valence bands to the bottom two conduction bands (see Table D.25).

Peak II at 1.380 eV is a doubly degenerate excitons localized at K and K' and consisting of transitions from the top two valence bands to the third and fourth conduction band (see Table D.26).

Peak III at 1.461 eV is a quadruply degenerate exciton localized at K and K' and consisting of transitions from the third and fourth valence bands to the third and fourth conduction bands (see Table D.27).

Peak IV at 1.483 eV is a quadruply degenerate exciton spread out in reciprocal space near K and K', and consisting of transitions between the top two valence bands and the bottom two conduction bands (see Table D.28).

Peak V at 1.492 eV is a quadruply degenerate exciton similar in character to Peak IV (see Table D.29).

Peak VI consists of two quadruply degenerate excitons at 1.519 eV and 1.526 eV, both of which are localized at K and K'. The first consists of transitions between the top two valence bands and third and fourth conduction band, the second consists of transitions between the third and fourth valence bands and the bottom two conduction bands (see Table D.30).

Peak VII at 1.594 eV is a quadruply degenerate exciton spread out in reciprocal space near K and K' and consisting of transitions between the top two valence bands and third and fourth conduction bands (see Table D.31).

Peak VIII consists of three quadruply degenerate excitons, although only two of those degenerate excitons are optically active in all three cases. All three are spread out in reciprocal space near K and K'. The first (at 1.6330 eV) consists of transitions between the top two valence bands and conduction bands. The second (at 1.6341 eV) and the third (at 1.6348 eV) consist of transitions between the third and fourth valence bands and the bottom two conduction bands (see Table D.32).

Peak IX at 1.663 eV is a quadruply degenerate exciton localized at K and K', consisting of transitions between the third and fourth valence bands and bottom two conduction bands (see Table D.33).

Figure 6.21 shows that the second and sixth peak are interlayer peaks, peaks VII and X are hybrid, and all other peaks are mostly intralayer peaks.

B^{XX} stacking

There are five distinct subbandgap peaks in the optical spectrum of B^{XX} stacked bilayers in our model, as shown and labelled in Fig. 6.15d. They are all quadruply degenerate. All except peak IV are strongly localized at K and K'.

Peak I at 1.334 eV and peak III at 1.505 eV consist of transitions between the top two valence bands and bottom two conduction bands (see Tables D.34 and D.36).

Peak II at 1.472 eV, peak IV at 1.612 eV, and peak V at 1.648 eV consist of transitions between the third and fourth valence bands and third and fourth conduction bands (see Tables D.35, D.37, and D.38).

Figure 6.22 shows that all peaks in B^{XX} stacked MoS_2 are almost entirely intralayer peaks, similar to AA stacking.

Conclusion

In summary, as shown in Figs. 6.15, and 6.18-6.22, AA and B^{XX} stacked MoS₂ bilayers have five subbandgap peaks each in their optical spectra, all of which are of pure intralayer character. B^{XX} stacking has a spin-degenerate electronic bandstructure, but AA stacking does not. In both stackings, the chalcogen pairs of top and bottom layers are stacked directly on top each other (see Fig. 6.1), resulting in the largest interlayer separations of all stackings (see Tab. 6.1). The character of the band edges in all stackings is dominated by p-orbitals (see Tabs. B.2-B.7), and the Slater-Koster parameters related to interlayer p-p hopping decrease exponentially with interlayer distance (see Eq. (6.2)). It is therefore likely that the lack of interlayer excitons in these two stackings is a consequence at least in part of the large interlayer separation.

B^{XM} and B^{MX} stackings have excitons which are purely located in individual layers (see Fig. 6.20). At the band gap, the electronic bands are strongly layer-polarized, with a small energy difference between bands corresponding to different layers (see Tab. B.5). This corresponds to the small separation between adjacent optical peaks in the optical spectra (see Fig. 6.15), which appear to come in five pairs for a total of ten optical peaks¹. This layer-symmetry breaking is possible because B^{XM} and B^{MX} are related to each other by inversion symmetry, but are not inversion symmetric by themselves.

B^{AB} and B^{MM} stacking both have spin-degenerate electronic band structures (see Tabs. B.3 and B.6) and both have nine optical peaks (see Figs. 6.15), including both intra- and interlayer excitons (see Figs. 6.18 and 6.21).

Note further that the three spin-degenerate stackings, AB, B^{MM}, and B^{XX}, have generally smaller optical peaks than the three spin-split stackings, B^{AA}, B^{XM}, and B^{MX} (see Fig. 6.15). Only spin-conserving transitions are optically allowed (see Appendices B and D for details on the orbital and spin character of the optical transitions involved in the optical peaks of

¹It would be interesting to look further into whether there is a sort of layer-valley coupling in these stackings, what the consequences of that would be, if so, and how this relates to spin-valley coupling

the different stacking geometries), so in the spin-hybridized transitions of the spin-degenerate bandstructures, only the spin-direct part of the transition couples to light. This is what may be causing the lower oscillator strength.

Compared to previous literature, we are able to qualitatively reproduce the optically active interlayer peak in AB and B^{MM} stacking. However, the interlayer peak in AB stacking in particular is comparatively dark (compared to luminescence of 20% – 30% of the A peak height observed in Ref. [53] and calculated in Ref. [52]), and with a slightly low excitation energy; it is more typically seen about 100 meV above the A peak[50, 52, 53]. We were also unable to see the interlayer peak in B^{MX} stacking, as seen in Refs. [52, 50].

Overall, we find that the stacking geometry has a strong impact on the optical properties of TMD homobilayers. The presence or absence of spin splitting, the interlayer separation, and the crystal symmetry all play roles in determining the properties of the excitons in these materials, resulting in qualitatively distinct optical spectra.

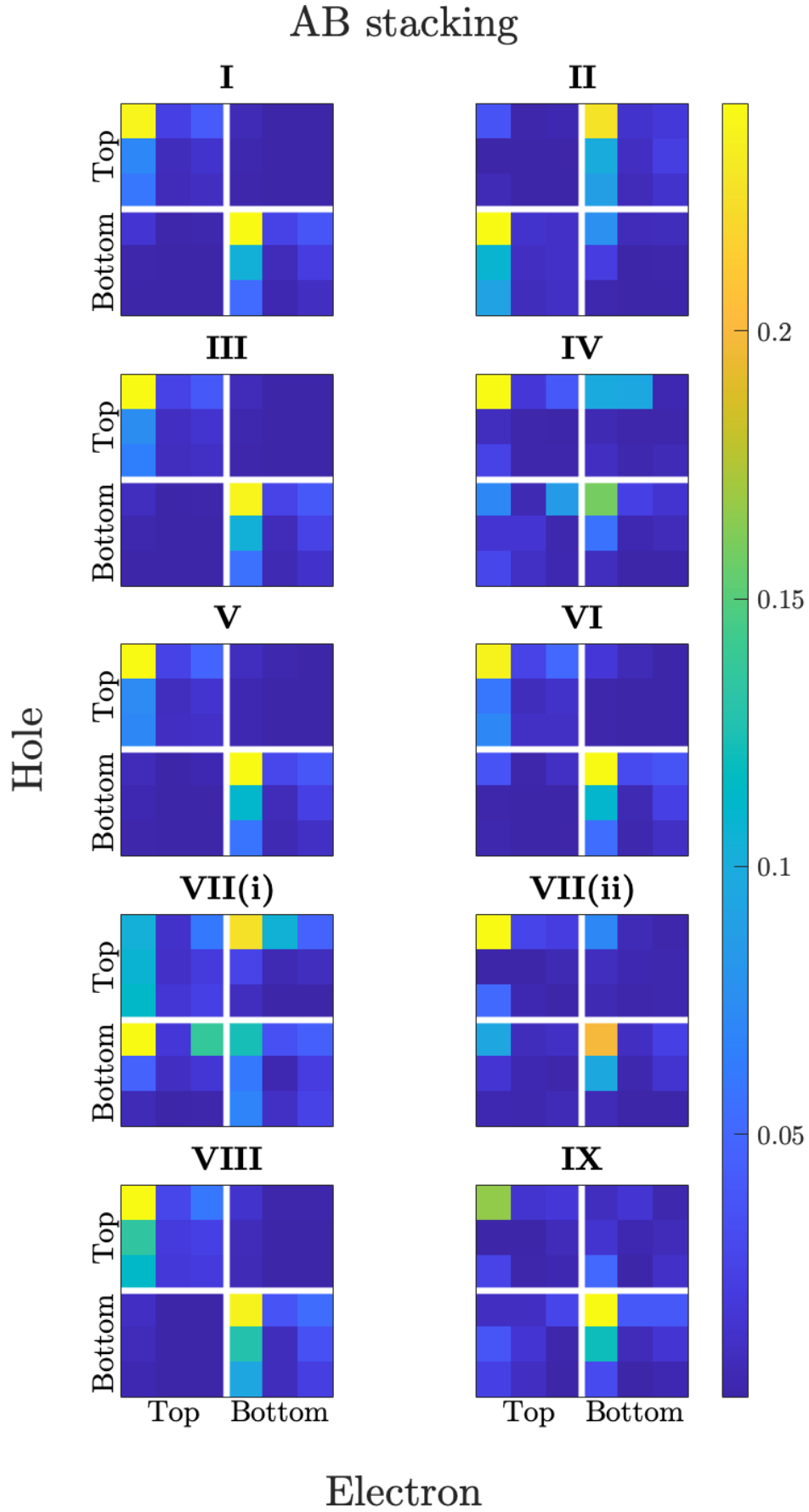


Figure 6.18: Illustration of the real space distribution of the optically active excitons in AB stacked MoS_2 bilayers. The matrix elements show the probability associated with an electron being localized on one atom and a hole on another, with the atomic positions being, in order, the top layer Mo, inner S, and outer S atoms, and the bottom layer Mo, inner S, and outer S atoms.

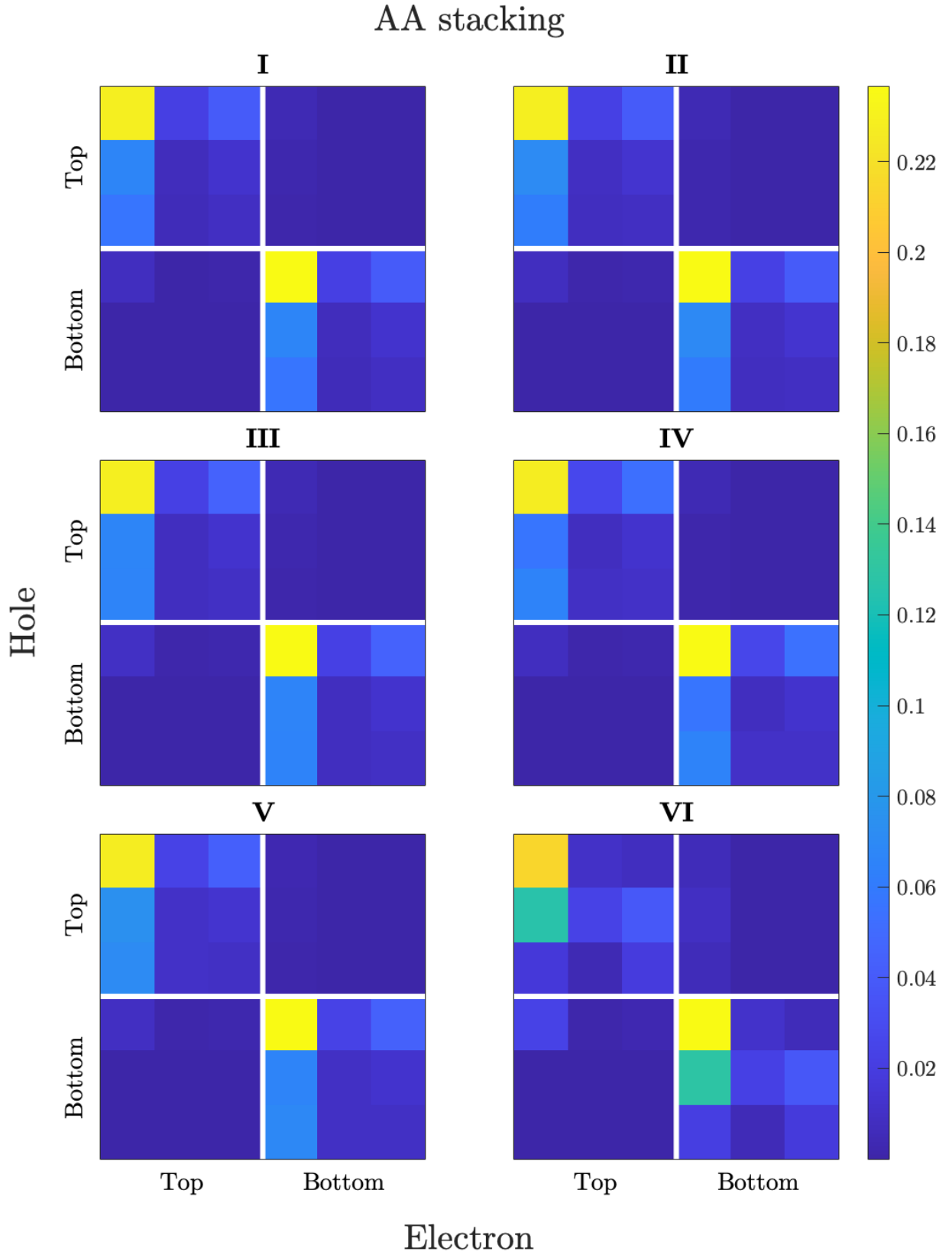


Figure 6.19: Illustration of the real space distribution of the optically active excitons in AA stacked MoS₂ bilayers. The matrix elements show the probability associated with an electron being localized on one atom and a hole on another, with the atomic positions being, in order, the top layer Mo, inner S, and outer S atoms, and the bottom layer Mo, inner S, and outer S atoms.

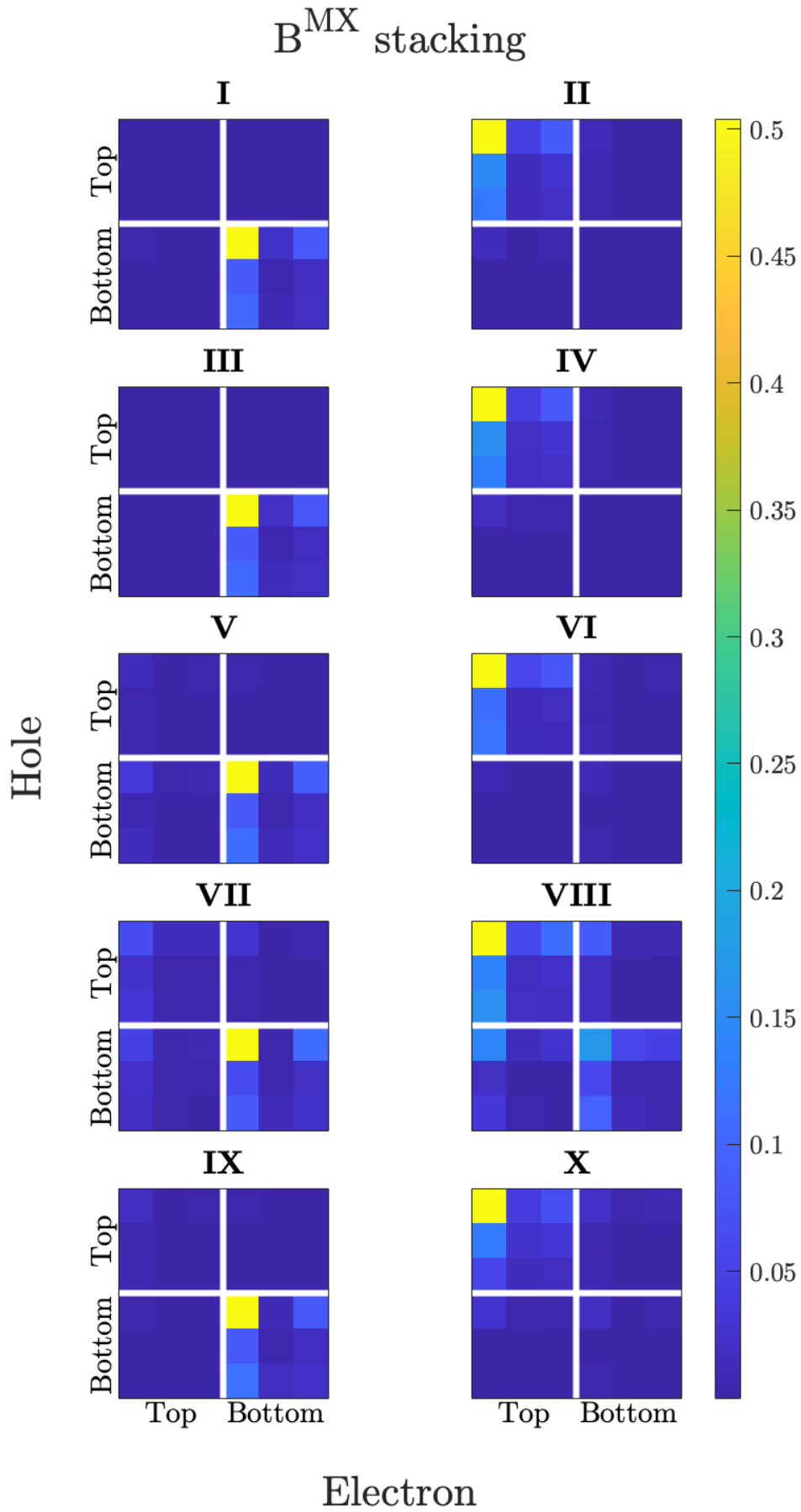


Figure 6.20: Illustration of the real space distribution of the optically active excitons in B^{MX} stacked MoS_2 bilayers. The matrix elements show the probability associated with an electron being localized on one atom and a hole on another, with the atomic positions being, in order, the top layer Mo, inner S, and outer S atoms, and the bottom layer Mo, inner S, and outer S atoms.

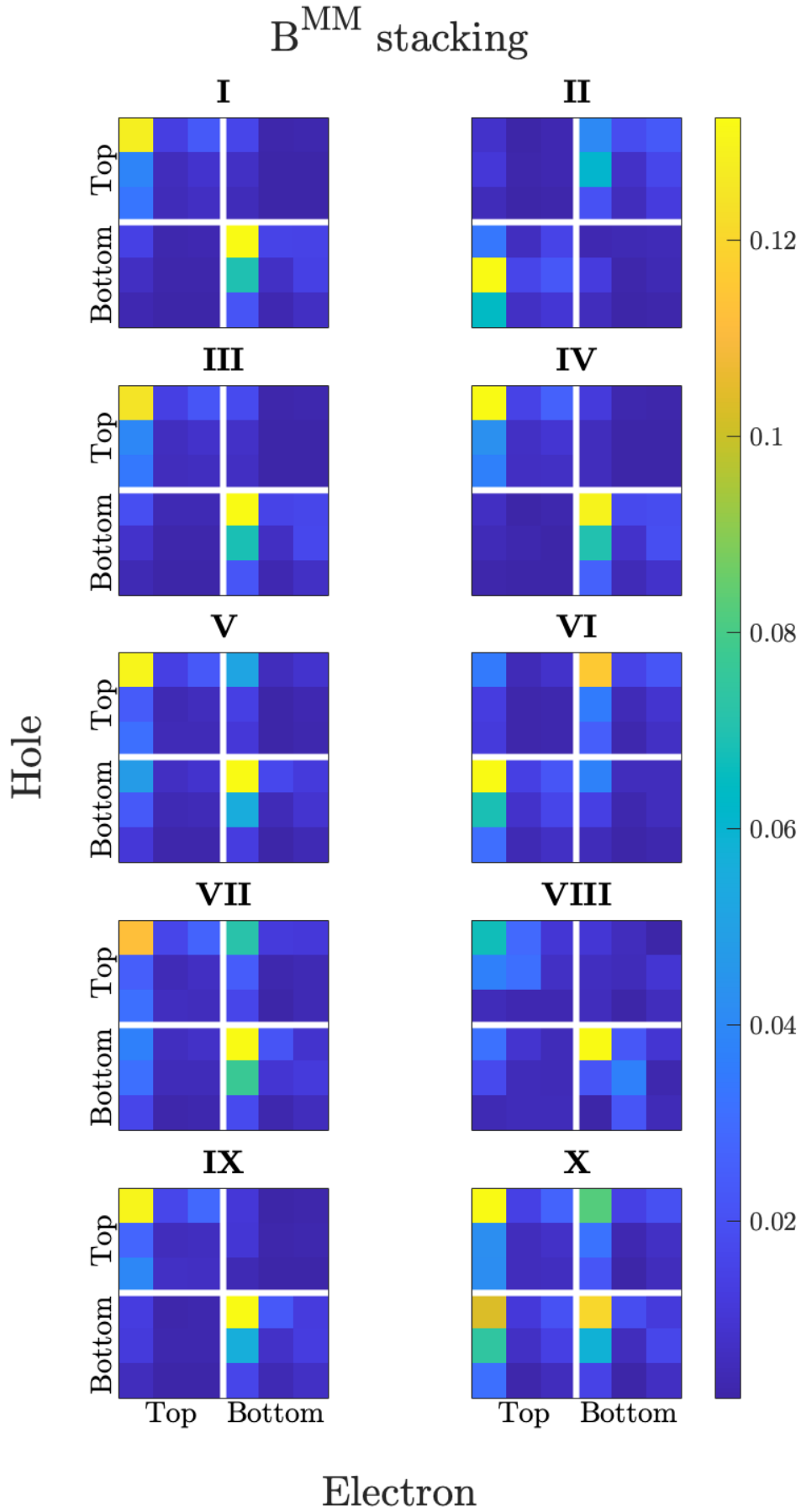


Figure 6.21: Illustration of the real space distribution of the optically active excitons in B^{MM} stacked MoS₂ bilayers. The matrix elements show the probability associated with an electron being localized on one atom and a hole on another, with the atomic positions being, in order, the top layer Mo, inner S, and outer S atoms, and the bottom layer Mo, inner S, and outer S atoms.

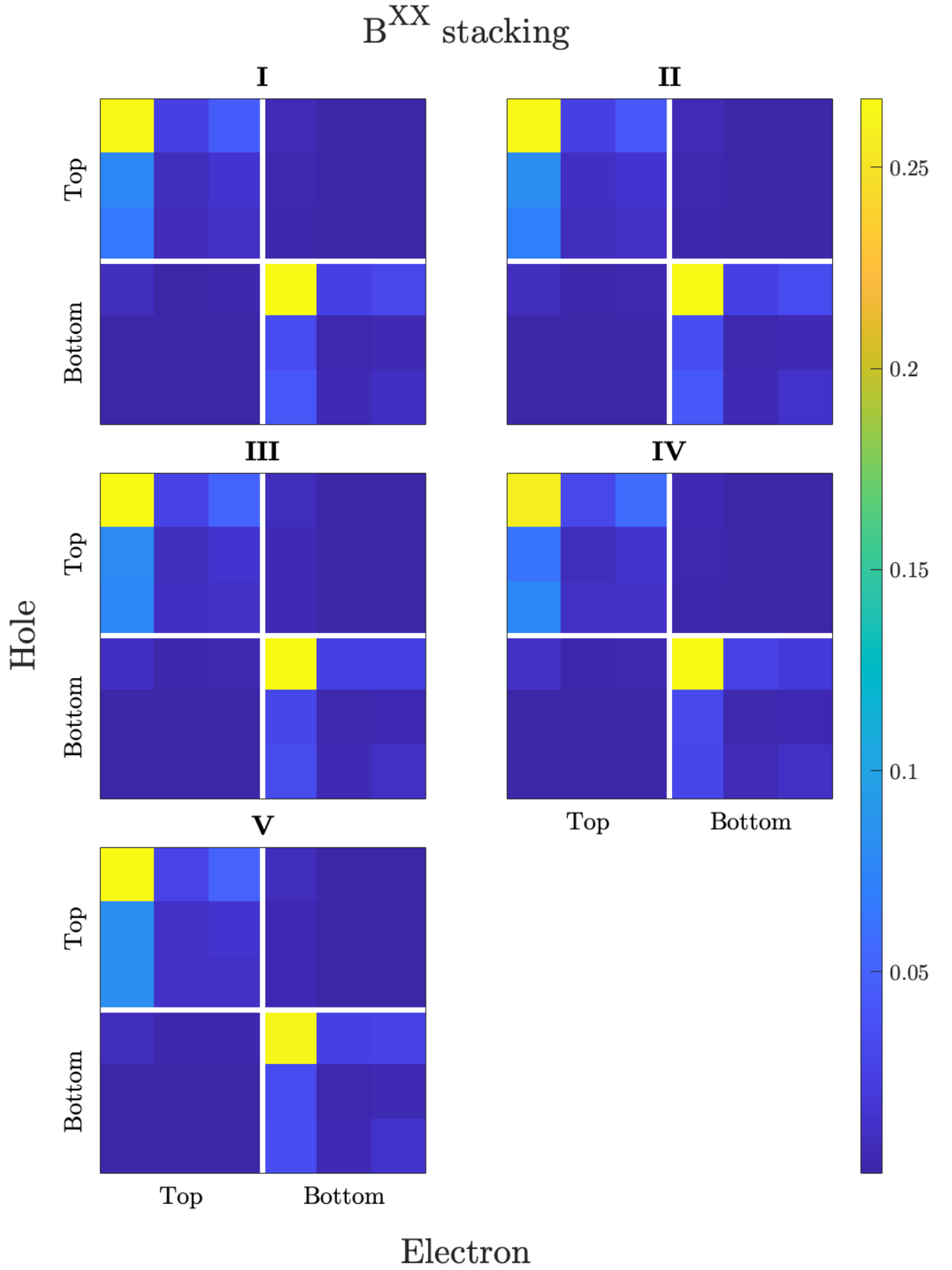


Figure 6.22: Illustration of the real space distribution of the optically active excitons in B^{XX} stacked MoS₂ bilayers. The matrix elements show the probability associated with an electron being localized on one atom and a hole on another, with the atomic positions being, in order, the top layer Mo, inner S, and outer S atoms, and the bottom layer Mo, inner S, and outer S atoms.

Chapter 7

Twisted MoS₂ homobilayers

In this chapter, I will apply the same model as discussed in the previous to twisted MoS₂ homobilayers. To do this, I will first introduce several theoretical concepts unique to commensurate twisted systems, as well as discuss atomic relaxation in the context of much larger moiré unit cells. I will then present electronic and optical spectra for MoS₂ bilayers with several different twist angles.

7.1 Commensurate lattices and moiré lattice vectors

We consider twisted TMD homobilayers where the center of rotation is located on a transition metal atom, and where a zero-degree twist angle corresponds to AA stacking, as illustrated in Fig. 7.1.

We consider commensurate twist angles, that is, twist angles that result in systems with finite lattice periodicity, and classify them by their periodicity. The moiré lattice vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ have to be integer multiples of the monolayer lattice vectors, and we write them in terms of the top layer lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ as

$$\mathbf{t}_1 = n\mathbf{a}_1 + m\mathbf{a}_2 ,$$

$$\mathbf{t}_2 = -m\mathbf{a}_1 + (n + m)\mathbf{a}_2 ,$$

where n and m are integers.

The corresponding twist angle is

$$\cos \theta = \frac{n^2 + 4nm + m^2}{2(n^2 + nm + m^2)} ,$$

and the number of atoms in the moiré supercell is given by

$$N = N_0 (n^2 + nm + m^2) ,$$

where N_0 is the number of atoms in the untwisted unit cell (in our case, $N_0 = 6$).

It is sensible to require that n and m be co-prime—if they are not, then the same physical system can be more efficiently described by their reduced equivalent (e.g. $n = 1, m = 3$ instead of $n = 2, m = 6$). One way of ensuring this, while simultaneously ensuring that angles get smaller with increased computational effort, is to require

$$m = n + 1 ,$$

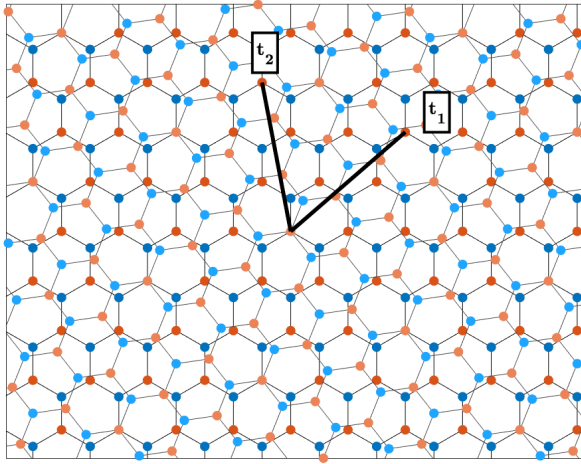
since, in this case,

$$\cos \theta = \frac{6n^2 + 6n + 1}{6n^2 + 6n + 2} ,$$

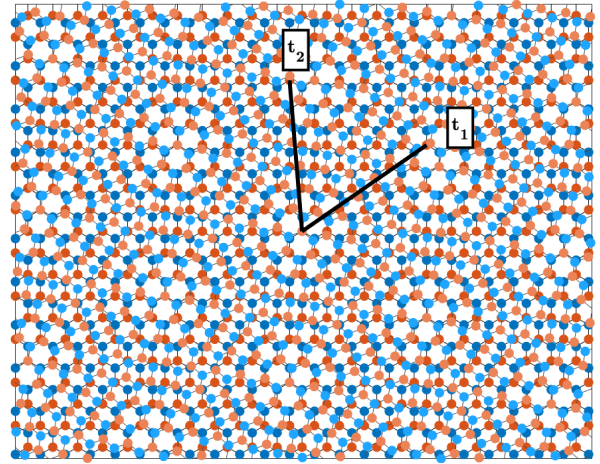
which means that if $n_1 > n_2$, then $\theta_1 < \theta_2$, and $\theta \rightarrow 0$ as $n \rightarrow \infty$.

n	m	θ	N_{atoms}	$n_k^{(18)}$	$n_k^{(30)}$	n	m	θ	N_{atoms}	$n_k^{(18)}$	$n_k^{(30)}$
1	2	21.79°	42	7	11	3	8	29.41°	582	2	3
1	3	32.20°	78	5	8	3	10	34.54°	834	2	3
1	4	38.21°	126	4	7	4	5	7.34°	366	2	4
1	5	42.10°	186	3	5	4	7	17.90°	456	2	3
1	6	44.82°	258	3	5	4	9	25.04°	798	2	3
1	7	46.83°	342	2	4	5	6	6.01°	546	2	3
1	8	48.36°	438	2	4	5	7	11.00°	654	2	3
1	9	49.58°	546	2	3	5	8	15.18°	774	2	3
1	10	50.57°	666	2	3	5	9	18.73°	906	1	2
2	3	13.17°	114	4	7	6	7	5.09°	762	2	3
2	5	27.80°	234	3	5	7	8	4.41°	1014	1	2
2	7	35.57°	402	2	4	7	9	8.26°	1158	1	2
2	9	40.35°	618	2	3	7	10	11.64°	1314	1	2
3	4	9.43°	222	3	5	8	9	3.89°	1464	1	2
3	5	16.43°	294	3	4	9	10	3.48°	1626	1	2
3	7	26.01°	474	2	3						

Table 7.1: Twist angles, number of atoms per unit cell, and k-grid finenesses equivalent to 18×18 and 30×30 monolayer k-grids for different commensurate lattices.



(a) Illustration of moiré grid for $\theta = 21.79^\circ$ twisted MoS₂



(b) Illustration of moiré grid for $\theta = 9.43^\circ$ twisted MoS₂

Figure 7.1: Illustration of moiré grids for different twist angles. Metal atoms are shown in red, chalcogen atoms in blue. The top layer is shown in more bold colours than the bottom layer. The top layer is rotated around a central metal atom relative to the bottom layer to form a commensurate lattice, with the resulting moiré lattice vectors t_1 and t_2 drawn as black arrows.

7.2 Atomic relaxation for twisted bilayers

The exact atomic structure of the unit cell is just as important in the case of twisted bilayers as it is in the case of different high-symmetric stacking configurations. However, the much larger unit cells make relaxation with DFT computationally impractical. Instead, we relax the atomic

structures using classical force fields as implemented in LAMMPS[201, 202].

The basic idea of classical force fields is to treat each simulated atom as a point mass subject to Newton's equations, with effective force fields chosen to suit the system in question[201].

As mentioned previously, the interlayer and intralayer interactions in TMD bilayers are qualitatively very differently, and are therefore approximated by two different force fields. For the strong intralayer interaction, we use a Stillinger–Weber potential[203], consisting of a two-body term V_2 depending on the distance r_{ij} of two atoms i and j , and a three-body term V_3 depending on the angle θ_{ijk} between the two bonds between atoms i and j , and i and k . It is

$$V_2(r_{ij}) = A \left(\frac{B}{r_{ij}} - 1 \right) \exp \left(\frac{\rho}{r_{ij} - r_{\max}} \right), \quad (7.1)$$

$$V_3(r_{ij}) = K \exp \left(\frac{\rho_1}{r_{ij} - r_{\max,12}} + \frac{\rho_2}{r_{ik} - r_{\max,13}} \right) \cdot (\cos(\theta_{ijk}) - \cos(\theta_0))^2. \quad (7.2)$$

Here, $r_{\max}$, $r_{\max,12}$, and $r_{\max,13}$ are cutoff radii above which the corresponding terms are zero, and A , B , ρ , K , ρ_1 , ρ_2 , and θ_0 are material dependent parameters.

For the van der Waals type interlayer interaction, we use a Kolmogorov–Crespi potential parameterized by Naik et al.[195]. The van der Waals interaction is often modelled by the Lennard–Jones potential as the sum of a long-ranged attraction term $\propto 1/r^6$ and a short-ranged Pauli repulsion term $\propto 1/r^{12}$, in which the latter term is numerical convenient and often sufficiently quantitatively accurate, but not strictly derived from physical principles[204]. This model of the Pauli repulsion falls short when considering stacked two-dimensional semiconductors, in which the overlap of the atomic orbitals which cause the repulsion is strongly dependent not only on the scalar distance r of the composite orbitals, but also on their relative orientation. Kolmogorov and Crespi[205] replace the Pauli repulsion term of the Lennard–Jones potential with an orientation-dependent, exponentially decaying repulsion term, resulting in

$$V_{ij} = \exp(-\lambda(r_{ij} - z_0)) V_p - A \left(\frac{r_{ij}}{z_0} \right)^{-6}, \quad (7.3)$$

where

$$V_\rho = C + f(\rho_{ij}) + f(\rho_{ji}) , \quad (7.4)$$

$$\rho_{ij} = \sqrt{r_{ij}^2 - (\mathbf{n}_i \cdot \mathbf{r}_{ij})^2} , \quad (7.5)$$

$$\rho_{ji} = \sqrt{r_{ji}^2 - (\mathbf{n}_j \cdot \mathbf{r}_{ji})^2} , \quad (7.6)$$

$$f(\rho) = \exp \left(- \left(\frac{\rho}{\delta} \right)^2 \right) \sum_{n=0}^2 C_{2n} \left(\frac{\rho}{\delta} \right)^2 , \quad (7.7)$$

and where r_{cut} is a cutoff radius above which the potential is set to zero, $\mathbf{n}_i$ and $\mathbf{n}_j$ are the surface normals at atomic sites i and j , respectively, λ , z_0 , A , C , C_0 , C_2 , C_4 , and δ are material parameters, given in Table 1 of Ref. [195] for TMDs.

7.3 The moiré Brillouin zone

Even with a cutoff energy, the number of atoms per unit cell (as detailed in Table 7.1 and the corresponding number of bands in even a small energy window seem at first glance to be computationally prohibitive—particularly given that, as established in Chapter 6, an 18×18 k-grid is required for converged exciton eigenenergies, and a 30×30 k-grid for the optical spectrum.

However, assuming that the convergence is a function of k-grid density rather than k-grid number, the situation is not quite as dire as that. The reciprocal lattice vector length is inversely proportional to the length of the real space lattice vectors, since

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)} , \quad (7.8)$$

where (i, j, k) is an even permutation of $(1, 2, 3)$. ($\mathbf{a}_3$ can be chosen to be $\hat{\mathbf{e}}_z$ for the two-dimensional case). This means that the area of the first Brillouin zone is inversely proportional to the area of the real space unit cell A_{uc}^θ , which can be expressed as

$$A_{\text{uc}}^\theta = \frac{N_{\text{atom}}^{\theta=0^\circ}}{N_{\text{atom}}^\theta} A_{\text{uc}}^{\theta=0^\circ} , \quad (7.9)$$

where $A^{\theta=0^\circ}$ and $N_{\text{atom}}^{\theta=0^\circ} = 6$ are the unit cell area and number of atoms per unit cell for the untwisted bilayer, and A^θ and N_{atom}^θ are the area and number of atoms per unit cell of the twisted bilayer with twist angle θ . Therefore, the number of k-points per dimension $n_k^{(x)}$ in a twisted system with twist angle θ equivalent in k-point density to $n_k = x$ in the untwisted bilayer is given by

$$n_k^{(x)} = \sqrt{\frac{N_{\text{atom}}^{\theta=0^\circ}}{N_{\text{atom}}^\theta}} x. \quad (7.10)$$

The number of k-points per dimension corresponding to converged eigenvalues ($n_k = 18$) and spectra ($n_k = 30$) in the untwisted bilayer are detailed in Table 7.1 for a variety of twist angles.

For small angles particularly, $n_k = 1$ (corresponding to Γ -point sampling) may be sufficient for converged exciton binding energies. For some systems, $n_k = 2$ seems sufficient. The potential problem here is that 2 is not divisible by three¹, and therefore the high-symmetry points of the mini Brillouin zone are not included in the grid. When computationally possible, I will therefore attempt to use at least $n_k = 3$.

7.4 Dependence of electronic structure on twist angle

Next, I will analyse the impact of twist angle on the electronic structure of twisted MoS₂ homobilayers. Figures 7.2 and 7.3 show the (relaxed, sixth-nearest neighbour) band structures for different twist angles. The most obvious impact is on the number and curvature of bands, which is due to the band folding described in the previous section. Figures 7.2 and 7.3 also show the impact of including sixth nearest neighbour hoppings to the electronic bandstructures of twisted bilayers. As the number of bands increases with increasing unit cell size (and therefore, in our choice of systems, decreasing twist angle), it is difficult to make out details of the impact of longer-ranged hoppings on the systems with small twist angle. In the systems with larger twist angles, Fig. 7.2, it can be seen that, as before, the conduction manifold is more strongly

¹citation needed

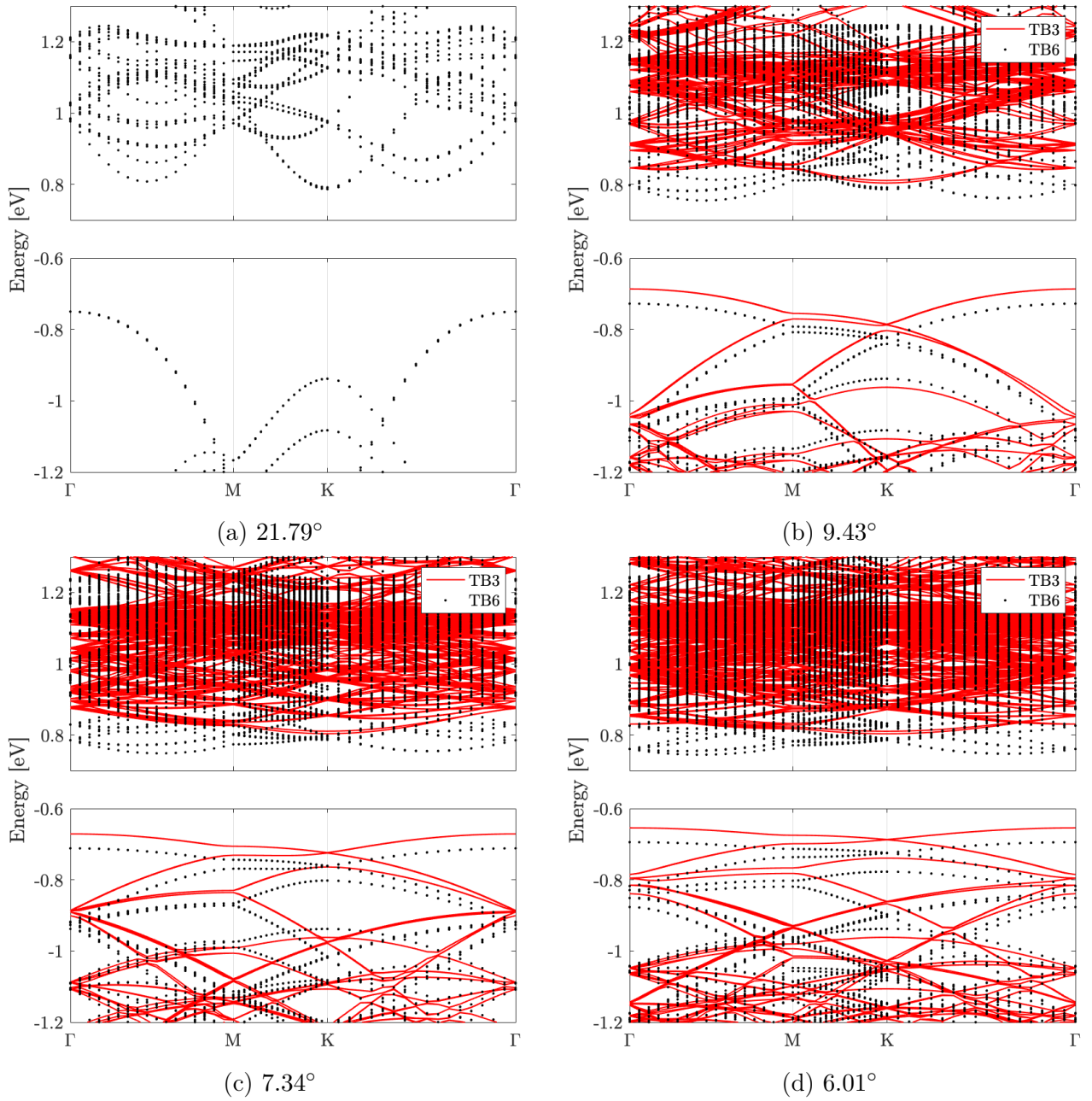


Figure 7.2: Bandstructures for different relaxed twisted MoS_2 homobilayers with up to sixth-nearest neighbour hoppings and spin-orbit coupling.

impacted by longer-ranged hoppings than the valence manifold.

Figure 7.4 shows the average interlayer distance, as well as the direct and indirect gap energies depending on twist angle. The dependence appears to be very smooth, with the interlayer distance decreasing with decreasing twist angles. This dependence is stronger with smaller twist angles, and appears to be flattening out with larger twist angles.

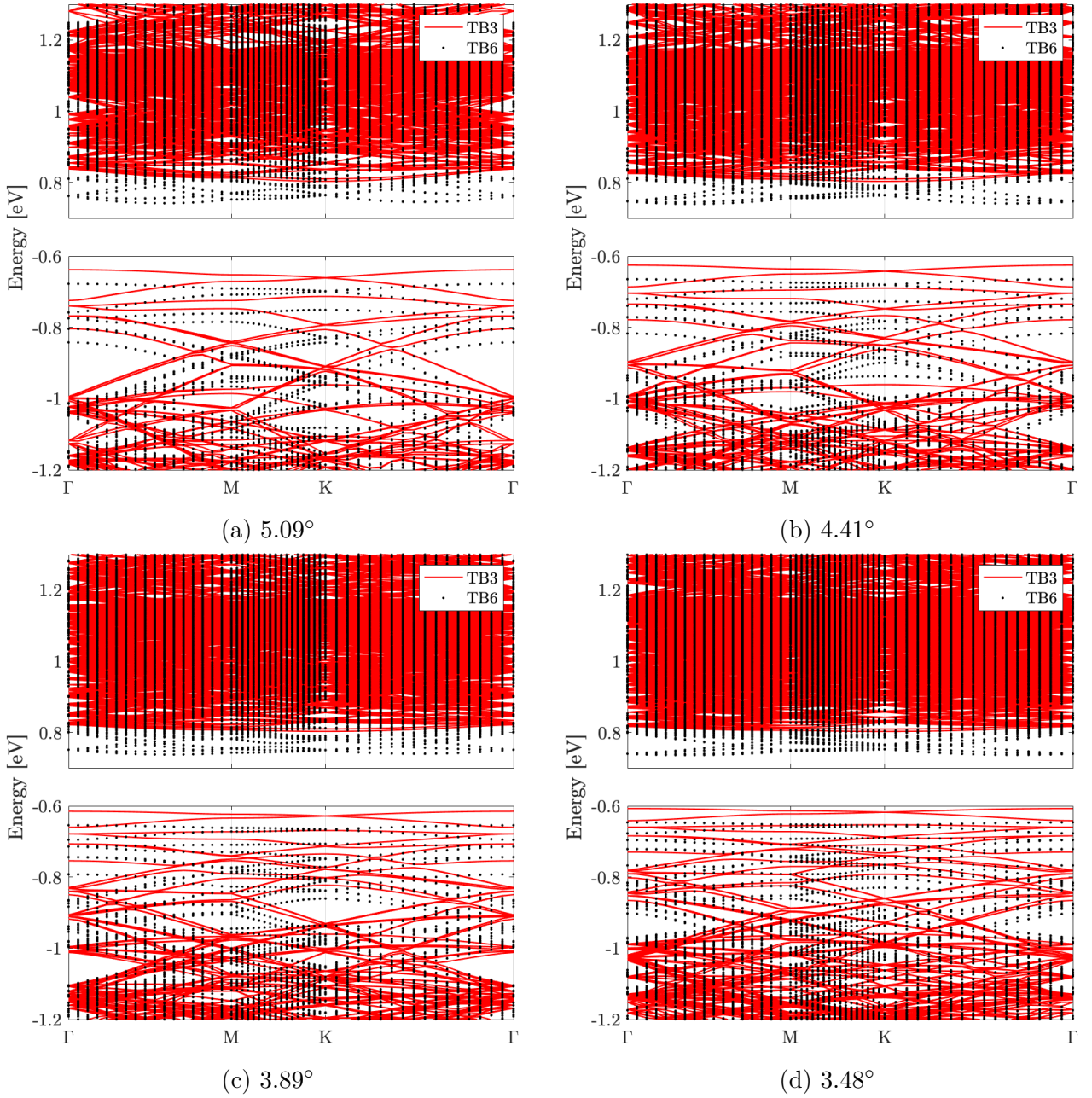


Figure 7.3: Bandstructures for different relaxed twisted MoS_2 homobilayers with up to sixth-nearest neighbour hoppings and spin-orbit coupling.

Liu et al.[55] measured the stacking configuration and twist angle dependence of the interlayer separation of MoS_2 bilayers. They only considered relatively large twist angles, between 13° - 47° . They found that for the systems they considered, the interlayer separation did not strongly depend on twist angle for the twisted systems. Instead, all four twisted systems had an interlayer separation smaller than that for AA and B^{xx} stacking, but larger than the other high-symmetry stackings.

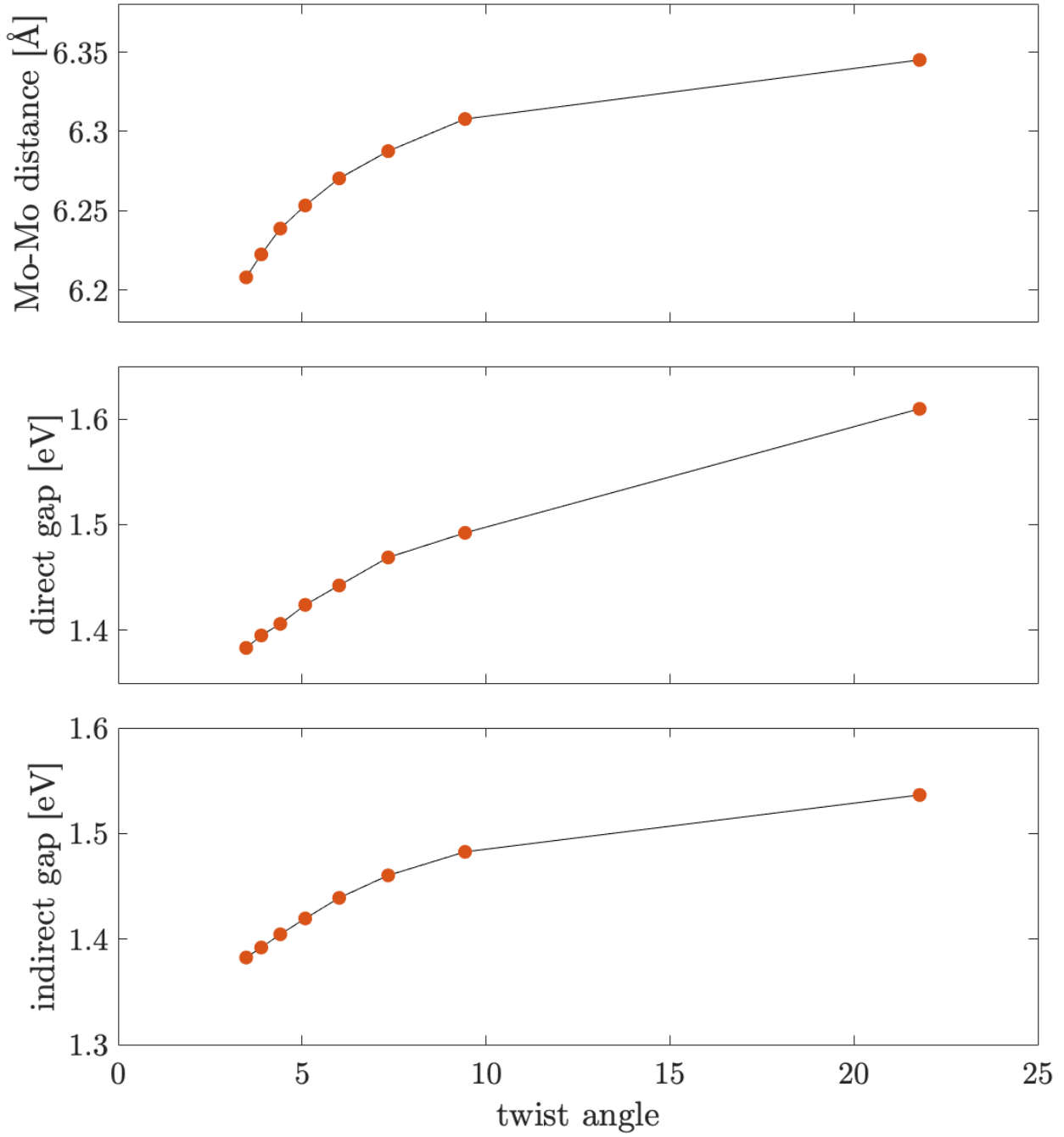


Figure 7.4: Dependence of interlayer distance, and direct and indirect bandgaps on twist angle for relaxed tight-binding calculations including up to sixth-nearest neighbour hoppings and spin-orbit coupling.

We are able to reproduce the high-symmetry stacking dependence of the interlayer separation reported by Liu et al., see Tab. 6.1. Similar to what they report, we find that 22° stacking has an interlayer separation smaller than AA and B^{XX} stacking, and larger than AB, B^{MX} , and B^{MM} stacking. The other three angles considered in Ref. [55] are all located in the more

21.79°		5.09°	
$c_{\min}$	9: 0.808 36: 0.787 46: 0.808	$c_{\min}$	11: 0.742 46: 0.745
$v_{\max}$	1: -0.750 36: -0.938	$v_{\max}$	1: -0.678
direct	7: 1.610	direct	9: 1.424
indirect	1.537	indirect	1.420
9.43°		4.41°	
$c_{\min}$	9: 0.755 36: 0.786 47: 0.761	$c_{\min}$	8: 0.740 48: 0.741
$v_{\max}$	1: -0.728	$v_{\max}$	1: -0.665
direct	7: 1.492	direct	6: 1.406
indirect	1.483	indirect	1.405
7.34°		3.89°	
$c_{\min}$	10: 0.749 36: 0.786 46: 0.754	$c_{\min}$	12: 0.738 45: 0.740
$v_{\max}$	1: -0.712	$v_{\max}$	1: -0.654
direct	8: 1.469	direct	9: 1.395
indirect	1.460	indirect	1.392
6.01°		3.48°	
$c_{\min}$	8: 0.745 48: 0.747	$c_{\min}$	7: 0.736 49: 0.737
$v_{\max}$	1: -0.712	$v_{\max}$	1: -0.646
direct	7: 1.443	direct	6: 1.383
indirect	1.439	indirect	1.382

Table 7.2: Location and magnitude of conduction band minima $c_{\min}$, valence band maxima $v_{\max}$, and direct and indirect gaps in eV for different twist angles in twisted MoS₂ homobilayers in the sixth nearest neighbour model. The location of the band extrema refers to k-point index of a 54 point bandstructure calculation with 18 evenly spaced k-points each between Γ , M, K, and Γ , so 36 corresponds to the K point, 9 to the Q point, etc.

flattened-out regime of Fig. 7.4. In this way, the two conflicting statements of twist-angle dependence or no twist-angle dependence may be reconcilable, although further research is needed to be certain.

A reason that a twist-angle may be expected is that in a relaxed unit cell, the larger unit cell size of smaller twist angles results in a relatively smaller fraction of areas with AA like stacking, which is energetically unfavourable and results in larger interlayer distances.

The dependence of the indirect gap energy on the twist angle is likely an actual dependence of the indirect gap on the interlayer dependence. This dependence was observed in DFT calculations again in Liu et al.[55], in which direct and indirect bandgaps were calculated for B^{MX} stacking with artificially varied interlayer separation. They found a strong dependence of the

indirect gap, which decreased with decreasing interlayer separation, but only weak dependence of the direct gap.

The dependence of the direct gap on twist angle that we observe in the middle figure in Fig. 7.4 seems on first glance to be a contradiction of this. This is a consequence of band folding and will be discussed in more detail in section 7.5.

Somewhat related to this fact is the observation that in twisted systems, the direct gap is no longer necessarily located at a high-symmetry point. In fact, looking at Table 7.2, the direct gap is usually located in the vicinity of the Q point, but only at the Q point in the case of 5.09° and 3.89° . This is despite the fact that the band extrema tend to still be located at high-symmetry points at least for the larger twist angles. This can be understood when looking at the band structure plots in Figs. 7.2 and 7.3, particularly the band structure for the 21.79° twisted system shown in the top left panel of Fig. 7.2. Here, the bottom conduction band has a steep minimum at Q, and the top valence band has a somewhat shallower maximum at Γ , and the minimum of the distance between the two is somewhere between Γ and Q.

It is important to note that this results in some convergence problems for the medium angles. The high symmetry points Γ and K are included in a 3×3 k-grid, but e.g. the point 7/18th of the way between Γ and M needs a much finer grid to be included. For very small angles, the bands become so flat that not including the actual minimum of the direct gap does not matter, and for very large angles, finer k-grids are accessible. However, for some of the medium angles, the BSE matrix sizes and therefore the k-grid fineness currently achievable in this code is not necessarily sufficient to capture the low-energy excitons accurately.

7.5 Dependence of optical spectra on twist angle

Figure 7.5 shows the optical spectra of twisted MoS_2 homobilayers in vacuum dependent on twist angle, with 21.79° on top in dark blue and 3.89° on the bottom in dark red.

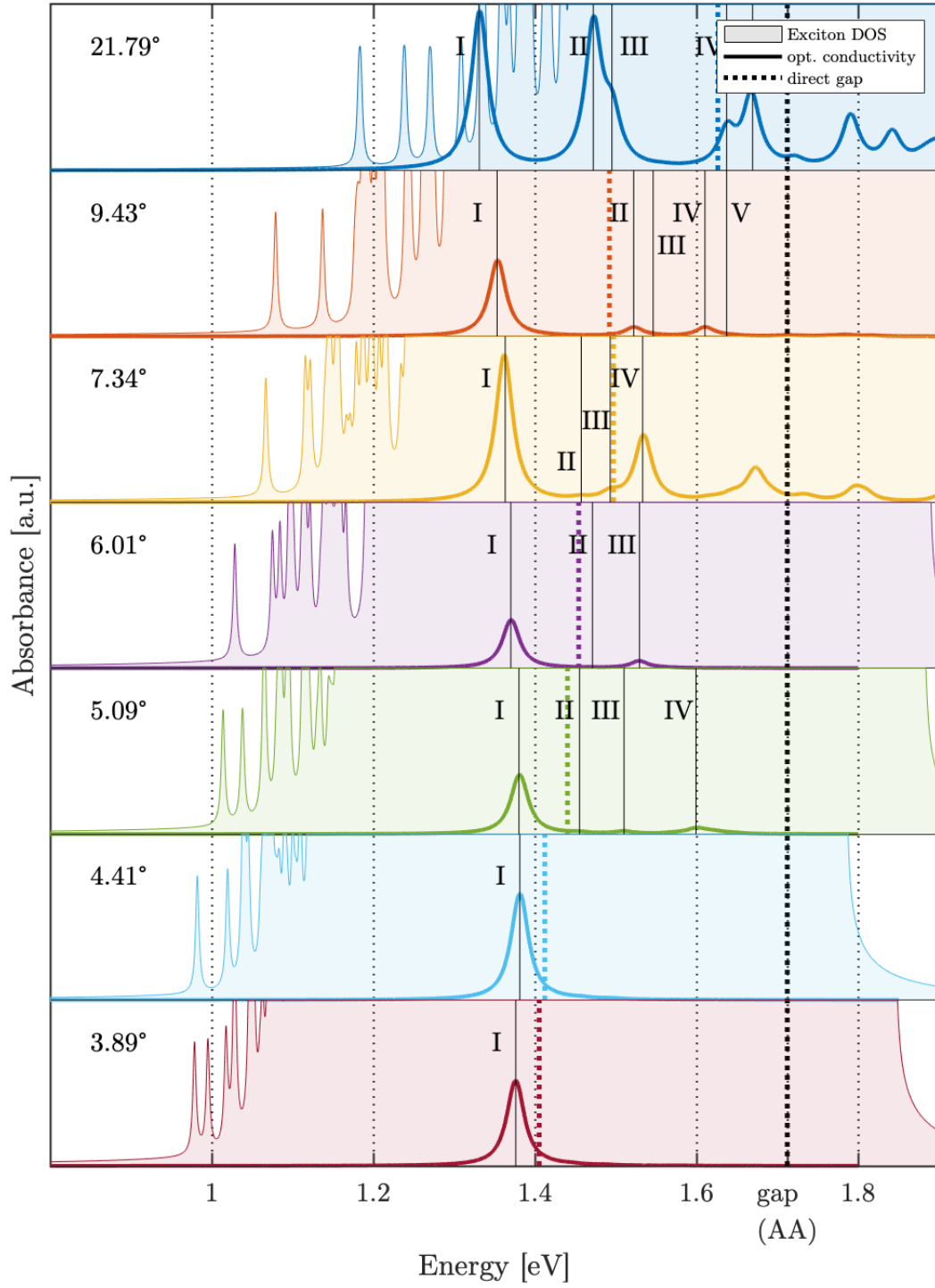


Figure 7.5: Comparison of optical absorption spectrum and exciton DOS for different twist angles.

There are two features of these spectra in particular which are unexpected at first glance.

Firstly, the overall optical conductivity appears to decrease with twist angle, and the number of peaks appears to decrease, from a complex looking spectrum with several peaks for the 21.79° system to a single, small peak very close to the direct bandgap (indicated as a dotted vertical line in the same color as the corresponding spectrum) in the 3.89° system.

Secondly, the energy of the first optical peak seems to barely depend on the twist angle. This seems at odds with the previous observation that the binding energy of the first excitons does not strongly depend on the twist angle but that the direct bandgap does. Figure 7.5 also shows the exciton joint density of states (JDOS), that is, roughly the number of excitons for a given energy regardless of whether or not those excitons are optically active. This is shown with a thin, filled in curve. The energy of the first peak of the JDOS corresponds to the first exciton energy given in Table 7.3.

It is at this point that we need to ask ourselves two questions. Firstly, is the assumption that 0.5 eV above the direct gap is a sufficiently high cutoff energy for convergence justified? Looking at Fig. 7.5, the answer to this is clearly no. And secondly, why exactly does the direct gap depend on the twist angle at all? The answer to this is slightly more complicated, but boils down to the following: it does not, at least not directly. Instead, the direct gap depends on the size of the moiré cell.

The direct gap of twisted bilayers is not the same as the direct layer of untwisted bilayers, even in the absence of interlayer hopping. A calculation of the tight-binding band structure of a moiré system without interlayer interaction would be effectively a supercell calculation of an untwisted system (not including the effect of atomic relaxation), which means that the monolayer bandstructure is folded into the moiré Brillouin zone, as illustrated in Fig. 7.6. This means that the direct gap of the twisted calculation could be resulting from an indirect gap from a unit cell calculation projected onto a direct gap.

This has two consequences.

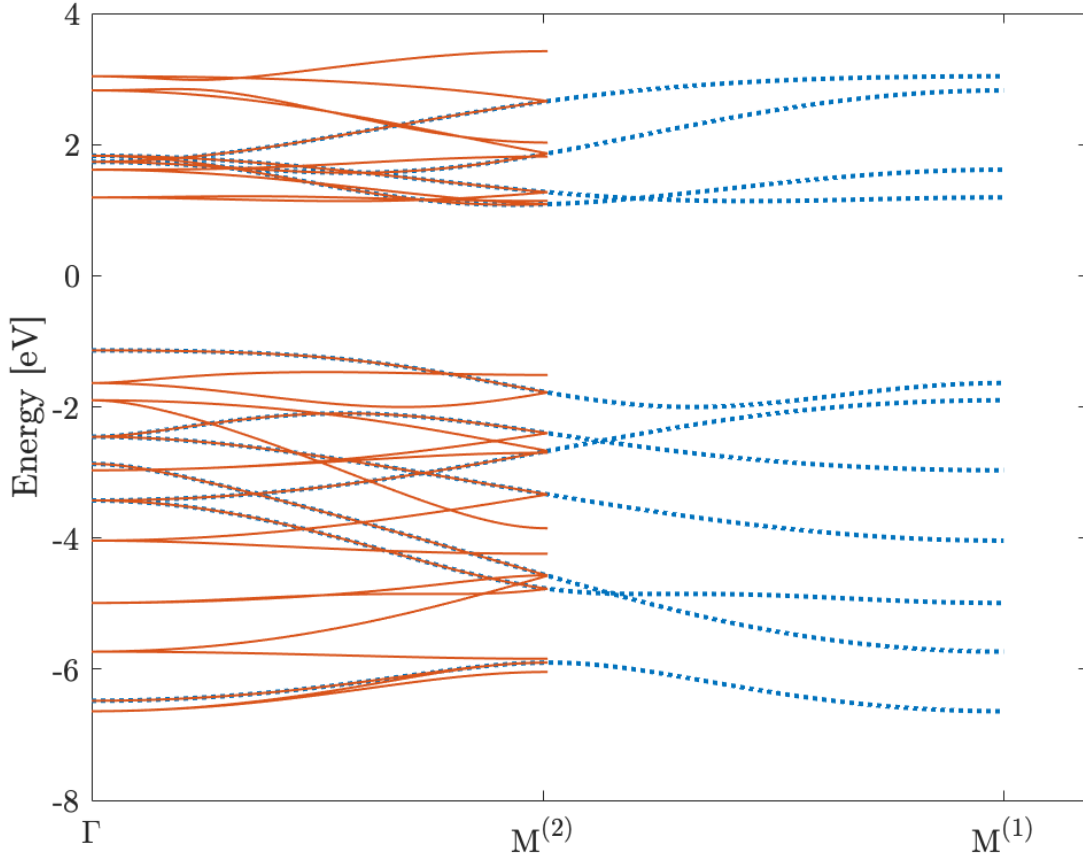


Figure 7.6: Illustration of the band folding resulting from using a 2×2 supercell calculation (red solid line) of an MoS_2 monolayer compared to a unitcell calculation (blue dotted line) between Γ and M , where $M^{(2)}$ is the M point of the supercell calculation and $M^{(1)}$ is the M point of the unit cell calculation.

Firstly, the direct gap in some twisted calculations is “secretly” momentum indirect, and the resulting low-energy excitons will be optically inactive, as can be clearly seen in Figure 7.5. This is due to momentum conservation. Photon momenta are too small to directly excite an exciton with non-zero momentum. And secondly, the direct gap can also have a twist angle dependence. This, again, can be due to two factors. Firstly, the indirect gap that is being projected onto a direct gap can have interlayer distance dependence and therefore twist angle dependence. And secondly, smaller twist angles in our choice of angles correspond to a larger moiré cell and therefore a larger number of projected bands in the moiré Brillouin zone, which means that statistically there is a higher chance of having a small indirect gap projected onto a direct gap.

This explanation is further supported by the band transitions which contribute most to the first optically active excitons, see Tables D.39, D.44, D.49, D.53, D.56, D.60, and D.61 in Appendix D. These bands get further away from the gap as the twist angle decreases.

This means among other things that calculating the exciton binding energy by subtracting the excitation energy from the direct bandgap energy (as shown in Table 7.3) is inaccurate, although Table 7.3 still accurately shows the binding energies of the lowest-energy, optically dark excitons.

To calculate the binding energy of the lowest-energy optically active excitons, I instead calcu-

θ	n_k	E^{gap}	E^{cutoff}	E^{exc}	E^{bind}
21.79°	2 (5)	1.726	2.0	1.222	0.504
			2.2	1.221	0.505
	3 (8)	1.725	2.0	1.233	0.492
			2.2	1.226	0.499
	9 (24)	1.626	2.2	1.182	0.444
			2.3	1.182	0.444
9.43°	1 (6)	1.525	2.5	1.014	0.511
	3 (18)	1.520	1.9	1.078	0.442
			2.0	1.078	0.442
	6 (36)	1.492	1.8	1.079	0.413
7.34°	1 (8)	1.497	2.2	1.019	0.478
	2 (16)	1.497	2.0	1.067	0.430
6.01°	1 (10)	1.455	2.1	0.999	0.456
	3 (29)	1.454	1.8	1.028	0.426
5.09°	1 (11)	1.440	1.95	0.999	0.441
	2 (22)	1.440	1.8	1.014	0.426
4.41°	1 (13)	1.412	1.85	0.982	0.430
3.89°	1 (16)	1.405	1.85	0.979	0.426
3.48°	1 (16)	1.386	1.8	0.967	0.409
	2 (32)	1.386	1.65	0.973	0.403

Table 7.3: Binding energies of lowest energy excitons in twisted systems.

late the difference between the excitation energy and the transition energy of the main transition involved in the exciton. This is shown in Table 7.4. Both binding energies are shown in Figure 7.7 for the same convergence parameters for each respective twist angle.

θ	n_k	v	c	E_{trans}	E_{exc}	E_{bind}
21.79°	9×9	v_1	c_1	1.725	1.331	0.394
9.43°	6×6	v_7	c_1	1.724	1.353	0.371
7.34°	2×2	v_{11}	c_8	1.799	1.360	0.439
6.01°	3×3	v_{14}	c_5	1.724	1.368	0.366
5.09°	2×2	v_{22}	c_7	1.757	1.378	0.379
4.41°	1×1	v_{30}	c_{34}	1.832	1.377	0.455
3.89°	1×1	v_{40}	c_{35}	1.805	1.372	0.433

Table 7.4: Binding energies of lowest-energy optically active excitons in twisted MoS_2 homobilayers in vacuum.

The binding energies of both lowest energy excitons and lowest energy optically active excitons do not depend strongly on twist angle, the latter being in agreement with experimental results[57].

However, since the optically active excitons are at higher energy, they are less well converged at the same cutoff energy. They also appear to be less well converged with k-grid, which may explain the spikes at 3.89° , 4.41° , and 6.01° , which all have k-grids smaller than 3×3 .

The reader may at this point be wondering why I am still presenting results of a calculation that is clearly unconverged.

Assuming as a next approximation that 0.5 eV above the transition energy corresponding to the bands involved in the lowest energy optically active exciton (an actual convergence study would be needed, but is not feasible for reasons which are about to become apparent), the necessary BSE matrix sizes are listed in Table 7.5. Unfortunately, with the current computing power available to me, it is not possible to store most of these matrices, let alone diagonalize them, with the exception of the 21.79° twisted system.

However, I believe it is still possible to derive at least some qualitative information from the calculations which I was able to perform. It can be seen from the convergence studies in the previous chapter that, while the energy and magnitude of the peaks in the optical spectra

θ	n_k	E_{cutoff} (eV)	BSE rank	memory
21.79°	9×9	2.225	15,224	1.8 GB
9.43°	6×6	2.224	348,144	969 GB
7.34°	2×2	2.299	175,896	248 GB
6.01°	3×3	2.224	620,120	3.1 TB
5.09°	2×2	2.257	664,368	3.5 TB
4.41°	1×1	2.332	432,480	1.5 TB
3.89°	1×1	2.305	652,608	3.4 TB

Table 7.5: BSE matrix sizes for a bandgap of 0.5 eV above the transition energy of the main transition involved in the lowest-energy optically active excitons, including an estimate of memory needed to store the matrix in double precision. This is a minimum size for convergence of the exciton binding energy (not the spectrum), and only includes the k-grid sizes included in the calculations presented in this chapter.

change with increasing cutoff energy in the unconverged systems, they do not do so unsystematically, and the two-peak structure is present even for quite small cutoff energies (see Fig. 5.6).

In the remainder of this chapter, I will analyse the properties of the optically active excitons in the optical spectra of twisted MoS₂ homobilayers.

7.6 Impact of twist angle on layer character of optically active excitons in untwisted MoS₂ homobilayers

Finally, we can analyze the composite bands and the layer character of the optically active excitons in twisted MoS₂.

Note that because of the large number of optically inactive band transitions, I will start referring to the n -th conduction band and n -th valence band as c_n and v_n , respectively.

21.79°

Peak I at 1.331 eV is a doubly degenerate exciton strongly localized at K and K', consisting of a transition from v_1 to the c_1 at K and from v_2 to c_2 at K' (see Table D.39). (Note however, that the

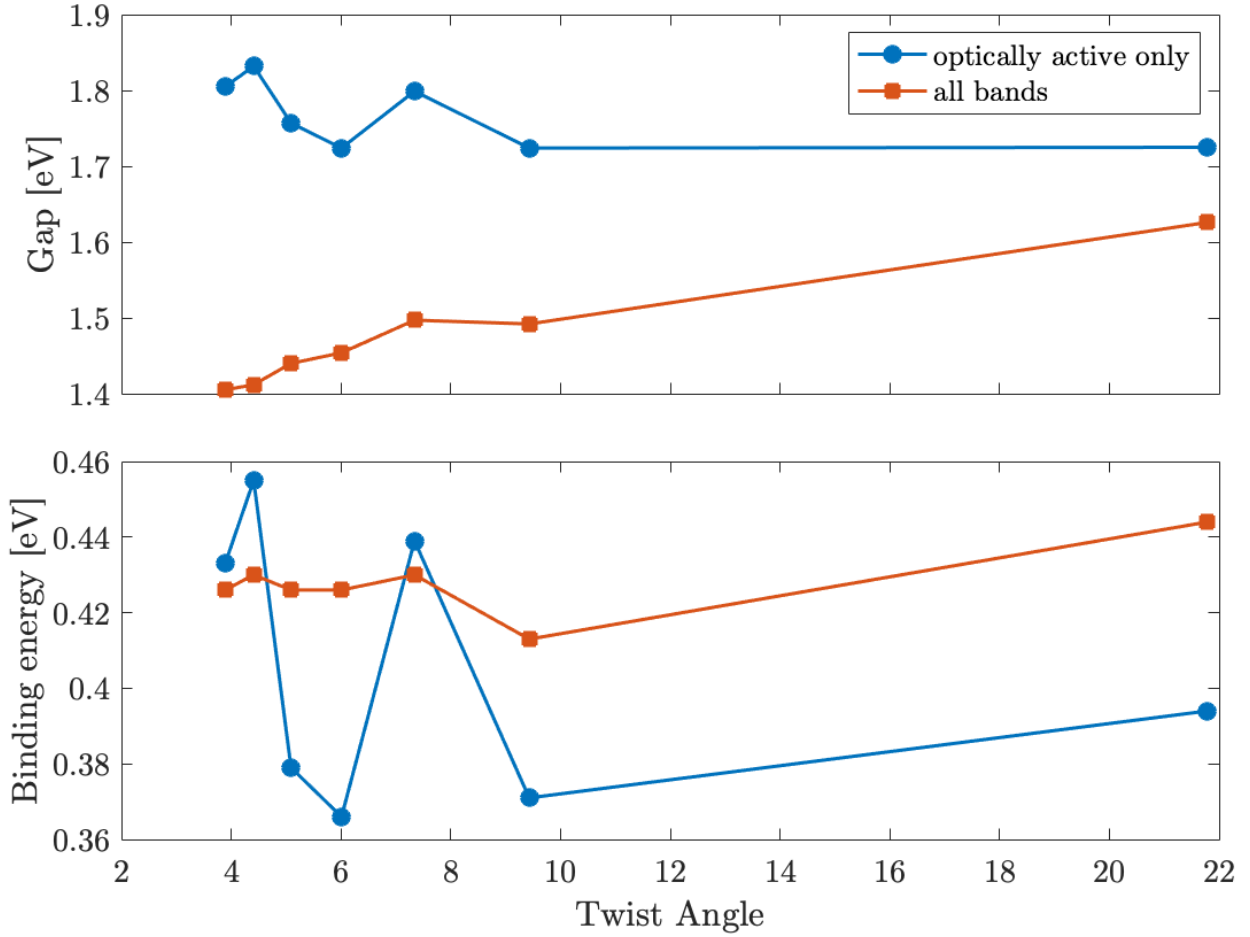


Figure 7.7: Comparison of direct gap (top) and lowest-exciton binding energy (bottom) for all excitons in the calculation (blue) vs. only optically active excitons (red). Note that "optically active bandgap" here refers to the transitions energy of the band transitions which most contributes to the lowest energy optically active exciton.

first optically active exciton is not the lowest energy excitation, but rather the 49th lowest one.)

Peak II at 1.472 eV consists of two excitons very close in energy, both localized at K and K'. The first one is doubly degenerate and consists of transitions between v_3 and c_2 . The second one is not degenerate, and consists of transitions between v_4 and c_4 (see Table D.40).

Peak III at 1.495 eV is a doubly degenerate exciton strongly localized at K and K', containing transitions from v_1 to c_1 and v_2 to c_2 (see Table D.41).

Peak IV is composed of two nondegenerate excitons at 1.637 eV and 1.638 eV. The first consists of transitions between v_3 and c_3 at K and K'. The second consists of transitions between v_4 and

c_4 at K' only (see Table D.43). No equivalent exciton at K is optically active. This is unlikely to be physical. The moiré lattice still has threefold rotational symmetry and so, therefore, should the energy landscape in reciprocal space. This may be due to a bug in the code.

Peak V is composed of one doubly degenerate exciton at 1.667 eV and one nondegenerate exciton at 1.669 eV. Both are spread around near K and K' . The first contains transitions from v_1 to c_3 , and second contains transitions from v_2 to v_4 (see Table D.43).

Figure 7.8 shows the real space distribution of the optically active excitons in 21.79° twisted MoS_2 bilayers. The internal ordering of the orbitals in the model is such that the first half corresponds to one layer and the second to another, and also that within a layer, all of the d-orbitals on the Mo atoms come first, and then the p-orbitals on the S atoms.

All optically active excitons in this stacking appear to be intralayer excitons, and the constituent electrons and holes are located almost exclusively on the Mo atoms.

Note that, in Fig. 7.8, there is a strong layer asymmetry between top and bottom layer, for example in Peak II (top right). Similar asymmetries can be seen for the other twist angles, Figs. 6.18-7.14. There are several possible reasons for this. It may simply be a numerical problem. However, consider the layer asymmetry of excitons in B^{MX} stacked bilayers, see Fig. 6.20. B^{MX} and B^{XM} stacked bilayers form a symmetry pair, in which both stackings have layer asymmetry, that is, the top layer is physically distinct from the bottom layer. The same is true for the twisted systems. It is possible that symmetry would be restored by twisting a given system anticlockwise instead of clockwise. However, further research would be needed to confirm this.

9.43°

Peak I consists of two doubly degenerate excitons, one at 1.353 eV, and one at 1.354 eV. Both are localized near K and K' and contains transitions from v_7 to c_1 and v_8 to c_2 (see Table D.44).

Peak II consists of one nondegenerate exciton at 1.520 eV and one doubly degenerate exciton at 1.523 eV. Both are strongly localized at K and K' and contain transitions from v_7 to c_1 and v_8 to c_2 (see Table D.45).

Peak III at 1.546 eV is a nondegenerate exciton spread out in reciprocal space and consisting of transitions between v_{12} and c_{16} , and v_{11} and c_{15} (see Table D.46).

Peak IV consists of three doubly degenerate excitons near 1.609 eV, and one nondegenerate exciton at 1.612 eV. All constituent excitons are spread out in reciprocal space and consist of transitions between v_7 , v_8 , v_9 and c_2 - c_{11} (see Table D.47).

Peak V at 1.637 eV is a nondegenerate exciton spread out in reciprocal space and consisting of transitions between v_7 - v_{10} and c_8 - c_{24} (see Table D.48).

Figure 7.9 shows the real space distribution of the optically active excitons in 9.43° twisted MoS_2 bilayers. Again, all of the constituent electrons and holes are localized on the Mo atoms, but the layer character of the peaks is much more interesting than in the previous system. The first peak is an intralayer peak, but the second and fourth peak are hybrid, and the third and fifth peak are intralayer peaks.

7.34°

Note that due to computational problems, the only data included in this chapter for a 7.34° twist angle was calculated using a 2×2 k-grid. This means that due to symmetry, most of the excitons are spread out in k-space, since the direct gap is not included in the gap. The gap is significantly larger at the Γ point than anywhere else, and most excitons involved in the subbandgap optical peaks are spread around every k-point except Γ .

Peak I is composed of one nondegenerate exciton at 1.360 eV and one doubly degenerate exciton

at 1.363 eV. The first consists of transitions from v_{11} and v_{12} to c_7 and c_8 . The second consists of transitions from v_{11} to c_{11} and v_{12} to c_{12} (see Table D.49).

Peak II at 1.457 eV consists of a nondegenerate exciton consisting of transitions from v_{13} to c_{11} and v_{14} to c_{12} (see Table D.50).

Peak III at 1.493 eV consists of a two nondegenerate excitons very close to each other in energy. They are the only excitons in this series which are somewhat localized, in between K and K'. It consists of transitions from v_{12} - v_{14} to c_8 - c_{13} (see Table D.51).

Peak IV is composed of six nondegenerate excitons with energies from 1.532 eV - 1.535 eV. They consist of transitions from valence states similar to previous excitons in this spectrum to conduction bands as high as c_{80} (see Table D.52).

Figure 7.10 shows the real space distribution of the optically active excitons in 7.34° twisted MoS₂ bilayers. The second peak is almost purely interlayer, all other peaks are intralayer peaks.

6.01°

Peak I is composed of two doubly degenerate excitons and four nondegenerate excitons. The first degenerate exciton pair has an energy of 1.368 eV, all other excitons are found near 1.371 eV. Some are well localized at K and K', others are more spread out in reciprocal space. They mostly consist of transitions from v_{14} and v_{15} to c_5 and c_8 , but some of the more spread out excitons include transitions from bands much further away from the gap (see Table D.53).

Peak II is composed of a single nondegenerate exciton at 1.471 eV. It contains transitions from v_{15} to c_{39} and v_{14} to c_{40} (see Table D.54). It is intralayer in character (see Fig. 7.11).

Peak III is composed of two nondegenerate excitons, one at 1.528 eV and one at 1.529 eV. The first appears to be localized at K' and the second at K, which again seems unlikely to be

physical. The first contains transitions from v_{14} to c_5 and c_{10} , the second contains transitions from v_{15} to c_8 and c_4 (see Table D.55).

Figure 7.11 shows the real space distribution of the optically active excitons in 6.01° twisted MoS_2 bilayers. The second peak is almost purely interlayer, all other peaks are intralayer peaks with small interlayer contributions.

5.09°

Peak I consists of two pairs of doubly degenerate excitons, one at 1.378 eV and one at 1.382 eV. All are spread out in reciprocal space away from Γ . They contain transitions from v_{22} and v_{23} to c_6 , c_7 , c_{11} , and c_{12} (see Table D.56).

Peak II contains a single nondegenerate exciton at 1.455 eV. It is spread around reciprocal space with the main contribution arising from inbetween K and K', and it involves transitions from v_{23} and v_{24} to c_8 and c_{11} (see Table D.57).

Peak III consists of two nondegenerate excitons at 1.509 eV and 1.510 eV. Both are localized inbetween K and K', and contain the same transitions as peak II (see Table D.58).

Peak IV consists of three nondegenerate excitons near 1.599 eV. The first and third are strongly localized at the Γ point, and the second is spread out in reciprocal space. The first contains transitions from v_{18} , v_{20} , and v_{23} to c_{14} , c_{24} , and c_{25} . The third contains transitions from the same valence bands as the first, to c_{25} , c_{28} , and c_{30} . The second contains transitions from v_{22} and v_{23} to c_{125} and c_{172} (see Table D.59).

Figure 7.12 shows the real space distribution of the optically active excitons in 5.09° twisted MoS_2 bilayers. The second peak is almost purely interlayer, peaks I and III are intralayer peaks, and peak IV is a hybrid peak.

4.41°

The remaining two angles have been computed using only Γ point grids, so all following excitons are trivially localized at Γ .

The only peak, peak I, consists of two pairs of doubly degenerate excitons, one at 1.378 eV and one at 1.382 eV. The first contains transitions from v_{29} - v_{32} to c_{29} , c_{30} , c_{33} , and c_{34} . The second contains transitions from the same valence bands as the first, to c_{33} , c_{34} , and c_{47} - c_{50} (see Table D.60).

Figure 7.13 shows both these excitons are almost entirely intralayer.

3.89°

The only peak, peak I, consists of two pairs of degenerate excitons at 1.372 eV and 1.377 eV. both contain transitions from v_{40} - v_{47} to c_{31} - c_{38} (see Table D.61).

Figure 7.14 shows both these excitons are almost entirely intralayer.

7.7 Conclusion

In summary, I attempted to calculate the electronic and optical spectra of twisted MoS₂ homobilayers with twist angles ranging from 21.79° to 3.89°.

To do that, I first considered the relaxed atomic structures calculated from classical force fields. I found that, for small twist angles, the interlayer separation is a monotonic function of twist angle, and was able to reproduce the relative ordering of smaller to larger interlayer separations for high-symmetry and large-twist angle stackings seen in previous theoretical work[55].

I was then able to calculate the electronic band structures of all twist angles with up to sixth-nearest neighbour hopping compared to third-nearest neighbour hopping in Ref. [5], and found that the conduction manifold is qualitatively different between TB3 and TB6 calculations.

Next, I tried to calculate the optical absorption spectra of twisted MoS_2 homobilayers. Unfortunately, I found that with the current methodology, I am not able to converge optical spectra of anything but the largest twist-angled systems. However, even so, I am able to see hybrid and interlayer excitons in twisted systems, as seen in principle in experimental work[58]. I am also able to see the relatively twist-angle independent exciton binding energy of the intralayer A peak[57], which is the lowest-energy optically active exciton in all of the different spectra.

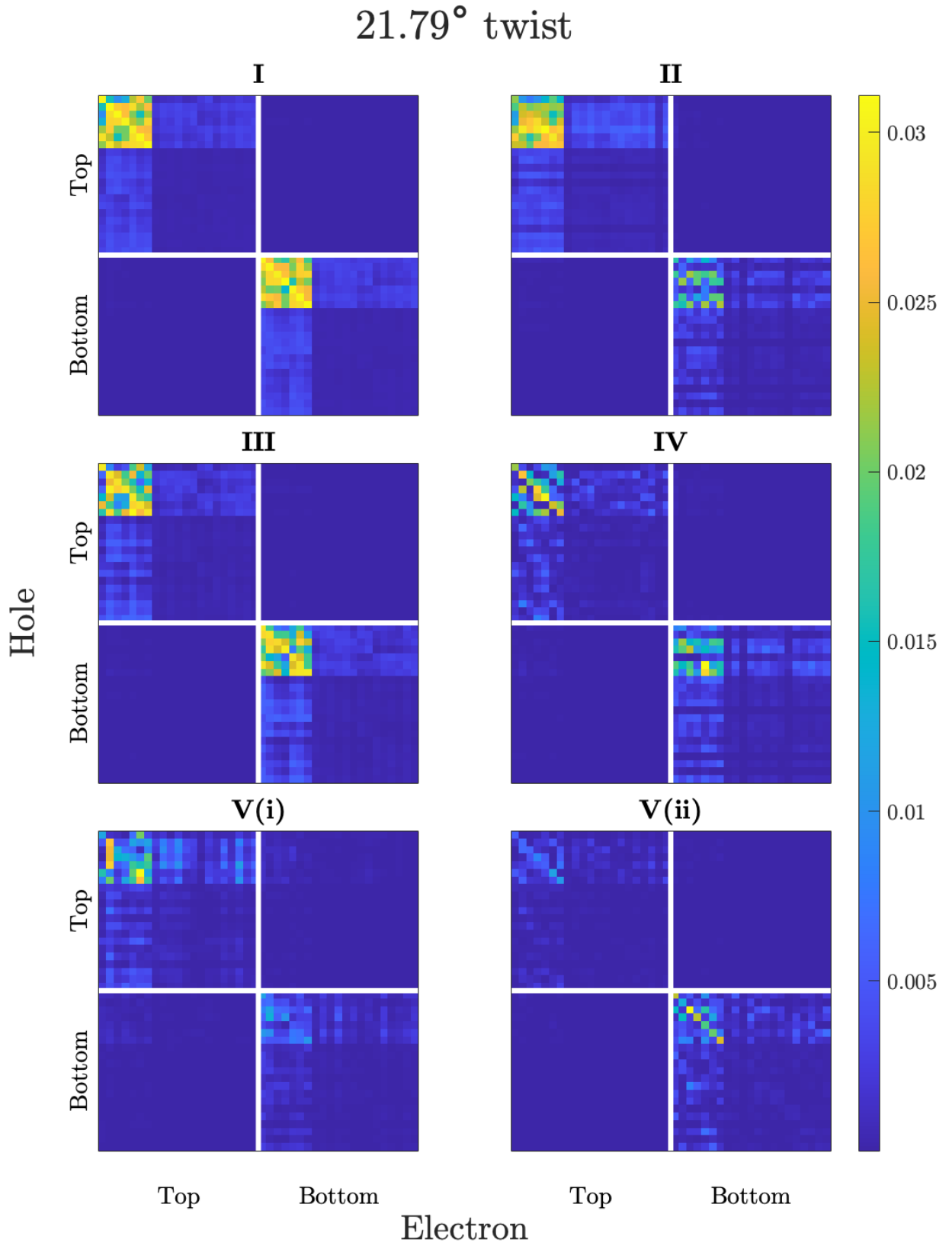


Figure 7.8: Illustration of the real space distribution of the optically active excitons in 21.79° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

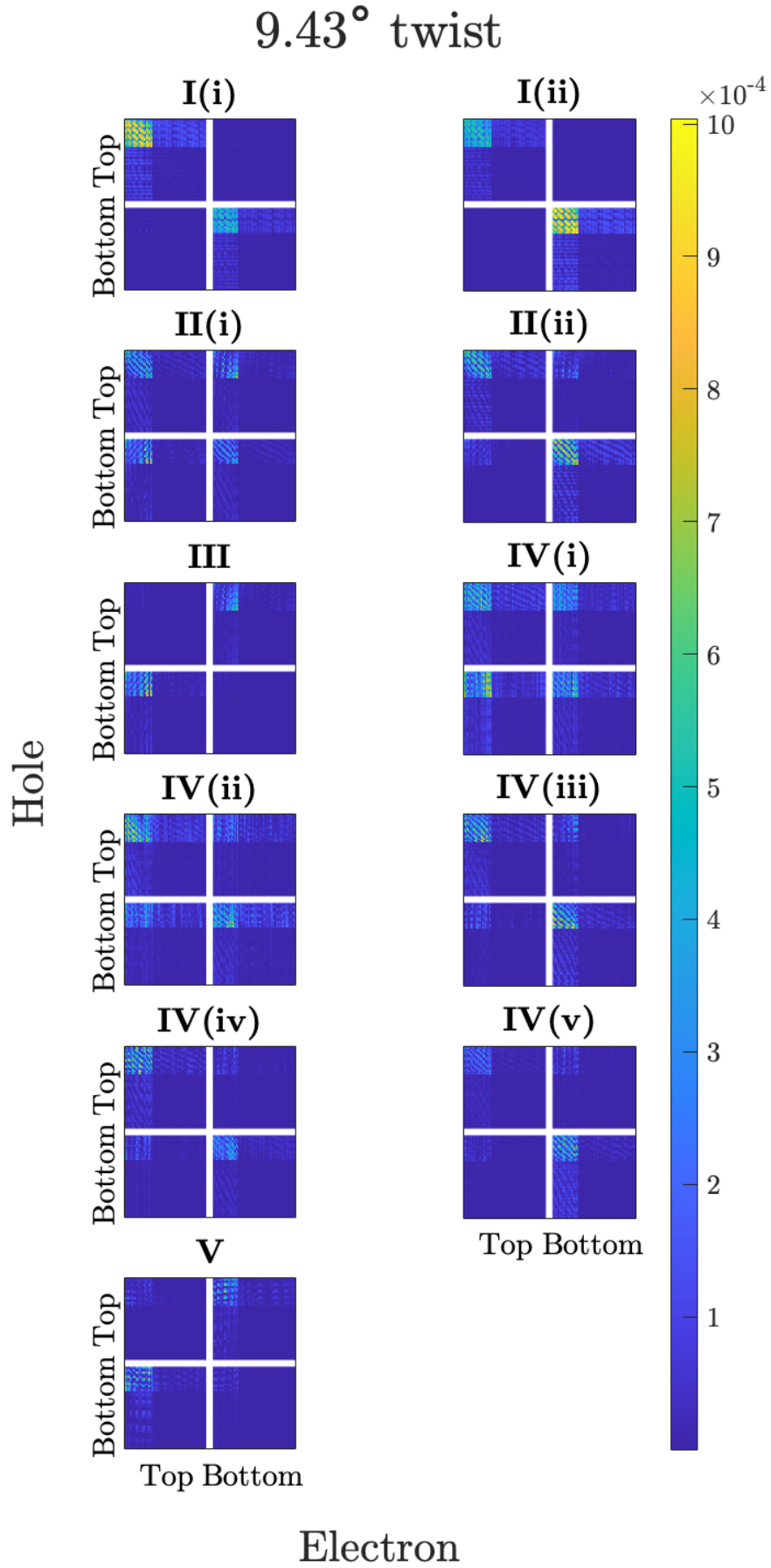


Figure 7.9: Illustration of the real space distribution of the optically active excitons in 9.43° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

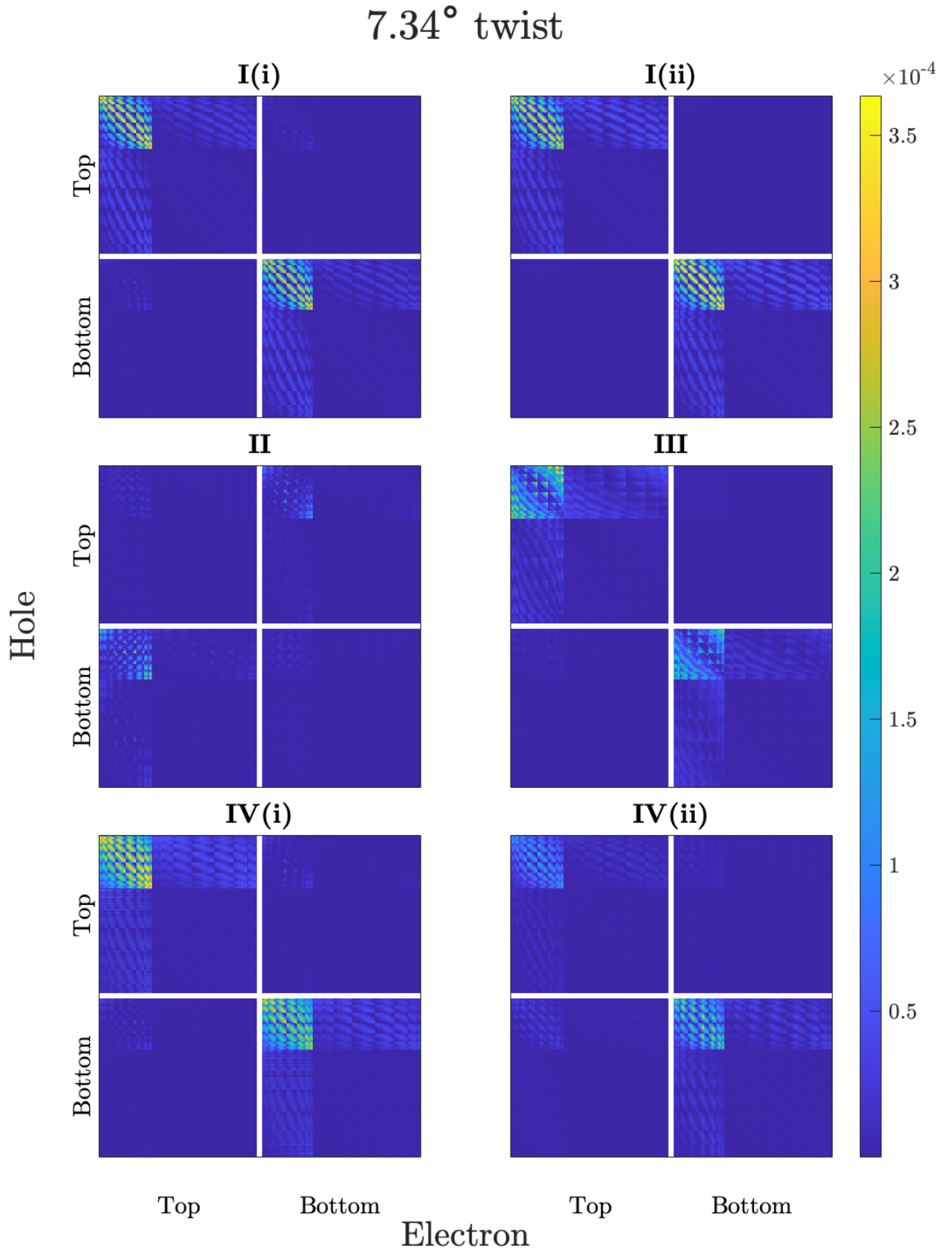


Figure 7.10: Illustration of the real space distribution of the optically active excitons in 7.34° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

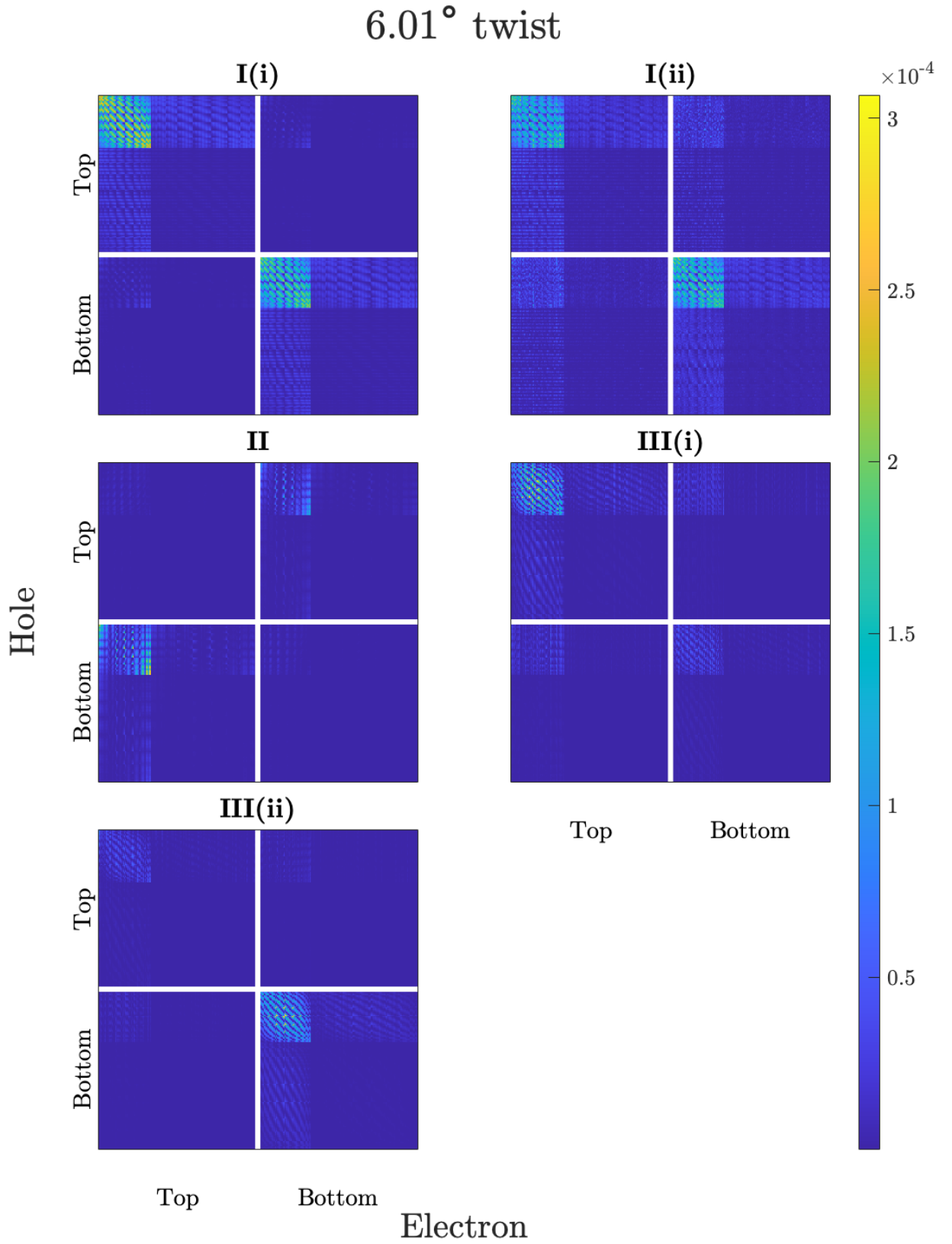


Figure 7.11: Illustration of the real space distribution of the optically active excitons in 6.01° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

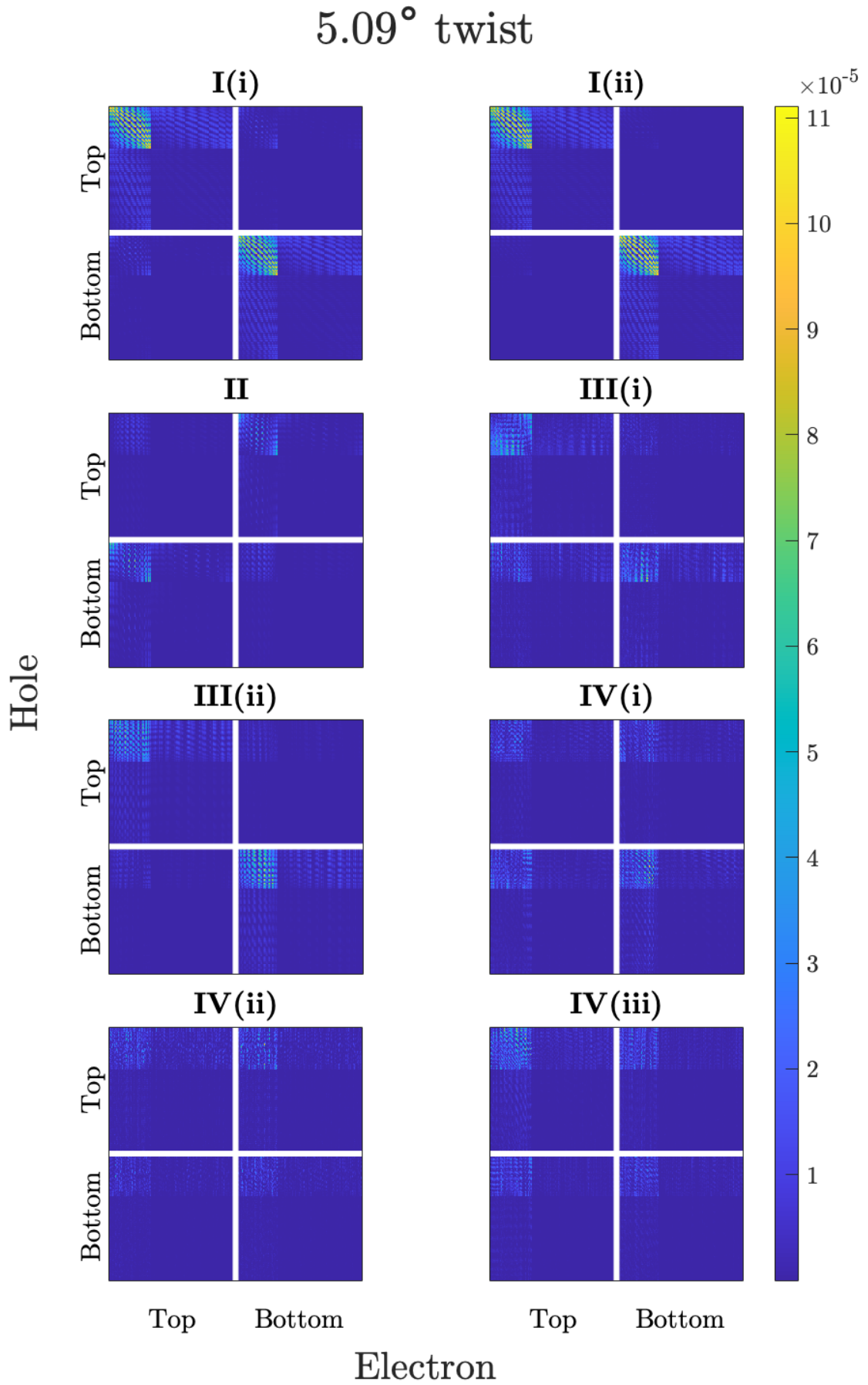


Figure 7.12: Illustration of the real space distribution of the optically active excitons in 5.09° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

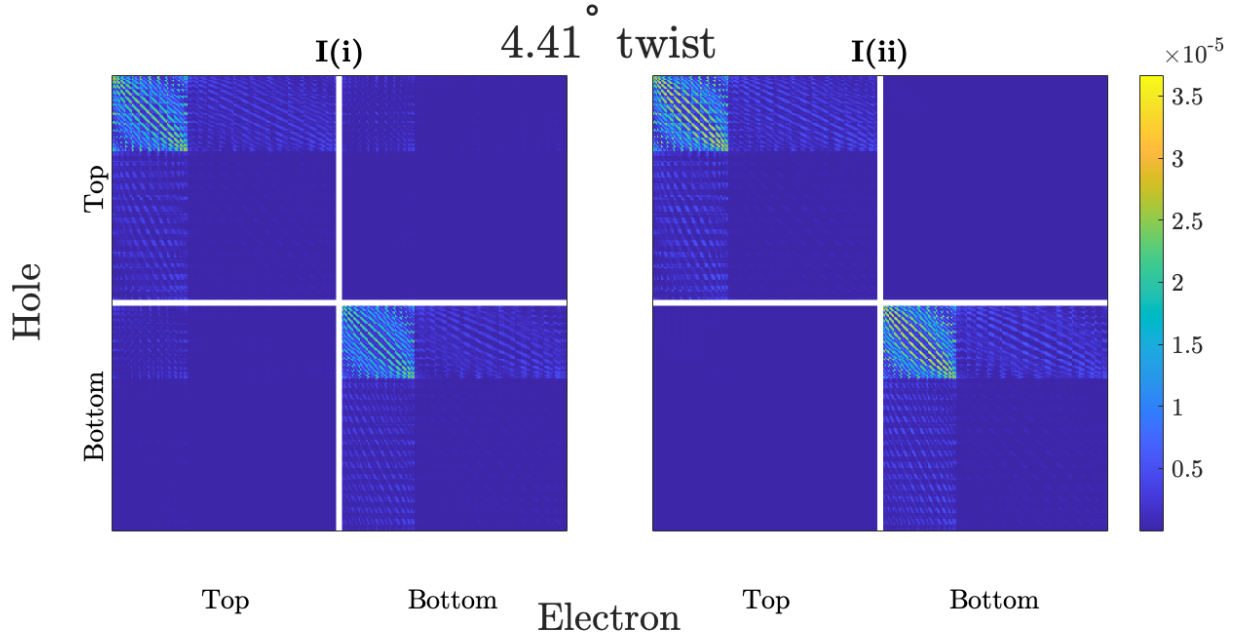


Figure 7.13: Illustration of the real space distribution of the optically active excitons in 4.41° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

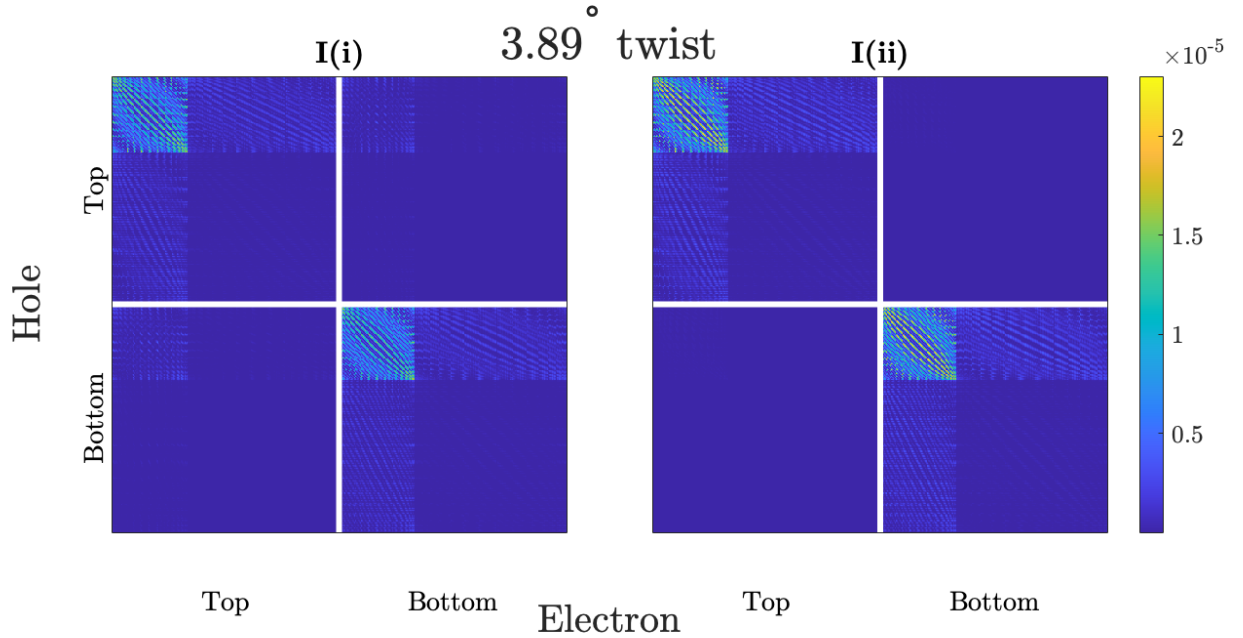


Figure 7.14: Illustration of the real space distribution of the optically active excitons in 3.89° twisted MoS_2 bilayers. The matrix elements show the probability associated with an electron on one atom and a hole on another, with the first half of the atoms being on one layer and the second on the other, and within a layer first all the Mo atoms, and then all the S atoms.

Chapter 8

Conclusion

8.1 Convergence

The overall conclusion of this work is that modelling excitons in twisted bilayers of transition metal dichalcogenides by solving the Bethe–Salpeter in a tight-binding basis is a very promising approach. However, it is not (yet) feasible to do so with a tight-binding model with a basis size as comparatively large as this one, nor for very small twist angles. The smallest angle described in this work is 3.48° , which is still more than twice as large as the largest angles studied in most experimental work, and the results presented here are nowhere near converged.

However, there is information which can be gained from this nonetheless. In particular, I believe the knowledge obtained from this work allows for a well informed approximations leading to reductions in system size.

Firstly, we have found in the untwisted systems that the cutoff energy plays a more important role than the k-grid fineness in the convergence of the low-energy features of the optical spectrum, see Figures 5.6 and 5.7. We have also seen from the binding energy dependence of the energy of the lowest lying optical peak on twist angle, Fig. 7.7, that it is important to include the K and K' points in the k-grid. A good minimum size of the k-grid would therefore be a

triangular Brillouin zone sampling, including only Γ , K, and K'. This is the smallest uniform Brillouin zone grid which includes both K and K', at three k-points.

The second informed reduction in system size is the choice of orbitals included in the tight-binding model. The electrons and holes involved in the optical peaks of both the twisted and untwisted spectra are all strongly localized on the Mo atoms. This suggests a reduced basis including only the five d-orbitals located on the Mo atoms might be sufficient for a good description of the character of the optically active excitons. A good first approach would be to use the five-band tight-binding model described by MacDonald et al.[161], or even a three-band tight-binding model as described in Ref. [206], and include spin-orbit and interlayer coupling as a in the same way as in the model described in this work, by an onsite spin-orbit coupling term and Slater–Koster parameters for the interlayer van-der-Waals interaction, respectively.

8.2 Electronic Properties

We developed a eleven-orbital per spin per layer tight-binding model including up to sixth-nearest neighbour intralayer hopping and selected interlayer hoppings based on previous work done by Refs. [1] and [5]. The sixth-nearest neighbour tight-binding model is successful in that the description of the electronic bandstructure is markedly improved compared to the third-nearest neighbour model. However, there are still qualitative differences compared to the DFT bandstructure, even without considering spin, and the impact on the low energy optical properties is minor. For future research, it would be interesting to focus more improving the description of the interlayer hopping, which appears to be underestimated.

8.3 Optical Properties

I modelled the optical properties of MoS₂ mono and bilayers by calculating their excitonic spectra. To do this, I solved the Bethe–Salpeter equation in the tight-binding bases described

above.

8.3.1 MoS₂ monolayers

I am able to reproduce the low-energy parts of the optical spectrum of monolayer MoS₂ of a much more computationally intensive GW-BSE calculation[6] reasonably well, see Figure 5.8. In particular, the relative height and separation of the A and B peaks can be reproduced very accurately.

8.3.2 Stacking configurations

Next, I focused on the five high-symmetry stackings of TMD bilayers. One of the most important factors in modelling the interlayer interaction in TMD bilayers is the interlayer separation. I calculated the atomic structures of the small unit cells of the high-symmetry stackings using DFT calculations with Quantum Espresso, and was able to reproduce the interlayer separation observed in experiments[55] up to 0.1Å.

The stacking configuration has a significant qualitative impact on the properties of the optically active excitons in MoS₂ bilayers. I found that two of the high-symmetry stackings include interlayer excitons, AB and B^{MM} stacking. B^{MX} and B^{XM} transform into each other through inversion and are not, themselves, inversion symmetric. This leads to energy splitting between excitons in top and bottom layers, leading to layer-asymmetric excitons.

8.3.3 Twisted systems

Lastly, I focused on the optical properties of twisted TMD bilayers. The resulting unit cells are too large to easily model their atomic structure using DFT. Nevertheless, as before, the atomic structure has a significant impact on the electronic and excitonic properties. We model their atomic structure using classical force fields with LAMMPS. Rather than resulting in the

superposition of two rigidly flat monolayers with a constant interlayer separation, the interlayer separation depends on the local stacking configuration, resulting in a buckled unit cell. The horizontal, in-layer, distortion of the composite atoms, by contrast, is negligible, allowing us to justify using the monolayer tight-binding model for the intralayer hoppings.

The optical properties of twisted MoS₂ bilayers are similarly computationally expensive to model, not only because of the size of unit cell, but also because most of the low-energy excitons in their spectra are “secretly momentum indirect” and are therefore optically dark. It might be possible to reduce the size of the calculation by including a minimum cutoff energy in addition to a maximum cutoff energy, although this would have to be pretty heuristic. A more rigorous approach in this direction involves so-called band unfolding, in which the band-structure of twisted systems is mapped back onto the untwisted Brillouin zone, as described for instance in Ref. [207].

The first peak in all stacking and twisting geometries studied in this work are all intralayer excitons. This matched with the observation that the direct gap in the untwisted systems is not dependent on the interlayer distance, see Figure 6.14, as well as the fact that the first peaks all appear at roughly the same energy. However, the higher energy peaks have a very interesting excitonic structure, and it would be very interesting to see how this holds up in converged calculations. This includes the fact that all twist angles for which more than one peak has been calculated include hybrid or interlayer excitons.

8.4 Final thoughts

This project has not gone according to plan, but in the end, that is as it should be. A perfect prediction is only possible based on perfect initial information, which would have made the project redundant.

Excitons in twisted MoS₂ bilayers have very rich physics, and if I have contributed even a

little to the knowledge we as the scientific community have about them (never mind the large amounts of knowledge I personally gained), then I consider this project to have been successful.

Bibliography

- [1] S. Fang et al. “*Ab initio* tight-binding Hamiltonian for transition metal dichalcogenides”. In: *Phys. Rev. B* 92 (2015), p. 205108.
- [2] H. M. Hill et al. “Observation of Excitonic Rydberg States in Monolayer MoS₂ and WS₂ by Photoluminescence Excitation Spectroscopy”. In: *Nano Lett.* 15 (2015), pp. 2992–2997.
- [3] J. Deslippe et al. “BerkeleyGW: A massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures”. In: *Comput. Phys. Commun.* 183 (2012), pp. 1269–1289.
- [4] H. Fang et al. “Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides”. In: *Proc. Natl. Acad. Sci. USA* 111 (2014), pp. 6198–1202.
- [5] V. Vitale et al. “Flat band properties of twisted transition metal dichalcogenide homo- and heterobilayers of MoS₂, MoS₂, WS₂ and WSe₂”. In: *2D Materials* 8 (2021), p. 045010.
- [6] D. Y. Qiu, F. H. da Jornada, and S. G. Louie. “Screening and many-body effects in two-dimensional crystals: Monolayer MoS₂”. In: *Phys. Rev. B* 93.235435 (2016).
- [7] M. Bieniek et al. “Theory of Excitons in Atomically Thin Semiconductors: Tight-Binding Approach”. In: *Nanomaterials* 12(9).1582 (2022).
- [8] P. R. Wallace. “The Band Theory of Graphite”. In: *Phys. Rev.* 71 (2021), pp. 622–634.
- [9] G. Connell, J. Wilson, and A. Yoffe. “Effects of pressure and temperature on exciton absorption and band structure of layer crystals: Molybdenum disulfide”. In: *J. Phys. Chem. Solids* 30 (1969), pp. 287–296.

- [10] J. Wilson and A. Yoffe. “The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties”. In: *Adv. Phys.* 18 (1969), pp. 193–335.
- [11] F. L. Claus. *Solid Lubricants and Self-Lubricating Solids*. Ed. by New York: Academic Press. 1972.
- [12] K. S. Novoselov et al. “Electric Field Effect in Atomically Thin Carbon Films”. In: *Science* 306 (2004), pp. 666–669.
- [13] K. S. Novoselov et al. “Two-dimensional gas of massless Dirac fermions in graphene”. In: *Nature* 438 (2005), pp. 197–200.
- [14] Y. Zhang et al. “Experimental observation of the quantum Hall effect and Berry’s phase in graphene”. In: *Nature* 438 (2005), pp. 197–200.
- [15] K. S. Novoselov et al. “Two-dimensional atomic crystals”. In: *Proc. Natl. Acad. Sci. USA* 102 (2005), pp. 10451–10453.
- [16] URL: <https://www.nobelprize.org/prizes/physics/2010/press-release/> (visited on 11/29/2022).
- [17] P. Ajayan, P. Kim, and K. Banerjee. “Two-dimensional van der Waals materials”. In: *Physics Today* 69.38 (9 2016).
- [18] A. K. Geim and I. V. Grigorieva. “Van der Waals heterostructures”. In: *Nature* 499.419 (2013).
- [19] L. A. Ponomarenko et al. “Tunable metal-insulator transition in double-layer graphene heterostructures”. In: *Nat. Phys.* 7.958-961 (2011).
- [20] G. Li et al. “Observation of Van Hove singularities in twisted graphene layers”. In: *Nat. Phys.* 6 (2010), pp. 109–113.
- [21] Y. Cao et al. “Correlated insulator behaviour at half-filling in magic-angle graphene superlattices”. In: *Nature* 556 (2018), pp. 80–84.
- [22] Y. Cao et al. “Unconventional superconductivity in magic-angle graphene superlattices”. In: *Nature* 556 (2018), pp. 43–50.

- [23] G. Chen et al. “Evidence of a gate-tunable Mott insulator in a trilayer graphene moiré superlattice”. In: *Nat. Phys.* 15 (2019), pp. 237–241.
- [24] M. Chhowalla et al. “The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets”. In: *Nature Chemistry* 5 (2013), pp. 263–275.
- [25] Q. H. Wang et al. “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides”. In: *Nat. Nanotechnol.* 7 (2012), pp. 699–712.
- [26] Z. Lei et al. “Recent Development of Metallic (1T) Phase of Molybdenum Disulfide for Energy Conversion and Storage”. In: *Advanced Energy Materials* 8 (19 2018).
- [27] P. Palczynski. “Characterisation of atomically-thin transition metal dichalcogenides”. PhD thesis. Imperial College London, 2019. URL: <http://hdl.handle.net/10044/1/80167>.
- [28] A. Splendiani et al. “Emerging Photoluminescence in Monolayer MoS₂”. In: *Nano Lett.* 10.1271 (2010).
- [29] K. F. Mak et al. “Atomically Thin MoS₂: A New Direct-Gap Semiconductor”. In: *Phys. Rev. Lett* 105 (2010), p. 136805.
- [30] G. Eda et al. “Photoluminescence from Chemically Exfoliated MoS₂”. In: *Nano. Lett.* 11 (2011), pp. 5111–5116.
- [31] P. Tonndorf et al. “Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂”. In: *Opt. Express* 21 (2013), pp. 4908–4916.
- [32] W. Zhao et al. “Evolution of Electronic Structure in Atomically Thin Sheets of WS₂ and WSe₂”. In: *ACS Nano* 7 (2013), pp. 791–797.
- [33] C. Ruppert, O. B. Aslan, and T. F. Heinz. “Optical Properties and Band Gap of Single- and Few-Layer MoTe₂ Crystals”. In: *Nano Lett.* 14 (2014), pp. 6231–6236.
- [34] I. G. Lezama et al. “Indirect-to-Direct Band Gap Crossover in Few-Layer MoTe₂”. In: *Nano Lett.* 15 (2015), pp. 2336–2342.
- [35] E. S. Kadantsev and P. Hawrylak. “Electronic structure of a single MoS₂ monolayer”. In: *Solid State Commun.* 152 (2012), p. 909.

- [36] A. Ramasubramaniam. “Large excitonic effects in monolayer and molybdenum and tungsten dichalcogenides”. In: *Phys. Rev. B* 86 (2012), p. 115409.
- [37] W. Jin et al. “Direct Measurement of the Thickness-Dependent Electronic Band Structure of MoS₂ Using Angle-Resolved Photoemission Spectroscopy”. In: *Phys. Rev. Lett.* 111 (2013), p. 106801.
- [38] D. H. Lien et al. “Engineering Light Outcoupling in 2D Materials”. In: *Nano Lett.* 15 (2015), pp. 1356–1361.
- [39] C. R. Dean et al. “Boron nitride substrates for high-quality graphene electronics”. In: *Nat. Nanotech.* 5 (2010), pp. 722–726.
- [40] O. A. Ajayi et al. “Approaching the intrinsic photoluminescence linewidth in transition metal dichalcogenide monolayers”. In: *2D Mater.* 4.031011 (2017).
- [41] F. Cadiz et al. “Excitonic Linewidth Approaching the Homogeneous Limit in MoS₂-Based van der Waals Heterostructures”. In: *Phys. Rev. X* 7.021026 (2017).
- [42] K. He et al. “Tightly Bound Excitons in Monolayer WSe₂”. In: *Phys. Rev. Lett.* 113 (2014), p. 026803.
- [43] A. Arora et al. “Excitonic resonances in thin films of WSe₂: From monolayer to bulk material”. In: *Nanoscale* 7 (2015), pp. 10412–10429.
- [44] A. Chernikov et al. “Exciton Binding Energy and Nonhydrogenic Rydberg Series in Monolayer WS₂”. In: *Phys. Rev. Lett.* 113 (2014), p. 076802.
- [45] A. Arora et al. “Exciton band structure in layered MoSe₂: From a monolayer to the bulk limit”. In: *Nanoscale* 7 (2015), pp. 20769–20775.
- [46] G. Wang et al. “Giant Enhancement of the Optical Second-Harmonic Emission of WSe₂ Monolayers by Laser Excitation at Exciton Resonances”. In: *Phys. Rev. Lett.* 114 (2015), p. 097403.
- [47] A. Y. Joe et al. “Electrically controlled emission from singlet and triplet exciton species in atomically thin light-emitting diodes”. In: *Phys. Rev. B* 103.L161411 (2021).

- [48] L. A. Jauregui et al. “Electrical control of interlayer exciton dynamics in atomically thin heterostructures”. In: *Science* 366 (2019), pp. 870–875.
- [49] E. V. Calman et al. “Indirect Excitons and Trions in MoSe₂/WSe₂ van der Waals Heterostructures”. In: *Nano Lett.* 20 (2020), pp. 1869–1875.
- [50] E. Lorchat et al. “Excitons in Bilayer MoS₂ Displaying a Colossal Electric Field Splitting and Tunable Magnetic Response”. In: *PRL* 125 (2021), p. 037401.
- [51] P. Rivera et al. “Observation of long-lived interlayer excitons in monolayer MoSe₂-WSe₂ heterostructures”. In: *Nat. Commun.* 6.6242 (2015).
- [52] I. C. Gerber et al. “Interlayer excitons in bilayer MoS₂ with strong oscillator strength up to room temperature”. In: *Phys. Rev. B* 99.035443 (2019).
- [53] N. Leisgang et al. “Giant Stark splitting of an exciton in bilayer MoS₂”. In: *Nat. Nanotech.* 15.901 (2020).
- [54] A. M. Van der Zande et al. “Tailoring the Electronic Structure in Bilayer Molybdenum Disulfide via Interlayer Twist”. In: *Nano Lett.* 14 (2014), pp. 3869–3875.
- [55] K. Liu et al. “Evolution of interlayer coupling in twisted molybdenum disulfide bilayers”. In: *Nature Communications* 5.4966 (2014).
- [56] S. Huang et al. “Probing the Interlayer Coupling of Twisted Bilayer MoS₂ Using Photoluminescence Spectroscopy”. In: *Nano Lett.* 14 (2014), pp. 5500–5508.
- [57] M. Liao et al. “Precise control of the interlayer twist angle in large scale MoS₂ homostructures”. In: *Nat. Commun.* 11.2153 (2020).
- [58] M. Grzeszczyk et al. “The optical response of artificially twisted MoS₂ bilayers”. In: *Sci. Rep.* 11.17037 (2021).
- [59] K. D. Bronsema, J. L. De Boer, and F. Jellinek. “On the structure of molybdenum diselenide and disulfide”. In: *Z. Anorg. Allg. Chem.* 540.15 (1968).
- [60] R. Coehoorn et al. “Electronic structure of MoSe₂, MoS₂, and WSe₂. I. Band-structure calculations and photoelectron spectroscopy”. In: *Phys. Rev. B* 35.6195 (1987).

- [61] W. Schutte, J. L. de Boer, and F. Jellinek. “Crystal structures of tungsten disulfide and diselenide”. In: *J. Solid State Chem.* 70.207 (1987).
- [62] G. Kresse and J. Hafner. “*Ab initio* molecular dynamics for open-shell transition metals”. In: *Phys. Rev. B* 48.13115 (1993).
- [63] J. Kunstmann et al. “Momentum-space indirect interlayer excitons in transition-metal dichalcogenide van der Waals heterostructures”. In: *Nat. Phys.* 14 (2018), pp. 801–805.
- [64] S. Mouri et al. “Thermal dissociation of inter-layer excitons in MoS₂/MoSe₂ heterobilayers”. In: *Nanoscale* 9 (2017), pp. 6674–6679.
- [65] D. A. Ruiz-Tijerina and V. I. Fal’ko. “Interlayer hybridization and moiré superlattice minibands for electrons and excitons in heterobilayers of transition-metal dichalcogenides”. In: *Phys. Rev. B* 99.125424 (2019).
- [66] C. Jin et al. “Observation of moiré excitons in WSe₂/WS₂ heterostructure superlattices”. In: *Nature* 567 (2019), pp. 76–80.
- [67] L. Zhang et al. “Highly valley-polarized singlet and triplet interlayer excitons in van der Waals heterostructure”. In: *Phys. Rev. B* 100.041402 (2019).
- [68] W. Li et al. “Dipolar interactions between localized interlayer excitons in van der Waals heterostructures”. In: *Nat. Mater.* 19 (2020), pp. 624–629.
- [69] L. Sigl et al. “Signatures of a degenerate many-body state of interlayer excitons in a van der Waals heterostack”. In: *Phys. Rev. Res.* 2.042044 (2020).
- [70] P. Rivera et al. “Valley-polarized exciton dynamics in a 2D semiconductor heterostructure”. In: *Science* 351 (2016), pp. 688–691.
- [71] K. Tran et al. “Evidence for moiré excitons in van der Waals heterostructures”. In: *Nature* 567 (2019), pp. 71–75.
- [72] K. L. Seyler et al. “Signatures of moiré-trapped valley excitons in MoSe₂/WSe₂ heterobilayers”. In: *Nature* 567 (2019), pp. 766–790.
- [73] J. Choi et al. “Moiré potential impedes interlayer exciton diffusion in van der Waals heterostructures”. In: *Sci. Adv.* 6.eaba8866 (2020).

- [74] B. Miller et al. “Long-Lived Direct and Indirect Interlayer Excitons in van der Waals Heterostructures”. In: *Nano Lett.* 17 (2017), pp. 5229–5237.
- [75] P. Nagler et al. “Interlayer exciton dynamics in a dichalcogenide monolayer heterostructure”. In: *2D Mater.* 4.025112 (2017).
- [76] T. Wang et al. “Giant Valley-Zeeman Splitting from Spin-Singlet and Spin-Triplet Interlayer Excitons in WSe₂/MoSe₂ Heterostructure”. In: *Nano Lett.* 20 (2020), pp. 694–700.
- [77] J. Choi et al. “Twist Angle-Dependent Interlayer Exciton Lifetimes in van der Waals Heterostructures”. In: *Phys. Rev. Lett.* 126.047401 (2021).
- [78] P. Nagler et al. “Giant magnetic splitting inducing near-unity valley polarization in van der Waals heterostructures”. In: *Nat. Commun.* 8.1551 (2017).
- [79] W. T. Hsu et al. “Negative circular polarization emissions from WSe₂/MoSe₂ commensurate heterobilayers”. In: *Nat. Commun.* 9.1356 (2018).
- [80] A. T. Hanbicki et al. “Double indirect interlayer exciton in a MoSe₂/WSe₂ van der Waals heterostructure”. In: *Acs Nano* 12 (2018), pp. 4719–4726.
- [81] J. Wang et al. “Optical generation of high carrier densities in 2D semiconductor heterobilayers”. In: *Sci. Adv.* 5 (9 2019).
- [82] H. Chen et al. “Ultrafast formation of interlayer hot excitons in atomically thin MoS₂/WS₂ heterostructures”. In: *Nat. Commun* 7.12512 (2016).
- [83] X. Zhu et al. “Effects of dielectric screening on the excitonic and critical points properties of WS₂/MoS₂ heterostructures”. In: *Nanoscale* 12 (2020), pp. 23732–23739.
- [84] X. Huang et al. “Recent progress on fabrication and flat-band physics in 2D transition metal dichalcogenides moiré superlattices”. In: *J Semicond* 44.011901 (2023).
- [85] J.-O. Carlsson and P. M. Martin. *Handbook of Deposition Technologies for Films and Coatings*. 3rd ed. 2010. Chap. 7, pp. 314–363.
- [86] URL: https://en.wikipedia.org/wiki/Molecular-beam_epitaxy (visited on 10/01/2023).

- [87] L. Meng, Y. L. Wang, L. Z. Zhang, et al. “Buckled silicene formation on Ir(111)”. In: *Nano Lett* 13.685 (2013).
- [88] Y. F. Hao, L. Wang, Y. Y. Liu, et al. “Oxygen-activated growth and bandgap tunability of large single-crystal bilayer graphene”. In: *Nat Nanotechnol.* 11 (2016), p. 426.
- [89] P. W. Sutter, J. I. Flege, and E. A. Sutter. “Epitaxial graphene on ruthenium”. In: *Nat Mater* 7.406 (2008).
- [90] C. Chang, W. Chen, Y. When, et al. “Recent process on two-dimensional materials”. In: *Acta Phys Chim Sin* 37.2108017 (2021).
- [91] G. Enlai et al. “Mechanical exfoliation of two-dimensional materials”. In: *Journal of the Mechanics and Physics of Solids* 115 (2018), pp. 248–262.
- [92] B. Radisavljevic, A. Radenovic, J. Brivio, et al. “Single-layer MoS₂ transistors”. In: *Nat. Nanotechnol.* 6 (2011), p. 147.
- [93] Y. Huang, E. Sutter, N. N. Shi, et al. “Reliable exfoliation of large-area high-quality flakes of graphene and other two-dimensional materials”. In: *ACS Nano* 9 (2015), p. 10612.
- [94] Y. Huang, X. Wang, X. Zhang, et al. “Raman spectral band oscillations in large graphene bubbles”. In: *Phys. Rev. Lett.* 120 (2018), p. 186104.
- [95] Y. Huang, Y. H. Pan, R. Yang, et al. “Universal mechanical exfoliation of large-area 2D crystals”. In: *Nat. Commun* 11 (2020), p. 2453.
- [96] F. Liiu, W. J. Wu, Y. S. Bai, et al. “Disassembling 2D van der Waals crystals into macroscopic monolayers and reassembling into artificial lattices”. In: *Science* 367.903 (2020).
- [97] Q. Fu, J. Q. Dai, X. Y. Huang, et al. “One-step exfoliation method for plasmonic activation of large-area 2D crystals”. In: *Adv Sci* 9.e2204247 (2022).
- [98] K. Kim, A. DaSilva, S. Q. Huang, et al. “Tunable moiré bands and strong correlations in small-twist-angle bilayer graphene”. In: *Proc Natl Acad Sci USA* 114 (2017), p. 3364.
- [99] X. D. Chen, W. Xin, W. S. Jiang, et al. “High-precision twist-controlled bilayer and trilayer graphene”. In: *Adv Mater* 28 (2016), p. 2563.

- [100] Y. Gillet, M. Giantomassi, and X. Gonze. “Efficient on-the-fly interpolation technique for Bethe–Salpeter calculations of optical spectra”. In: *Comput. Phys. Commun.* 203 (2016), pp. 83–93.
- [101] D. Sangalli et al. “Many-body perturbation theory calculations using the yambo code”. In: *J. Phys. Condens. Matter* 31.325902 (2019).
- [102] S. Ono et al. “TOMBO: All-electron mixed-basis approach to condensed matter physics”. In: *Comput. Phys. Commun.* 189 (2015), pp. 20–30.
- [103] C. Vorwerk et al. “Bethe–Salpeter equation for absorption and scattering spectroscopy: Implementation in the exciting code”. In: *Electron. Struct.* 1 (2019), p. 037001.
- [104] T. Sander, E. Maggio, and G. Kresse. “Beyond the Tamm–Dancoff approximation for extended systems using exact diagonalization”. In: *Phys. Rev. B* 92.0454209 (2015).
- [105] A. Marini et al. “Yambo: An ab initio tool for excited state calculations”. In: *Comput. Phys. Commun.* 180 (2009), pp. 1392–1403.
- [106] P. Giannozzi et al. “Advanced capabilities for materials modelling with Quantum ESPRESSO”. In: *J. Phys. Condens. Matter* 29.465901 (2017).
- [107] R. Soklaski, Y. Liang, and L. Yang. “Temperature effect on optical spectra of monolayer molybdenum disulfide”. In: *Appl. Phys. Lett.* 104.193110 (2014).
- [108] M. M. Ugeda et al. “Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor”. In: *Nat. Mater.* 13.1091 (2014).
- [109] H. Yu et al. “Dirac cones and Dirac saddle points of bright excitons in monolayer transition metal dichalcogenides”. In: *Nat. Commun.* 5.3876 (2014).
- [110] D. Y. Qiu, T. Cao, and S. G. Louie. “Nonanalyticity, Valley Quantum Phases, and Lightlike Exciton Dispersion in Monolayer Transition Metal Dichalcogenides”. In: *Phys. Rev. Lett.* 115.176801 (2015).
- [111] S. Latini, T. Olsen, and K. S. Thygesen. “Excitons in van der Waals heterostructures: The important role of dielectric screening”. In: *Phys. Rev. B* 92.245123 (2015).

- [112] A. Molina-Sánchez et al. “Temperature-dependent excitonic effects in the optical properties of single-layer MoS₂”. In: *Phys. Rev. B* 93.155435 (2016).
- [113] C. Robert et al. “Excitonic properties of semiconducting monolayer and bilayer MoTe₂”. In: *Phys. Rev. B* 94.155425 (2016).
- [114] V. Despoja, Z. Rukelj, and L. Marušić. “Ab initio study of electronic excitations and the dielectric function in molybdenum disulfide monolayer”. In: *Phys. Rev. B* 94.165446 (2016).
- [115] L. Guo et al. “Exchange-driven intravalley mixing of excitons in monolayer transition metal dichalcogenides”. In: *Nat. Phys.* 15.228 (2019).
- [116] Z. Ye et al. “Probing excitonic dark states in single-layer tungsten disulphide”. In: *Nature* 513 (2014), pp. 214–218.
- [117] T. Cheiwchanchamnangij and W. R. L. Lambrecht. “Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂”. In: *PRB* 85 (2012), p. 205302.
- [118] H. P. Komsa and A. V. Krasheninnikov. “Effects of confinements and environment on the electronic structure and exciton binding energy of MoS₂ from first principles”. In: *Phys. Rev. B* 86.241201 (2012).
- [119] D. Y. Qiu, F. H. da Jornada, and S. G. Louie. “Optical Spectrum of MoS₂: Many-Body Effects and Diversity of Exciton States”. In: *Phys. Rev. Lett.* 111.216805 (2013).
- [120] H. Shi et al. “Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂”. In: *Phys. Rev. B* 87 (2013), p. 155304.
- [121] M. Bernardi, M. Palummo, and J. C. Grossman. “Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials”. In: *Nano Lett.* 13 (2013), pp. 3664–3670.
- [122] H. J. Conley et al. “Bandgap Engineering of Strained Monolayer and Bilayer MoS₂”. In: *Nano Lett.* 13 (2013), pp. 3626–3630.
- [123] A. R. Klots et al. “Probing excitonic states in suspended two-dimensional semiconductors by photocurrent spectroscopy”. In: *Sci. Rep.* 4.6608 (2014).

- [124] A. Molina-Sánchez et al. “Effect of spin-orbit interaction on the optical spectra of single-layer, double-layer, and bulk MoS₂”. In: *Phys. Rev. B* 88.045412 (2013).
- [125] Y. Suzuki and K. Watanabe. “Excitons in two-dimensional atomic layer materials from time-dependent density functional theory: Mono-layer and bi-layer hexagonal boron nitride and transition-metal dichalcogenides”. In: *Phys. Chem. Phys.* 22 (2020), pp. 2908–2916.
- [126] Z. Li et al. “Interlayer Exciton Transport in MoSe₂/WSe₂ Heterostructures”. In: *ACS Nano* 15 (2021), pp. 1539–1547.
- [127] T. Deilmann, M. Rohlfing, and U. Wurstbauer. “Light-matter interaction in van der Waals hetero-structures”. In: *J. Phys. Condens. Matter* 32.333002 (2020).
- [128] J. He, K. Hummer, and C. Franchini. “Stacking effects on the electronic and optical properties of bilayer transition metal dichalcogenides MoS₂, MoSe₂, WS₂, and WSe₂”. In: *Phys. Rev. B* 89 (2014), p. 075409.
- [129] S. Gao, L. Yang, and C. D. Spataru. “Interlayer coupling and gate-tunable excitons in transition metal dichalcogenide heterostructures”. In: *Nano Lett.* 17 (2017), pp. 7809–7813.
- [130] R. Gillen and J. Maultzsch. “Interlayer excitons in MoSe₂/WSe₂ heterostructures from first principles”. In: *Phys. Rev. B* 97.165306 (2018).
- [131] E. Torun et al. “Interlayer and intralayer excitons in MoS₂/WS₂ and MoSe₂/WSe₂ heterobilayers”. In: *Phys. Rev. B* 97.245427 (2018).
- [132] X. Lu, X. Li, and L. Yang. “Modulated interlayer exciton properties in a two-dimensional moiré crystal”. In: *Phys. Rev. B* 100.155416 (2019).
- [133] H. Guo, X. Zhang, and G. Lu. “Shedding light on moiré excitons: A first-principles perspective”. In: *Sci. Adv.* 6.eabc5638 (2020).
- [134] T. G. Pedersen. “Exciton Stark shift and electroabsorption in monolayer transition-metal dichalcogenides”. In: *Phys. Rev. B* 94.125424 (2016).

- [135] Y. Cho and T. C. Berkelbach. “Environmentally sensitive theory of electronic and optical transitions in atomically thin semiconductors”. In: *Phys. Rev. B* 97.041409 (2018).
- [136] M. Selig et al. “Dark and bright exciton formation, thermalization, and photoluminescence in monolayer transition metal dichalcogenides”. In: *2D Mater.* 5.035017 (2018).
- [137] L. S. R. Cavalcante et al. “Stark shift of excitons and trions in two-dimensional materials”. In: *Phys. Rev. B* 98.245309 (2018).
- [138] M. Feierabend et al. “Dark exciton based strain sensing in tungsten-based metal dichalcogenides”. In: *Phys. Rev. B* 99.195454 (2019).
- [139] W. T. Hsu et al. “Dielectric impact on exciton binding energy and quasiparticle bandgap in monolayer WS₂ and WSe₂”. In: *2D Mater.* 6.025028 (2019).
- [140] M. R. Molas et al. “Energy Spectrum of Two-Dimensional Excitons in a Nonuniform Dielectric Medium”. In: *Phys. Rev. Lett.* 123.136801 (2019).
- [141] C. Robert et al. “Optical spectroscopy of excited exciton states in MoS₂ monolayers in van der Waals heterostructures”. In: *Phys. Rev. Mater.* 2.011001 (2018).
- [142] T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman. “Theory of neutral and charged excitons in monolayer transition metal dichalcogenides”. In: *Phys. Rev. B* 88.045318 (2013).
- [143] I. Kylänpää and H. P. Komsa. “Binding energies of exciton complexes in transition metal dichalcogenide monolayers and effect of dielectric environment”. In: *Phys. Rev. B* 92.205418 (2015).
- [144] M. Z. Mayers et al. “Binding energies and spatial structures of small carrier complexes in monolayer transition-metal dichalcogenides via diffusion Monte Carlo”. In: *Phys. Rev. B* 92.161404 (2015).
- [145] K. A. Velizhanin and A. Saxena. “Excitonic effects in two-dimensional semiconductors: Path integral Monte Carlo approach”. In: *Phys. Rev. B* 92.195305 (2015).
- [146] T. Olsen et al. “Simple Screened Hydrogen Model of Excitons in Two-Dimensional Materials”. In: *PRL* 116.056401 (2016).

- [147] D. W. Kidd, D. K. Zhang, and K. Varga. “Binding energies and structures of two-dimensional excitonic complexes in transition metal dichalcogenides”. In: *Phys. Rev. B* 93 (2016), p. 125423.
- [148] D. Xiao et al. “Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides”. In: *Phys. Rev. Lett.* 108.196802 (2012).
- [149] M. Trushin, M. O. Goerbig, and W. Belzig. “Optical absorption by Dirac excitons in single-layer transition-metal dichalcogenides”. In: *Phys. Rev. B* 94.041301 (2016).
- [150] M. Trushin, M. O. Goerbig, and W. Belzig. “Model Prediction of Self-Rotating Excitons in Two-Dimensional Transition-Metal Dichalcogenides”. In: *Phys. Rev. Lett.* 120.187401 (2019).
- [151] C. Zhang et al. “Absorption of light by excitons and trions in monolayers of metal dichalcogenide MoS₂: Experiments and theory”. In: *Phys. Rev. B* 89.205436 (2014).
- [152] M. M. Glazov et al. “Exciton fine structure and spin decoherence in monolayers of transition metal dichalcogenides”. In: *Phys. Rev. B* 89.201302 (2014).
- [153] M. M. Glazov et al. “Spin and valley dynamics of excitons in transition metal dichalcogenide monolayers”. In: *Phys. Status Solidi (B)* 252 (2015), pp. 2349–2362.
- [154] M. M. Glazov et al. “Intrinsic exciton-state mixing and nonlinear optical properties in transition metal dichalcogenide monolayers”. In: *Phys. Rev. B* 035311 (2017).
- [155] J. Zhou et al. “Berry Phase Modification to the Energy Spectrum of Excitons”. In: *Phys. Rev. Lett.* 115.166803 (2015).
- [156] M. Van der Donck and F. M. Peeters. “Spectrum of exciton states in monolayer transition metal dichalcogenides: Angular momentum and Landau levels”. In: *Phys. Rev. B* 99.115439 (2019).
- [157] A. J. Chaves et al. “Excitonic effects in the optical properties of 2D materials: An equation of motion approach”. In: *2D Mater.* 4.025086 (2017).
- [158] H. Haug and S. W. Koch. *Quantum theory of the optical and electronic properties of semiconductors*. Ed. by World Scientific. 2004.

- [159] T. C. Berkelbach, M. S. Hybertsen, and D. R. Reichman. “Bright and dark singlet excitons via linear and two-photon spectroscopy in monolayer transition-metal dichalcogenides”. In: *Phys. Rev. B* 92.085413 (2015).
- [160] A. Steinhoff et al. “Influence of Excited Carriers on the Optical and Electronic Properties of MoS₂”. In: *Nano Lett.* 14 (2014), pp. 3743–3748.
- [161] F. Wu, F. Qu, and A. H. MacDonald. “Exciton band structure of monolayer MoS₂”. In: *Phys. Rev. B* 91 (2015), p. 075310.
- [162] M. Bieniek, L. Szulakowska, and P. Hawrylak. “Band nesting and exciton spectrum in monolayer MoS₂”. In: *Phys. Rev. B* 101.125423 (2020).
- [163] E. Ridolfi, C. H. Lewenkopf, and V. M. Pereira. “Excitonic structure of the optical conductivity in MoS₂ monolayers”. In: *Phys. Rev. B* 97 (2018), p. 205409.
- [164] B. Scharf et al. “Excitonic Stark effect in MoS₂ monolayers”. In: *Phys. Rev. B* 94.245434 (2016).
- [165] G. H. Peng et al. “Distinctive Signatures of the Spin- and Momentum-Forbidden Dark Exciton States in the Photoluminescence of Strained WSe₂ Monolayers under Thermalization”. In: *Nano Lett.* 19 (2019), pp. 2299–2312.
- [166] P. Hohenberg and W. Kohn. “Inhomogeneous electron gas”. In: *Physical Review* 136.3B (1964), B864–B871.
- [167] W. Kohn and L. J. Sham. “Self-consistent equations including exchange and correlation effects”. In: *Physical Review* 140.4A (1965), A1133–A1138.
- [168] J. P. Perdew, K. Burke, and M. Ernzerhof. “Generalized Gradient Approximation Made Simple”. In: *Phys. Rev. Lett.* 77.3865 (1996).
- [169] P. Schwerdtfeger. “The Pseudopotential Approximation in Electronic Structure Theory”. In: *Chem. Phys. Chem.* 12 (2011), pp. 3143–3155.
- [170] D. Vanderbilt. “Optimally smooth norm-conserving pseudopotentials”. In: *Phys. Rev. B* 32 (12 1985), pp. 8412–8415.

- [171] G. B. Bachelet, D. R. Hamann, and M. Schlüter. “Pseudopotentials that work: From H to Pu”. In: *Phys. Rev. B* 26.8 (1982), pp. 4199–4228.
- [172] J. C. Slater and G. F. Koster. “Simplified LCAO Method for the Periodic Potential Problem”. In: *Phys. Rev.* 94.1498 (1954).
- [173] Z. A. H. Goodwin. “Theory and Simulation of Moiré Graphene Multilayers”. PhD thesis. Imperial College London, 2021. URL: <http://hdl.handle.net/10044/1/96089>.
- [174] N. Marzari et al. “Maximally localized Wannier functions: Theory and applications”. In: *Rev. Mod. Phys.* 84 (2012), pp. 1419–1475.
- [175] X. L. Yang, S. H. Guo, and F. T. Chan. “Analytic solution of a two-dimensional hydrogen atom. I. Nonrelativistic theory”. In: *Phys. Rev. A* 43.3 (1991).
- [176] P. Cudazzo, I. V. Tokatly, and A. Rubio. “Dielectric screening in two-dimensional insulators: Implications for excitonic and impurity states in graphane”. In: *Phys. Rev. B* 84 (2011), p. 085406.
- [177] M. Rohlfing and S. G. Louie. “Electron-hole excitations and optical spectra from first principles”. In: *Phys. Rev. B* 62 (2000), pp. 4927–4044.
- [178] L. V. Keldysh. “Coulomb interaction in thin semiconductor and semimetal films”. In: *Soviet Journal of Experimental and Theoretical Physics Letters* 29.658 (1979).
- [179] A. S. Rodin, A. Carvalho, and A. H. Castro Neto. “Excitons in anisotropic two-dimensional semiconducting crystals”. In: *Phys. Rev. B* 90.075429 (2014).
- [180] D. Van Tuan, M. Yang, and H. Dery. “Coulomb interaction in monolayer transition-metal dichalcogenides”. In: *Phys. Rev. B* 98.125308 (2018).
- [181] G. Berghäuser and E. Malic. “Analytical approach to excitonic properties of MoS₂”. In: *Phys. Rev. B* 89.125309 (2014).
- [182] M. N. Brunetti, O. L. Berman, and R. Y. Kezerashvili. “Optical absorption by indirect excitons in a transition metal dichalcogenide/hexagonal boron nitride heterostructure”. In: *J. Phys.: Condens. Matter* 30.225001 (2018).

- [183] T. G. Pedersen, K. Pedersen, and T. B. Kriestensen. “Optical matrix elements in tight-binding calculations”. In: *Phys. Rev. B* 63 (2001), p. 201101.
- [184] L. C. Lew Yan Voon and L. R. Ram-Mohan. “Tight-binding representation of the optical matrix elements: Theory and applications”. In: *Phys. Rev. B* 47.15500 (1993).
- [185] A. J. Read and R. J. Needs. “Calculation of optical matrix elements with nonlocal pseudopotentials”. In: *Phys. Rev. B* 44 (1991), p. 13071.
- [186] P. Giannozzi et al. “Quantum espresso: a modular and open-source software project for quantum simulation of materials”. In: *Journal of Physics: Condensed Matter* 21(39).395502 (2009).
- [187] D. R. Hamann. “Optimized norm-conserving Vanderbilt pseudopotentials”. In: *Phys. Rev. B* 88.085117 (2013).
- [188] M. Aghajanian. “Theory and simulation of electronic and optical properties of charged defects in two-dimensional semiconductors”. PhD thesis. Imperial College London, 2021. URL: <https://spiral.imperial.ac.uk/handle/10044/1/93714>.
- [189] A. Chaves et al. “Bandgap engineering of two-dimensional semiconductor materials”. In: *npj 2D Materials and Applications* 4.29 (2020).
- [190] C. D. H. Chisholm. *Group theoretical techniques in quantum chemistry*. Ed. by New York: Academic Press. 1976.
- [191] E. Kaxiras. *Atomic and Electronic Structure of Solids*. Ed. by Cambridge University Press. 2003.
- [192] H. Peelaers and C. G. Van de Walle. “Effects of strain on band structure and effective masses in MoS₂”. In: *Phys. Rev. B* 86 (2012), p. 241401.
- [193] F. Zahid et al. “A generic tight-binding model for monolayer, bilayer and bulk MoS₂”. In: *AIP Advances* 3 (2013), p. 052111.
- [194] H. V. Phuc et al. “Tuning the Electronic Properties, Effective Mass and Carrier Mobility of MoS₂ Monolayer by Strain Engineering: First-Principle Calculations”. In: *Journal of Electronic Materials* 47.1 (2018).

- [195] M. H. Naik et al. “Kolmogorov–Crespi Potential For Multilayer Transition-Metal Dichalcogenides: Capturing Structural Transformations in Moiré Superlattices”. In: *J. Phys. Chem. C* 123.15 (2019), pp. 9770–9778.
- [196] K. Yan et al. “Formation of bilayer Bernal graphene: layer-by-layer epitaxy via chemical vapor deposition”. In: *Nano Lett.* 11.3 (2011), pp. 1106–1110.
- [197] N. Cortés et al. “Stacking change in MoS₂ bilayers induced by interstitial Mo impurities”. In: *Scientific Reports* 8.2143 (2018).
- [198] W. Zhang et al. “Van der Waals stacked 2D layered materials for optoelectronics”. In: *2D Materials* 3.2 (2016), p. 022001.
- [199] D. Y. Qiu, F. H. da Jornada, and S. G. Louie. “Erratum: Optical Spectrum of MoS₂: Many-Body Effects and Diversity of Exciton States”. In: *Phys. Rev. Lett.* 115.119901 (2015).
- [200] P. Rivera et al. “Interlayer valley excitons in heterobilayers of transition metal dichalcogenides”. In: *Nat. Nanotechnol.* 13 (2018), pp. 1004–1015.
- [201] S. Plimpton. “Fast parallel algorithms for short-range molecular dynamics”. In: *Journal of Computational Physics* 117.1 (1995), pp. 1–19.
- [202] URL: <http://lammps.sandia.gov>.
- [203] J.-W. Jiang and Y.-P. Zhou. *Handbook of Stillinger-Weber potential parameters for two-dimensional atomic crystals*. 2017.
- [204] URL: https://en.wikipedia.org/wiki/Lennard-Jones_potential (visited on 12/15/2023).
- [205] A. N. Kolmogorov and V. H. Crespi. “Registry-dependent interlayer potential for graphitic systems”. In: *Phys. Rev. B* 71.235415 (2005).
- [206] G.-B. Liu et al. “Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides”. In: *Phys. Rev. B* 88.085433 (2013).

- [207] H. Nishi, Y. Matsuhita, and A. Oshiyama. “Band-unfolding approach to moiré induced band-gap opening and Fermi level velocity reduction in twisted bilayer graphene”. In: *Phys. Rev. B* 95.085420 (2017).

Appendix A

Tight-binding parameters

This appendix lists the tight-binding parameters for MoS_2 based on the wannierization procedure described in Sec. 3.4.

e_1	0.03416	$t_{7,8}^{(1)}$	-0.24128	$t_{9,6}^{(10)}$	0.04788	$t_{3,3}^{(20)}$	-0.00569
e_3	-1.89607	$t_{9,10}^{(1)}$	0.10471	$t_{11,6}^{(10)}$	0.00861	$t_{4,4}^{(20)}$	0.06339
e_4	-2.32423	$t_{10,11}^{(1)}$	-0.03880	$t_{4,2}^{(10)}$	0.07142	$t_{5,5}^{(20)}$	0.00132
e_6	-1.12487	$t_{4,1}^{(5)}$	-0.77670	$t_{10,8}^{(10)}$	-0.02343	$t_{6,6}^{(20)}$	0.01844
e_7	-0.91587	$t_{3,2}^{(5)}$	-1.36442	$t_{5,1}^{(10)}$	-0.04083	$t_{7,7}^{(20)}$	0.01087
e_9	-3.89192	$t_{5,2}^{(5)}$	2.10170	$t_{11,7}^{(10)}$	-0.00223	$t_{8,8}^{(20)}$	0.03471
e_{10}	-2.90729	$t_{9,6}^{(5)}$	0.84468	$t_{3,1}^{(10)}$	-0.01832	$t_{9,9}^{(20)}$	-0.00391
$t_{1,1}^{(1)}$	-0.18263	$t_{11,6}^{(5)}$	-0.93976	$t_{9,7}^{(10)}$	0.00085	$t_{10,10}^{(20)}$	0.06283
$t_{2,2}^{(1)}$	0.03120	$t_{10,7}^{(5)}$	1.36436	$t_{10,6}^{(10)}$	0.02272	$t_{11,11}^{(20)}$	-0.00818
$t_{3,3}^{(1)}$	-0.17461	$t_{9,8}^{(5)}$	-0.94087	$t_{1,1}^{(18)}$	0.01675	$t_{3,5}^{(20)}$	0.01228
$t_{4,4}^{(1)}$	0.86661	$t_{11,8}^{(5)}$	0.61748	$t_{2,2}^{(18)}$	-0.00142	$t_{6,8}^{(20)}$	-0.03404
$t_{5,5}^{(1)}$	-0.18730	$t_{4,1}^{(7)}$	0.05955	$t_{3,3}^{(18)}$	0.01802	$t_{9,11}^{(20)}$	-0.00164
$t_{6,6}^{(1)}$	-0.30627	$t_{10,7}^{(7)}$	0.00969	$t_{4,4}^{(18)}$	-0.05488	$t_{1,2}^{(20)}$	0.02130
$t_{7,7}^{(1)}$	0.28409	$t_{5,2}^{(7)}$	-0.04168	$t_{5,5}^{(18)}$	-0.01129	$t_{3,4}^{(20)}$	-0.00698
$t_{8,8}^{(1)}$	-0.56038	$t_{11,8}^{(7)}$	-0.23784	$t_{6,6}^{(18)}$	0.01620	$t_{4,5}^{(20)}$	-0.00637
$t_{9,9}^{(1)}$	-0.20667	$t_{3,2}^{(7)}$	0.03367	$t_{7,7}^{(18)}$	-0.00770	$t_{6,7}^{(20)}$	0.00714
$t_{10,10}^{(1)}$	0.91601	$t_{9,8}^{(7)}$	-0.22875	$t_{8,8}^{(18)}$	0.03941	$t_{7,8}^{(20)}$	0.01110
$t_{11,11}^{(1)}$	0.00180	$t_{9,6}^{(7)}$	-0.06907	$t_{9,9}^{(18)}$	0.04822	$t_{9,10}^{(20)}$	0.00448
$t_{3,5}^{(1)}$	-0.06863	$t_{11,6}^{(7)}$	-0.15333	$t_{10,10}^{(18)}$	-0.00753	$t_{10,11}^{(20)}$	-0.00057
$t_{6,8}^{(1)}$	0.40924	$t_{4,1}^{(10)}$	0.03620	$t_{11,11}^{(18)}$	-0.02455		
$t_{9,11}^{(1)}$	0.00026	$t_{10,7}^{(10)}$	-0.00142	$t_{3,5}^{(18)}$	-0.00695		
$t_{1,2}^{(1)}$	-0.25331	$t_{5,2}^{(10)}$	-0.00912	$t_{6,8}^{(18)}$	-0.00165		
$t_{3,4}^{(1)}$	-0.10659	$t_{11,8}^{(10)}$	-0.03215	$t_{9,11}^{(18)}$	0.05206		
$t_{4,5}^{(1)}$	-0.06865	$t_{3,2}^{(10)}$	-0.06115	$t_{1,1}^{(20)}$	0.01449		
$t_{6,7}^{(1)}$	-0.11030	$t_{9,8}^{(10)}$	-0.07957	$t_{2,2}^{(20)}$	-0.03304		

Table A.1: Hopping parameters for MoS₂ in eV.

$\delta z_{pp}[\text{\AA}]$	ν [eV]		$R[\text{\AA}]$		η	
	σ	π	σ	π	σ	π
2.617	4.077	-1.271	2.824	2.612	3.547	5.419
2.717	3.723	-1.112	2.888	2.688	3.590	5.497
2.817	3.397	-0.983	2.952	2.759	3.630	5.528
2.917	3.097	-0.885	3.017	2.822	3.666	5.498
3.017	2.824	-0.818	3.080	2.872	3.696	5.386
3.117	2.577	-0.792	3.143	2.899	3.722	5.158
3.217	2.355	-0.843	3.205	2.879	3.741	4.754
3.317	2.155	-1.138	3.265	2.739	3.754	4.045
3.417	1.975	-6.142	3.323	1.959	3.760	2.501

Table A.2: Fitting parameters for $p - p$ -hopping for MoS₂-MoS₂ bilayers. Taken from Table S2 in Vitale et al. Note that ν_π for $\delta z_{pp} = 3.417\text{\AA}$ is very large compared to adjacent layer separations. The Slater-Koster parameters resulting from these parameter sets are, however, sufficiently close that we do not require a finer separation resolution.[5]

$\delta z_{pd}[\text{\AA}]$	V [eV]		α		β		γ	
	σ	π	σ	π	σ	π	σ	π
4.208	-0.400	-4.256	-5.843	-10.332	2.386	1.710	-4.784	-2.388
4.309	-0.370	-4.508	-5.455	-10.186	2.245	1.689	-4.247	-2.412
4.409	-0.388	-4.751	-5.465	-10.050	2.171	1.666	-4.045	-2.423
4.508	-0.424	-4.988	-5.588	-9.925	2.120	1.642	-3.959	-2.422
4.609	-0.472	-5.222	-5.760	-9.813	2.081	1.616	-3.933	-2.410
4.708	-0.531	-5.461	-5.957	-9.713	2.049	1.589	-3.943	-2.387
4.809	-0.603	-5.705	-6.167	-9.627	2.022	1.561	-3.979	-2.357
4.909	-0.689	-5.949	-6.382	-9.549	1.998	1.533	-4.029	-2.318
5.008	-0.789	-6.197	-6.598	-9.482	1.976	1.504	-4.092	-2.272

Table A.3: Fitting parameters for $p_z - d_{z^2}$ -hopping for MoS₂-MoS₂ bilayers. Taken from Table S3 in Vitale et al.[5]

Appendix B

Orbital character at band edges

This appendix details the orbital character of the bandstructures near the band edges at Γ and K for both different stacking configurations and twist angles, based on sixth-nearest neighbour tight-binding calculations.

band	Γ	K
11	$p_x^{(e)}, p_x^{(o)}$	$d_{xz}^{(o)}, d_{yz}^{(o)}, d_{z^2}^{(e)}$
10	$p_y^{(e)}, p_y^{(o)}$	$d_{xz}^{(o)}, d_{yz}^{(o)}, d_{xy}^{(e)}, d_{x^2-y^2}^{(e)}$
9	$d_{x^2-y^2}^{(e)}, d_{yz}^{(o)}$	$p_x^{(o)}, p_y^{(o)}, p_z^{(e)}$
8	$d_{xy}^{(e)}, d_{xz}^{(o)}$	$p_z^{(o)}, p_x^{(e)}, p_y^{(e)}$
7	$p_z^{(o)}, p_z^{(e)}$	$p_x^{(o)}, p_y^{(o)}, p_x^{(e)}, p_y^{(e)}$
6	$d_{xz}^{(o)}, d_{yz}^{(o)}, d_{xy}^{(e)}, d_{x^2-y^2}^{(e)}$	$d_{xz}^{(o)}, d_{yz}^{(o)}, d_{z^2}^{(e)}$
5	$d_{xz}^{(o)}, d_{yz}^{(o)}, d_{xy}^{(e)}, d_{x^2-y^2}^{(e)}$	$d_{xy}^{(e)}, d_{x^2-y^2}^{(e)}$
4	$d_{z^2}^{(e)}$	$p_z^{(e)}, p_x^{(o)}, p_y^{(o)}$
3	$p_y^{(o)}, p_y^{(e)}$	$p_x^{(e)}, p_y^{(e)}, p_x^{(o)}, p_y^{(o)}$
2	$p_x^{(o)}, p_x^{(e)}$	$p_x^{(e)}, p_y^{(e)}, p_z^{(o)}$
1	$p_z^{(e)}, p_z^{(o)}$	$d_{xy}^{(e)}, d_{x^2-y^2}^{(e)}, d_{xz}^{(o)}, d_{yz}^{(o)}$

Table B.1: Orbital character of Γ and K band edges in monolayer MoS₂ without spin (comparable IV in [1]). Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

AA	Γ		K	
c ₄	1.706	$d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}, d_{yz\uparrow}^{(o,bot)}, d_{xz\uparrow}^{(o,bot)}$ $d_{x^2-y^2\uparrow}^{(e,top)}, d_{xy\uparrow}^{(e,top)}, p_{y\uparrow}^{(e,bot)}, p_{x\uparrow}^{(e,bot)}$ $p_{y\uparrow}^{(e,top)}, p_{x\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,bot)}, d_{xy\uparrow}^{(e,bot)}$	0.798	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$
c ₃	1.706	$d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,top)}, d_{yz\downarrow}^{(o,bot)}, d_{xz\downarrow}^{(o,bot)}$ $d_{x^2-y^2\downarrow}^{(e,top)}, d_{xy\downarrow}^{(e,top)}, p_{y\downarrow}^{(e,bot)}, p_{x\downarrow}^{(e,bot)}$ $p_{y\downarrow}^{(e,top)}, p_{x\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,bot)}, d_{xy\downarrow}^{(e,bot)}$	0.793	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$
c ₂	1.700	$d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,top)}, d_{yz\downarrow}^{(o,bot)}, d_{xz\downarrow}^{(o,bot)}$ $d_{x^2-y^2\downarrow}^{(e,top)}, d_{xy\downarrow}^{(e,top)}, p_{y\downarrow}^{(e,bot)}, p_{x\downarrow}^{(e,bot)}$ $p_{y\downarrow}^{(e,top)}, p_{x\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,bot)}, d_{xy\downarrow}^{(e,bot)}$	0.784	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$
c ₁	1.700	$d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}, d_{yz\uparrow}^{(o,bot)}, d_{xz\uparrow}^{(o,bot)}$ $d_{x^2-y^2\uparrow}^{(e,top)}, d_{xy\uparrow}^{(e,top)}, p_{y\uparrow}^{(e,bot)}, p_{x\uparrow}^{(e,bot)}$ $p_{y\uparrow}^{(e,top)}, p_{x\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,bot)}, d_{xy\uparrow}^{(e,bot)}$	0.780	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$
v ₁	-0.949	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$ $d_{z^2\uparrow}^{(e,bot)}, p_{z\uparrow}^{(e,top)}, d_{z^2\uparrow}^{(e,top)}, p_{z\uparrow}^{(e,bot)}$	-0.933	$p_{x\downarrow}^{(o,top)}, p_{y\downarrow}^{(o,top)}, p_{x\downarrow}^{(o,bot)}, p_{y\downarrow}^{(o,bot)}$
v ₂	-0.949	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$ $d_{z^2\downarrow}^{(e,bot)}, p_{z\downarrow}^{(e,top)}, d_{z^2\downarrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$	-0.950	$p_{x\downarrow}^{(o,top)}, p_{y\downarrow}^{(o,top)}, p_{x\downarrow}^{(o,bot)}, p_{y\downarrow}^{(o,bot)}$
v ₃	-1.256	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$ $d_{z^2\uparrow}^{(e,bot)}, p_{z\uparrow}^{(e,top)}, d_{z^2\uparrow}^{(e,top)}, p_{z\uparrow}^{(e,bot)}$	-1.077	$p_{x\uparrow}^{(o,top)}, p_{y\uparrow}^{(o,top)}, p_{x\uparrow}^{(o,bot)}, p_{y\uparrow}^{(o,bot)}$
v ₄	-1.256	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$ $d_{z^2\downarrow}^{(e,bot)}, p_{z\downarrow}^{(e,top)}, d_{z^2\downarrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$	-1.095	$p_{x\uparrow}^{(o,top)}, p_{y\uparrow}^{(o,top)}, p_{x\uparrow}^{(o,bot)}, p_{y\uparrow}^{(o,bot)}$

Table B.2: Orbital character and band energies (in eV) of Γ and K band edges in AA stacked MoS₂ bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

AB	Γ				K	
c ₄	1.715	$p_{y\uparrow}^{(e,\text{top})}, d_{x^2-y^2\uparrow}^{(e,\text{bot})}, d_{xy\uparrow}^{(e,\text{bot})}, p_{x\uparrow}^{(e,\text{top})}$ $d_{yz\uparrow}^{(o,\text{top})}, d_{yz\uparrow}^{(o,\text{bot})}, d_{xz\uparrow}^{(o,\text{bot})}, d_{xz\uparrow}^{(o,\text{top})}$			0.792	$p_{z\downarrow}^{(o,\text{bot})}$
c ₃	1.715	$p_{y\downarrow}^{(e,\text{top})}, d_{x^2-y^2\downarrow}^{(e,\text{bot})}, d_{xy\downarrow}^{(e,\text{bot})}, p_{x\downarrow}^{(e,\text{top})}$ $d_{yz\downarrow}^{(o,\text{top})}, d_{yz\downarrow}^{(o,\text{bot})}, p_{x\downarrow}^{(o,\text{bot})}, d_{xz\downarrow}^{(o,\text{top})}$			0.792	$p_{z\uparrow}^{(o,\text{top})}$
c ₂	1.670	$d_{xz\downarrow}^{(o,\text{bot})}, d_{yz\downarrow}^{(o,\text{bot})}, d_{xz\downarrow}^{(o,\text{top})}, d_{yz\downarrow}^{(o,\text{top})}$ $d_{xy\downarrow}^{(e,\text{bot})}, p_{x\downarrow}^{(e,\text{top})}, d_{x^2-y^2\downarrow}^{(e,\text{bot})}, p_{y\downarrow}^{(e,\text{top})}$			0.787	$p_{z\downarrow}^{(o,\text{top})}, p_{z\uparrow}^{(o,\text{bot})}$
c ₁	1.670	$d_{xz\uparrow}^{(o,\text{bot})}, d_{yz\uparrow}^{(o,\text{bot})}, d_{xz\uparrow}^{(o,\text{top})}, d_{yz\uparrow}^{(o,\text{top})}$ $d_{xy\uparrow}^{(e,\text{bot})}, p_{x\uparrow}^{(e,\text{top})}, d_{x^2-y^2\uparrow}^{(e,\text{bot})}, p_{y\uparrow}^{(e,\text{top})}$			0.787	$p_{z\downarrow}^{(o,\text{top})}, p_{z\downarrow}^{(o,\text{bot})}$
v ₁	-0.718	$p_{z\uparrow}^{(o,\text{top})}, p_{z\uparrow}^{(o,\text{bot})}, d_{x^2\uparrow}^{(e,\text{bot})}, p_{z\uparrow}^{(e,\text{top})}$			-0.938	$p_{x\downarrow}^{(o,\text{top})}, p_{y\downarrow}^{(o,\text{top})}$
v ₂	-0.718	$p_{z\downarrow}^{(o,\text{top})}, p_{z\downarrow}^{(o,\text{bot})}, p_{z\uparrow}^{(e,\text{bot})}, p_{z\downarrow}^{(e,\text{top})}$			-0.938	$p_{x\uparrow}^{(o,\text{bot})}, p_{y\uparrow}^{(o,\text{bot})}$
v ₃	-1.337	$p_{z\uparrow}^{(o,\text{top})}, p_{z\uparrow}^{(o,\text{bot})}, p_{z\uparrow}^{(e,\text{bot})}, d_{z^2\uparrow}^{(e,\text{top})}$			-1.088	$p_{x\downarrow}^{(o,\text{bot})}, p_{y\downarrow}^{(o,\text{bot})}$
v ₄	-1.337	$p_{z\downarrow}^{(o,\text{top})}, p_{z\downarrow}^{(o,\text{bot})}, p_{z\downarrow}^{(e,\text{bot})}, d_{z^2\downarrow}^{(e,\text{top})}$			-1.088	$p_{x\uparrow}^{(o,\text{top})}, p_{y\uparrow}^{(o,\text{top})}$

Table B.3: Orbital character and band energies (in eV) of Γ and K band edges in AB stacked MoS₂ bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

B ^{MX}	Γ			K	
c ₄	1.712	$d_{x^2-y^2\downarrow}^{(e,bot)}, p_{y\downarrow}^{(e,top)}, p_{x\downarrow}^{(e,top)}, d_{xy\downarrow}^{(e,bot)}$ $d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,top)}$	0.794	$p_{z\uparrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$	
c ₃	1.712	$d_{x^2-y^2\uparrow}^{(e,bot)}, p_{y\uparrow}^{(e,top)}, p_{x\uparrow}^{(e,top)}, d_{xy\uparrow}^{(e,bot)}$ $d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}$	0.791	$p_{z\uparrow}^{(o,bot)}$	
c ₂	1.668	$d_{xz\uparrow}^{(o,top)}, d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,bot)}, d_{yz\uparrow}^{(o,bot)}$ $p_{x\uparrow}^{(e,top)}, p_{y\uparrow}^{(e,top)}, d_{xy\uparrow}^{(e,bot)}, d_{x^2-y^2\uparrow}^{(e,bot)}$	0.787	$p_{z\downarrow}^{(o,top)}$	
c ₁	1.668	$d_{xz\downarrow}^{(o,top)}, d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,bot)}, d_{yz\downarrow}^{(o,bot)}$ $p_{x\downarrow}^{(e,top)}, p_{y\downarrow}^{(e,top)}, d_{xy\downarrow}^{(e,bot)}, d_{x^2-y^2\downarrow}^{(e,bot)}$	0.784	$p_{z\uparrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$	
v ₁	-0.695	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}, d_{z^2\uparrow}^{(e,bot)}, p_{z\uparrow}^{(e,top)}$	-0.937	$p_{x\downarrow}^{(o,bot)}, p_{y\downarrow}^{(o,bot)}$	
v ₂	-0.695	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}, p_{z\uparrow}^{(e,bot)}, p_{z\downarrow}^{(e,top)}$	-0.940	$p_{x\downarrow}^{(o,top)}, p_{y\downarrow}^{(o,top)}$	
v ₃	-1.343	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}, p_{y\downarrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$ $p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$	-1.082	$p_{x\uparrow}^{(o,bot)}, p_{y\uparrow}^{(o,bot)}$	
v ₄	-1.343	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}, p_{y\uparrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$ $p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}$	-1.085	$p_{x\uparrow}^{(o,top)}, p_{y\uparrow}^{(o,top)}$	

Table B.4: Orbital character and band energies (in eV) of Γ and K band edges in B^{MX} stacked MoS₂ bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

B^{XM}	Γ				K	
c_4	1.712	$d_{x^2-y^2\downarrow}^{(e,bot)}$, $p_{y\downarrow}^{(e,top)}$, $p_{x\downarrow}^{(e,top)}$, $d_{xy\downarrow}^{(e,bot)}$ $d_{yz\downarrow}^{(o,top)}$, $d_{xz\downarrow}^{(o,top)}$			0.794	$p_{z\uparrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$
c_3	1.712	$d_{x^2-y^2\uparrow}^{(e,bot)}$, $p_{y\uparrow}^{(e,top)}$, $p_{x\uparrow}^{(e,top)}$, $d_{xy\uparrow}^{(e,bot)}$ $d_{yz\uparrow}^{(o,top)}$, $d_{xz\uparrow}^{(o,top)}$			0.791	$p_{z\uparrow}^{(o,bot)}$
c_2	1.668	$d_{xz\uparrow}^{(o,top)}$, $d_{yz\uparrow}^{(o,top)}$, $d_{xz\uparrow}^{(o,bot)}$, $d_{yz\uparrow}^{(o,bot)}$ $p_{x\uparrow}^{(e,top)}$, $p_{y\uparrow}^{(e,top)}$, $d_{xy\uparrow}^{(e,bot)}$, $d_{x^2-y^2\uparrow}^{(e,bot)}$			0.787	$p_{z\downarrow}^{(o,top)}$
c_1	1.668	$d_{xz\downarrow}^{(o,top)}$, $d_{yz\downarrow}^{(o,top)}$, $d_{xz\downarrow}^{(o,bot)}$, $d_{yz\downarrow}^{(o,bot)}$ $p_{x\downarrow}^{(e,top)}$, $p_{y\downarrow}^{(e,top)}$, $d_{xy\downarrow}^{(e,bot)}$, $d_{x^2-y^2\downarrow}^{(e,bot)}$			0.784	$p_{z\uparrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$
v_1	-0.695	$p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$, $d_{z^2\uparrow}^{(e,bot)}$, $p_{z\uparrow}^{(e,top)}$			-0.937	$p_{x\downarrow}^{(o,bot)}$, $p_{y\downarrow}^{(o,bot)}$
v_2	-0.695	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$, $p_{z\uparrow}^{(e,bot)}$, $p_{z\downarrow}^{(e,top)}$			-0.940	$p_{x\downarrow}^{(o,top)}$, $p_{y\downarrow}^{(o,top)}$
v_3	-1.343	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$, $p_{y\downarrow}^{(e,top)}$, $p_{z\downarrow}^{(e,bot)}$ $p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$			-1.082	$p_{x\uparrow}^{(o,bot)}$, $p_{y\uparrow}^{(o,bot)}$
v_4	-1.343	$p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$, $p_{y\uparrow}^{(e,top)}$, $p_{z\downarrow}^{(e,bot)}$ $p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$			-1.085	$p_{x\uparrow}^{(o,top)}$, $p_{y\uparrow}^{(o,top)}$

Table B.5: Orbital character and band energies (in eV) of Γ and K band edges in B^{XM} stacked MoS₂ bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

B^{MM}	Γ				K	
c_4	1.719	$d_{x^2-y^2\downarrow}^{(e,bot)}$, $p_{y\downarrow}^{(e,top)}$, $p_{x\downarrow}^{(e,top)}$, $d_{xy\downarrow}^{(e,bot)}$ $d_{xz\downarrow}^{(o,bot)}$, $d_{xz\downarrow}^{(o,top)}$, $d_{yz\downarrow}^{(o,bot)}$, $d_{yz\downarrow}^{(o,top)}$ $d_{xz\uparrow}^{(o,bot)}$, $d_{xz\uparrow}^{(o,top)}$, $d_{yz\uparrow}^{(o,bot)}$, $d_{yz\uparrow}^{(o,top)}$			0.803	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$
c_3	1.719	$d_{x^2-y^2\uparrow}^{(e,bot)}$, $p_{y\uparrow}^{(e,top)}$, $p_{x\uparrow}^{(e,top)}$, $d_{xy\uparrow}^{(e,bot)}$ $d_{yz\uparrow}^{(o,top)}$, $d_{xz\uparrow}^{(o,top)}$ $d_{xz\downarrow}^{(o,bot)}$, $d_{xz\downarrow}^{(o,top)}$, $d_{yz\downarrow}^{(o,bot)}$, $d_{yz\downarrow}^{(o,top)}$ $d_{xz\uparrow}^{(o,bot)}$, $d_{xz\uparrow}^{(o,top)}$, $d_{yz\uparrow}^{(o,bot)}$, $d_{yz\uparrow}^{(o,top)}$			0.803	$p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$
c_2	1.674	$d_{xz\uparrow}^{(o,top)}$, $d_{yz\uparrow}^{(o,top)}$, $d_{xz\uparrow}^{(o,bot)}$, $d_{yz\uparrow}^{(o,bot)}$ $p_{x\uparrow}^{(e,top)}$, $p_{y\uparrow}^{(e,top)}$, $d_{xy\uparrow}^{(e,bot)}$, $d_{x^2-y^2\uparrow}^{(e,bot)}$			0.775	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$
c_1	1.674	$d_{xz\downarrow}^{(o,top)}$, $d_{yz\downarrow}^{(o,top)}$, $d_{xz\downarrow}^{(o,bot)}$, $d_{yz\downarrow}^{(o,bot)}$ $p_{x\downarrow}^{(e,top)}$, $p_{y\downarrow}^{(e,top)}$, $d_{xy\downarrow}^{(e,bot)}$, $d_{x^2-y^2\downarrow}^{(e,bot)}$			0.775	$p_{z\uparrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$
v_1	-0.744	$p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$, $d_{z^2\uparrow}^{(e,bot)}$, $p_{z\uparrow}^{(e,top)}$			-0.938	$p_{y\downarrow}^{(o,top)}$, $p_{x\downarrow}^{(o,top)}$
v_2	-0.744	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$, $p_{z\uparrow}^{(e,bot)}$, $p_{z\downarrow}^{(e,top)}$			-0.938	$p_{y\uparrow}^{(o,bot)}$, $p_{x\uparrow}^{(o,bot)}$
v_3	-1.330	$p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$, $p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$ $p_{z\downarrow}^{(e,bot)}$, $p_{z\downarrow}^{(e,top)}$, $d_{z^2\uparrow}^{(e,bot)}$, $d_{z^2\downarrow}^{(e,top)}$ $p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$			-1.083	$p_{x\downarrow}^{(o,bot)}$, $p_{y\downarrow}^{(o,bot)}$
v_4	-1.330	$p_{z\uparrow}^{(o,top)}$, $p_{z\uparrow}^{(o,bot)}$, $p_{z\downarrow}^{(o,top)}$, $p_{z\downarrow}^{(o,bot)}$ $p_{z\uparrow}^{(e,bot)}$, $p_{z\uparrow}^{(e,top)}$, $d_{z^2\uparrow}^{(e,bot)}$, $d_{z^2\downarrow}^{(e,top)}$			-1.083	$p_{x\uparrow}^{(o,top)}$, $p_{y\uparrow}^{(o,top)}$

Table B.6: Orbital character and band energies (in eV) of Γ and K band edges in B^{MM} stacked MoS₂ bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

B^{XX}	Γ		K	
c_4	1.707	$d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,top)}, d_{yz\downarrow}^{(o,bot)}, d_{xz\downarrow}^{(o,bot)}$ $d_{xy\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,top)}, p_{y\downarrow}^{(e,bot)}, p_{x\downarrow}^{(e,bot)}$ $p_{y\downarrow}^{(e,top)}, p_{x\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,bot)}, d_{xy\downarrow}^{(e,bot)}$	0.791	$p_{z\uparrow}^{(o,top)}$
c_3	1.707	$d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}, d_{yz\uparrow}^{(o,bot)}, d_{xz\uparrow}^{(o,bot)}$ $d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}$ $d_{xy\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,top)}, p_{y\uparrow}^{(e,bot)}, p_{x\uparrow}^{(e,bot)}$ $p_{y\uparrow}^{(e,top)}, p_{x\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,bot)}, d_{xy\uparrow}^{(e,bot)}$	0.791	$p_{z\downarrow}^{(o,bot)}$
c_2	1.699	$d_{yz\downarrow}^{(o,top)}, d_{xz\downarrow}^{(o,top)}, d_{yz\downarrow}^{(o,bot)}, d_{xz\downarrow}^{(o,bot)}$ $d_{xy\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,top)}, p_{y\downarrow}^{(e,bot)}, p_{x\downarrow}^{(e,bot)}$ $p_{y\downarrow}^{(e,top)}, p_{x\downarrow}^{(e,top)}, d_{x^2-y^2\downarrow}^{(e,bot)}, d_{xy\downarrow}^{(e,bot)}$	0.786	$p_{z\downarrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$
c_1	1.699	$d_{yz\uparrow}^{(o,top)}, d_{xz\uparrow}^{(o,top)}, d_{yz\uparrow}^{(o,bot)}, d_{xz\uparrow}^{(o,bot)}$ $d_{xy\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,top)}, p_{y\uparrow}^{(e,bot)}, p_{x\uparrow}^{(e,bot)}$ $p_{y\uparrow}^{(e,top)}, p_{x\uparrow}^{(e,top)}, d_{x^2-y^2\uparrow}^{(e,bot)}, d_{xy\uparrow}^{(e,bot)}$	0.786	$p_{z\downarrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}$
v_1	-0.943	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}, d_{z^2\downarrow}^{(e,bot)}, p_{z\downarrow}^{(e,top)}$ $d_{z^2\downarrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$	-0.941	$p_{y\downarrow}^{(o,top)}, p_{x\downarrow}^{(o,top)}$
v_2	-0.943	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}, d_{z^2\uparrow}^{(e,bot)}, p_{z\uparrow}^{(e,top)}$ $d_{z^2\uparrow}^{(e,top)}, p_{z\uparrow}^{(e,bot)}$	-0.941	$p_{y\uparrow}^{(o,bot)}, p_{x\uparrow}^{(o,bot)}$
v_3	-1.259	$p_{z\downarrow}^{(o,top)}, p_{z\downarrow}^{(o,bot)}, d_{z^2\downarrow}^{(e,top)}, p_{z\downarrow}^{(e,bot)}$	-1.086	$p_{x\downarrow}^{(o,bot)}, p_{y\downarrow}^{(o,bot)}$
v_4	-1.259	$p_{z\uparrow}^{(o,top)}, p_{z\uparrow}^{(o,bot)}, d_{z^2\uparrow}^{(e,top)}, p_{z\uparrow}^{(e,bot)}$	-1.086	$p_{x\uparrow}^{(o,top)}, p_{y\uparrow}^{(o,top)}$

Table B.7: Orbital character and band energies (in eV) of Γ and K band edges in B^{XX} stacked MoS_2 bilayers with spin. Qualitatively, the composition is the same between third- and sixth-nearest neighbour model.

Appendix C

Optically active excitonic states

This appendix lists the indices, energies, and degeneracies of the optically active excitons in both different stacking configurations and different twist angles, resulting from BSE calculations based on sixth nearest neighbour tight-binding calculations.

C.1 Untwisted systems

AB		
Peak	energy (eV)	exciton state indices
I	1.3322	5, 6, 7, 8
II	1.3800	16
III	1.4757	25, 26, 27, 28
IV	1.4892	44
V	1.5053	57, 58, 59 60
VI	1.6030	133, 134, 135, 136
VII	1.6334	177, 178, 193
VIII	1.6523	229, 230, 231, 232
IX	1.6757	255

Table C.1: Indices of most optically active excitons contributing to peaks as labelled in Fig. 6.15b, for AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

AA		
Peak	energy (eV)	exciton state indices
I	1.3343	7, 8
II	1.4726	25, 26, 27, 28
III	1.5048	57, 58
IV	1.6125	155, 156
V	1.6476	215, 216
VI	1.6616	239

Table C.2: Indices of most optically active excitons contributing to peaks as labelled in Fig. 6.15a, for AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

B^{MX}		
Peak	energy (eV)	exciton state indices
I	1.3300	1, 2
II	1.3336	7, 8
III	1.4682	19, 20
IV	1.4717	25, 26
V	1.5014	57, 58
VI	1.5066	61, 62
VII	1.6022	131, 132
VIII	1.6082	143, 144, 145, 146, 147, 148
IX	1.6442	215, 216
X	1.6473	223, 226

Table C.3: Indices of most optically active excitons contributing to peaks as labelled in Fig. 6.15e, for B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

B^{MM}		
Peak	energy (eV)	exciton state indices
I	1.3266	5, 6, 7, 8
II	1.3869	13, 15
III	1.4610	25, 26, 27, 28
IV	1.4723	37, 38, 39, 40
V	1.4918	41, 42, 43, 44
VI	1.5270	69, 70, 71, 73, 75, 76
VII	1.5944	125, 126, 127, 128
VIII	1.5968	135
IX	1.6340	174, 176, 182, 184, 186, 188
X	1.6680	241, 242, 244

Table C.4: Indices of most optically active excitons contributing to peaks as labelled in Fig. 6.15c, for B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

B^{XX}		
Peak	energy (eV)	exciton state indices
I	1.3341	5, 6, 7, 8
II	1.4722	17, 18, 19, 20
III	1.5049	57, 58, 59, 60
IV	1.6117	137, 138, 139, 140
V	1.6479	213, 214, 215, 216

Table C.5: Indices of most optically active excitons contributing to peaks as labelled in Fig. 6.15d, for B^{XX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

Appendix D

Most relevant transitions for optically active excitonic states

D.1 Untwisted systems

This appendix lists the most relevant valence to conduction transitions contributing to the optically active excitons in both untwisted and twisted MoS₂ homobilayers as detailed in the previous section, appendix C. In all tables, the first three columns per exciton correspond to k-point index (see Figures D.1 and D.2 for the meaning of the numeric k-point indices; K and K' are labelled as letters), the the conduction and valence band indices. In both cases, "0" refers to the lowest energy band. The fourth column lists the magnitude of this contribution relative to the complete exciton probability distribution as a percentage.

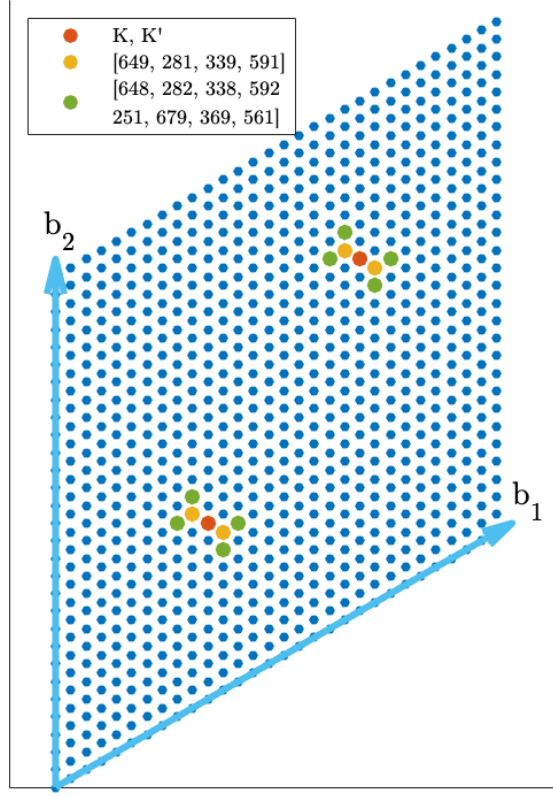


Figure D.1: Location in reciprocal space of indices of optically active excitons mentioned in the tables in this appendix. Note the broken symmetry; this is likely an artifact of the finite, asymmetric Brillouin zone.

5 (1.332 eV)				6 (1.332 eV)				7 (1.332 eV)				8 (1.332 eV)			
K'	0	27	4.71 %	K	0	27	4.72 %	K	1	26	4.66 %	K'	1	26	4.64 %
K	1	26	4.68 %	K'	1	26	4.69 %	K'	0	27	4.63 %	K	0	27	4.62 %
K	0	27	4.55 %	K'	0	27	4.56 %	K'	1	26	4.62 %	K	1	26	4.61 %
K'	1	26	4.50 %	K	1	26	4.51 %	K	0	27	4.57 %	K'	0	27	4.56 %
K'	1	27	2.51 %	K	1	27	2.50 %	K	0	26	2.47 %	K'	0	26	2.48 %
K	0	26	2.48 %	K'	0	26	2.47 %	K'	1	27	2.44 %	K	1	27	2.45 %
K	1	27	2.41 %	K'	1	27	2.40 %	K'	0	26	2.43 %	K	0	26	2.45 %
K'	0	26	2.40 %	K	0	26	2.39 %	K	1	27	2.42 %	K'	1	27	2.44 %

Table D.1: Most important transitions contributing to optically active excitons 5-8 (peak I) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

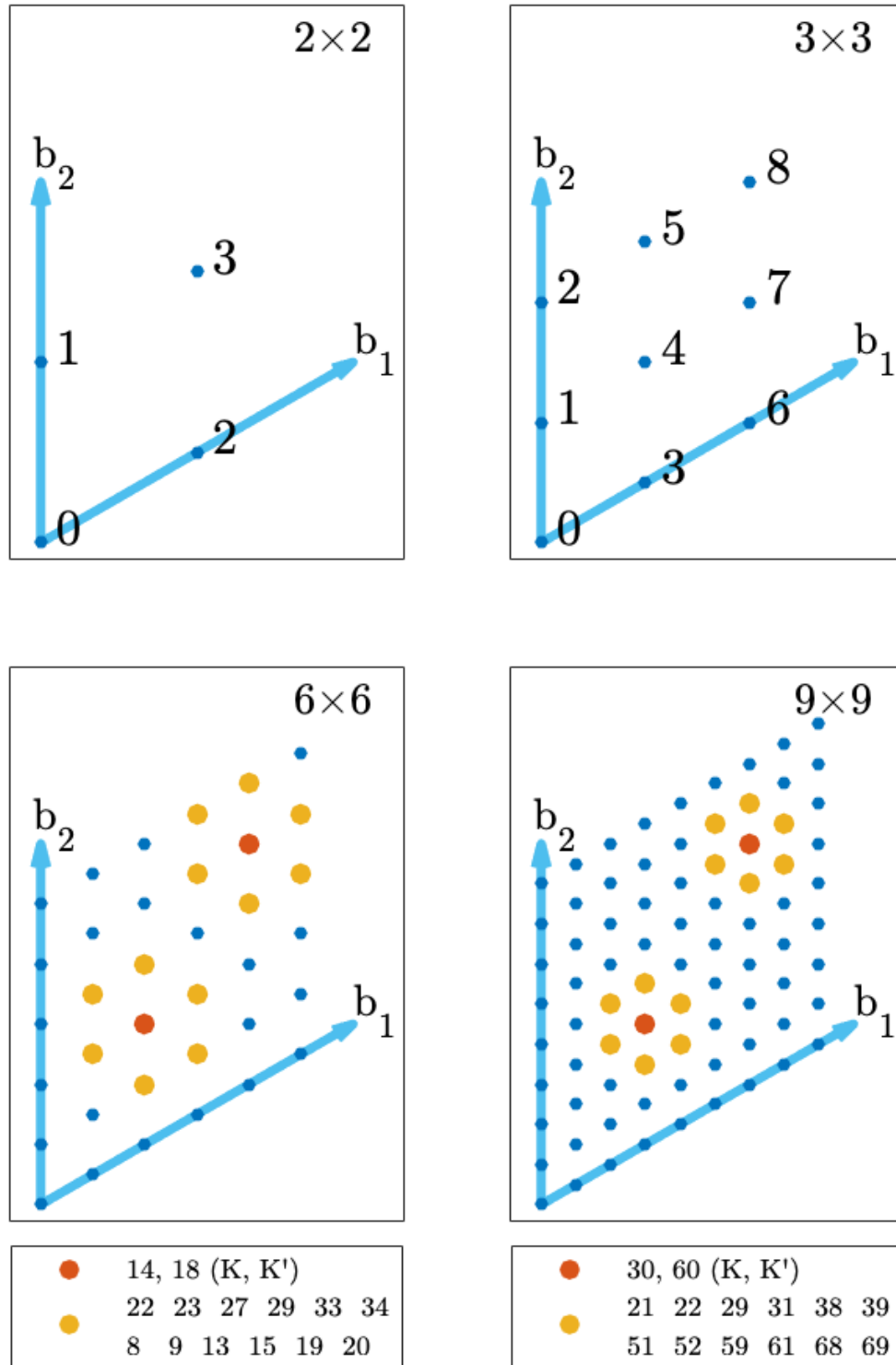


Figure D.2: Location in reciprocal space of indices of optically active excitons mentioned in the tables in this appendix for the coarsest k -grids used for the twisted systems.

5 (1.380 eV)			
K'	2	26	9.33 %
K	2	26	9.24 %
K	3	27	8.83 %
K'	3	27	8.74 %

Table D.2: Most important transitions contributing to optically active exciton 16 (peak II) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

25 (1.476 eV)				26 (1.476 eV)				27 (1.476 eV)				28 (1.476 eV)			
K'	2	24	6.16 %	K	2	24	6.17 %	K'	3	25	6.17 %	K	3	25	6.16 %
K	2	24	6.16 %	K'	2	24	6.17 %	K	3	25	6.17 %	K'	3	25	6.16 %
K	3	25	6.08 %	K'	3	25	6.08 %	K	2	24	6.08 %	K'	2	24	6.08 %
K'	3	25	6.08 %	K	3	25	6.08 %	K'	2	24	6.08 %	K	2	24	6.08 %

Table D.3: Most important transitions contributing to optically active excitons 25-28 (peak III) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

44 (1.489 eV)			
649	1	27	2.37%
281	1	27	2.37%
339	0	26	2.36%
591	0	26	2.36%
591	1	27	2.35%
339	1	27	2.35%
281	0	26	2.35%
649	0	26	2.35%
620	1	26	2.26%
310	1	26	2.25%
620	0	27	2.25%
310	0	27	2.24%

Table D.4: Most important transitions contributing to optically active exciton 44 (peak IV) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

57 (1.505 eV)				58 (1.505 eV)				59 (1.505 eV)				60 (1.505 eV)			
K	0	27	8.61%	K'	0	27	8.63%	K	1	26	8.61%	K'	1	26	8.63%
K'	0	27	8.59%	K	0	27	8.61%	K'	1	26	8.58%	K	1	26	8.60%
K	1	26	8.57%	K'	1	26	8.59%	K	0	27	8.56%	K'	0	27	8.59%
K'	1	26	8.55%	K	1	26	8.57%	K'	0	27	8.55%	K	0	27	8.57%
K'	1	27	4.59%	K	1	27	4.56%	K'	0	26	4.58%	K	0	26	4.56%
K'	0	26	4.56%	K	0	26	4.54%	K'	1	27	4.57%	K	1	27	4.54%
K	1	27	4.56%	K'	1	27	4.54%	K	0	26	4.57%	K'	0	26	4.54%
K	0	26	4.54%	K'	0	26	4.52%	K	1	27	4.54%	K'	1	27	4.52%

Table D.5: Most important transitions contributing to optically active excitons 57-60 (peak V) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

133 (1.603 eV)				134 (1.603 eV)				135 (1.603 eV)				136 (1.603 eV)			
592	1	26	1.86%	592	0	26	1.77%	251	0	27	1.86%	679	1	27	1.77%
338	1	26	1.86%	338	0	26	1.77%	679	0	27	1.86%	251	1	27	1.77%
251	0	27	1.85%	679	1	27	1.76%	592	1	26	1.85%	592	0	26	1.76%
679	0	27	1.85%	251	1	27	1.76%	338	1	26	1.85%	338	0	26	1.76%
679	1	26	1.75%	679	0	26	1.67%	592	0	27	1.75%	592	1	27	1.67%
251	1	26	1.75%	251	0	26	1.67%	338	0	27	1.75%	338	1	27	1.67%
592	0	27	1.75%	592	1	27	1.67%	679	1	26	1.75%	679	0	26	1.67%
338	0	27	1.75%	338	1	27	1.67%	251	1	26	1.75%	251	0	26	1.67%

Table D.6: Most important transitions contributing to optically active excitons 133-136 (peak VI) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

177 (1.633 eV)				178 (1.633 eV)				193 (1.635 eV)			
592	3	26	2.91%	592	2	26	3.33%	619	1	24	2.01%
338	3	26	2.91%	338	2	26	3.33%	311	1	24	2.01%
679	2	27	2.91%	679	3	27	3.32%	340	0	25	2.01%
251	2	27	2.91%	251	3	27	3.32%	590	0	25	2.01%
679	3	26	2.75%	679	2	26	3.07%	590	1	24	1.95%
251	3	26	2.75%	251	2	26	3.07%	340	1	24	1.95%
592	2	27	2.75%	592	3	27	3.06%	311	0	25	1.95%
338	2	27	2.75%	338	3	27	3.06%	619	0	25	1.95%

Table D.7: Most important transitions contributing to optically active excitons 177, 178, and 192 (peak VII) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

229 (1.652 eV)				230 (1.652 eV)				231 (1.652 eV)				232 (1.652 eV)			
K	2	24	14.24%	K'	2	24	14.24%	K'	3	25	14.24%	K	3	25	14.23%
K'	2	24	14.24%	K	2	24	14.24%	K	3	25	14.24%	K'	3	25	14.23%
K'	3	25	14.22%	K	3	25	14.22%	K	2	24	14.22%	K'	2	24	14.22%
K	3	25	14.22%	K'	3	25	14.22%	K'	2	24	14.22%	K	2	24	14.22%

Table D.8: Most important transitions contributing to optically active excitons 229-232 (peak VIII) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

255 (1.676 eV)			
561	3	27	3.29%
369	3	27	3.29%
282	2	26	3.29%
648	2	26	3.29%
648	3	27	3.05%
282	3	27	3.05%
369	2	26	3.05%
561	2	26	3.05%

Table D.9: Most important transitions contributing to optically active exciton 255 (peak IX) in AB-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

7 (1.334 eV)				8 (1.334 eV)			
K'	2	27	7.55%	K	2	27	7.55%
K	2	27	7.54%	K'	2	27	7.54%
K'	0	26	6.71%	K	0	26	6.71%
K	0	26	6.71%	K'	0	26	6.71%

Table D.10: Most important transitions contributing to optically active excitons 7 and 8 (peak I) in AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

25 (1.4726 eV)				26 (1.4726 eV)				27 (1.4732 eV)				28 (1.4732 eV)			
K'	3	25	5.50%	620	3	25	5.50%	619	1	27	5.46%	311	1	27	5.46%
K	3	25	5.50%	310	3	25	5.50%	311	1	27	5.46%	619	1	27	5.46%
K'	1	24	4.93%	620	1	24	4.93%	650	1	27	5.45%	280	1	27	5.45%
K	1	24	4.93%	310	1	24	4.93%	280	1	27	5.45%	650	1	27	5.45%
								590	1	27	5.43%	340	1	27	5.43%
								340	1	27	5.43%	590	1	27	5.43%
								621	1	27	5.41%	309	1	27	5.41%
								309	1	27	5.41%	621	1	27	5.41%
								649	1	27	5.19%	281	1	27	5.19%
								281	1	27	5.19%	649	1	27	5.19%
								591	1	27	5.16%	339	1	27	5.16%
								339	1	27	5.16%	591	1	27	5.16%

Table D.11: Most important transitions contributing to optically active (pair of degenerate) excitons 25-28 (peak II) in AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

57 (1.505 eV)				58 (1.505 eV)			
K'	2	27	19.47%	K	2	27	19.47%
K	2	27	19.47%	K'	2	27	19.47%
K'	0	26	14.14%	K	0	26	14.14%
K	0	26	14.14%	K'	0	26	14.14%

Table D.12: Most important transitions contributing to optically active excitons 57 and 58 (peak III) in AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

155 (1.613 eV)				156 (1.613 eV)			
338	3	27	3.78%	592	3	27	3.78%
592	3	27	3.78%	338	3	27	3.78%
251	3	27	2.86%	679	3	27	2.86%
679	3	27	2.86%	251	3	27	2.86%
338	1	26	2.73%	592	1	26	2.72%
592	1	26	2.73%	338	1	26	2.72%
251	1	26	2.05%	679	1	26	2.05%
679	1	26	2.05%	251	1	26	2.05%

Table D.13: Most important transitions contributing to optically active excitons 155 and 156 (peak IV) in AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

215 (1.648 eV)				216 (1.648 eV)			
K	3	25	19.79%	310	3	25	19.79%
K'	3	25	19.79%	620	3	25	19.79%
K	1	24	14.06%	310	1	24	14.06%
K'	1	24	14.06%	620	1	24	14.06%

Table D.14: Most important transitions contributing to optically active excitons 215 and 216 (peak V) in AA-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

1 (1.330 eV)				2 (1.330 eV)			
K	0	27	11.96%	K'	0	27	11.96%
K'	0	27	11.96%	K	0	27	11.96%

Table D.15: Most important transitions contributing to optically active excitons 1 and 2 (peak I) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

7 (1.334 eV)				8 (1.334 eV)			
K'	1	26	14.11%	K	1	26	14.11%
K	1	26	14.11%	K'	1	26	14.11%

Table D.16: Most important transitions contributing to optically active excitons 7 and 8 (peak II) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

19 (1.468 eV)				20 (1.468 eV)			
K'	2	25	12.43%	620	2	25	12.43%
K	2	25	12.43%	310	2	25	12.43%

Table D.17: Most important transitions contributing to optically active excitons 19 and 20 (peak III) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

25 (1.472 eV)				26 (1.472 eV)			
K'	3	24	8.53%	620	3	24	8.54%
K	3	24	8.53%	310	3	24	8.54%
K'	0	24	3.86%	620	0	24	3.86%
K	0	24	3.86%	310	0	24	3.86%

Table D.18: Most important transitions contributing to optically active excitons 25 and 26 (peak IV) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

57 (1.501 eV)				58 (1.501 eV)			
K'	0	27	26.77%	K	0	27	26.77%
K	0	27	26.77%	K'	0	27	26.77%

Table D.19: Most important transitions contributing to optically active excitons 57 and 58 (peak V) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

61 (1.507 eV)				62 (1.507 eV)			
K	1	26	19.74%	K'	1	26	19.74%
K'	1	26	19.74%	K	1	26	19.74%

Table D.20: Most important transitions contributing to optically active excitons 61 and 62 (peak VI) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

131 (1.602 eV)				132 (1.602 eV)			
679	0	27	5.57%	251	0	27	5.57%
251	0	27	5.57%	679	0	27	5.57%
592	0	27	4.49%	338	0	27	4.49%
338	0	27	4.49%	592	0	27	4.49%

Table D.21: Most important transitions contributing to optically active excitons 131 and 132 (peak VII) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

143 (1.6080 eV)				144 (1.6080 eV)			
338	1	27	5.77%	592	1	27	5.76%
592	1	27	5.77%	338	1	27	5.76%
251	1	27	3.96%	679	1	27	3.96%
679	1	27	3.96%	251	1	27	3.96%
145 (1.6083 eV)				146 (1.6083 eV)			
679	1	27	2.99%	251	1	27	3.00%
251	1	27	2.99%	679	1	27	3.00%
678	1	27	1.77%	252	1	27	1.77%
252	1	27	1.77%	678	1	27	1.77%
592	1	26	1.60%	338	1	26	1.60%
338	1	26	1.60%	592	1	26	1.60%
562	1	27	1.28%	368	1	27	1.27%
368	1	27	1.28%	562	1	27	1.27%
147 (1.6092 eV)				148 (1.6092 eV)			
341	0	27	3.76%	589	0	27	3.75%
589	0	27	3.76%	341	0	27	3.75%
338	0	27	2.43%	592	0	27	2.43%
592	0	27	2.43%	338	0	27	2.43%
341	1	27	2.40%	589	1	27	2.40%
589	1	27	2.40%	341	1	27	2.40%
340	1	27	2.09%	590	1	27	2.09%
590	1	27	2.09%	340	1	27	2.09%
311	1	27	2.07%	619	1	27	2.07%
619	1	27	2.07%	311	1	27	2.07%
251	0	27	1.99%	679	0	27	1.99%
679	0	27	1.99%	251	0	27	1.99%

Table D.22: Most important transitions contributing to optically active excitons 143-148 (peak VIII) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

215 (1.644 eV)				216 (1.644 eV)			
K	2	25	30.17%	K'	2	25	30.17%
K'	2	25	30.17%	K	2	25	30.17%

Table D.23: Most important transitions contributing to optically active excitons 215 and 216 (peak IX) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

223 (1.647 eV)				226 (1.647 eV)			
K	1	24	13.04%	K'	1	24	14.43%
K'	1	24	13.04%	K	1	24	14.43%
K	0	24	7.72%	K'	0	24	6.83%
K'	0	24	7.72%	K	0	24	6.83%
K	3	24	6.90%	K'	3	24	6.44%
K'	3	24	6.90%	K	3	24	6.44%

Table D.24: Most important transitions contributing to optically active excitons 223 and 226 (peak X) in B^{MX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

D.1.1 AB-stacked MoS₂ homobilayers

D.1.2 AA-stacked MoS₂ homobilayers

D.1.3 B^{MX}-stacked MoS₂ homobilayers

D.1.4 B^{MM}-stacked MoS₂ homobilayers

5 (1.327 eV)				6 (1.327 eV)				7 (1.327 eV)				8 (1.327 eV)			
K'	0	27	4.71%	K	0	27	4.72%	K	1	26	4.66%	K'	1	26	4.64%
K	1	26	4.68%	K'	1	26	4.69%	K'	0	27	4.63%	K	0	27	4.62%
K	0	27	4.55%	K'	0	27	4.56%	K'	1	26	4.62%	K	1	26	4.61%
K'	1	26	4.50%	K	1	26	4.51%	K	0	27	4.57%	K'	0	27	4.56%
K'	1	27	2.51%	K	1	27	2.50%	K	0	26	2.47%	K'	0	26	2.48%
K	0	26	2.48%	K'	0	26	2.47%	K'	1	27	2.44%	K	1	27	2.45%
K	1	27	2.41%	K'	1	27	2.40%	K'	0	26	2.43%	K	0	26	2.45%
K'	0	26	2.40%	K	0	26	2.39%	K	1	27	2.42%	K'	1	27	2.44%

Table D.25: Most important transitions contributing to optically active excitons 5-8 (peak I) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

13 (1.380 eV)				15 (1.380 eV)			
K'	3	27	9.67%	K	2	26	9.33%
K	2	26	9.14%	K'	2	26	9.24%
K	3	27	8.90%	K'	3	27	8.83%
K'	2	26	8.42%	K	3	27	8.74%

Table D.26: Most important transitions contributing to optically active excitons 13 and 15 (peak II) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

25 (1.461 eV)				26 (1.461 eV)				27 (1.461 eV)				28 (1.461 eV)			
K'	2	24	6.16%	K	2	24	6.17%	K'	3	25	6.17%	K	3	25	6.16%
K	2	24	6.16%	K'	2	24	6.17%	K	3	25	6.17%	K'	3	25	6.16%
K	3	25	6.08%	K'	3	25	6.08%	K	2	24	6.08%	K'	2	24	6.08%
K'	3	25	6.08%	K	3	25	6.08%	K'	2	24	6.08%	K	2	24	6.08%

Table D.27: Most important transitions contributing to optically active excitons 25-28 (peak III) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

37 (1.483 eV)				38 (1.483 eV)				39 (1.483 eV)				40 (1.483 eV)			
649	0	26	1.68%	281	1	26	1.54%	339	1	27	1.68%	591	0	27	1.54%
281	0	26	1.68%	649	1	26	1.54%	591	1	27	1.68%	339	0	27	1.54%
339	1	27	1.67%	591	0	27	1.53%	649	0	26	1.67%	281	1	26	1.53%
591	1	27	1.67%	339	0	27	1.53%	281	0	26	1.67%	649	1	26	1.53%
591	0	26	1.65%	339	1	26	1.53%	281	1	27	1.65%	649	0	27	1.52%
339	0	26	1.65%	591	1	26	1.53%	649	1	27	1.65%	281	0	27	1.52%
281	1	27	1.64%	649	0	27	1.52%	591	0	26	1.64%	339	1	26	1.52%
649	1	27	1.64%	281	0	27	1.52%	339	0	26	1.64%	591	1	26	1.52%

Table D.28: Most important transitions contributing to optically active excitons 37-40 (peak IV) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

41 (1.492 eV)				42 (1.492 eV)				43 (1.492 eV)				44 (1.492 eV)			
K'	0	27	2.27%	339	0	26	2.37%	K'	1	26	2.27%	649	1	27	2.37%
K	0	27	2.26%	591	0	26	2.37%	K	1	26	2.26%	281	1	27	2.37%
K'	1	26	2.25%	649	1	27	2.36%	K'	0	27	2.25%	339	0	26	2.36%
K	1	26	2.25%	281	1	27	2.36%	K	0	27	2.25%	591	0	26	2.36%
591	1	26	2.17%	281	0	26	2.35%	281	0	27	2.17%	591	1	27	2.35%
339	1	26	2.17%	649	0	26	2.35%	649	0	27	2.17%	339	1	27	2.35%
281	0	27	2.17%	591	1	27	2.35%	591	1	26	2.17%	281	0	26	2.35%
649	0	27	2.17%	339	1	27	2.35%	339	1	26	2.17%	649	0	26	2.35%
281	1	26	2.16%	K	0	27	2.26%	591	0	27	2.16%	K	1	26	2.26%
649	1	26	2.16%	K'	0	27	2.25%	339	0	27	2.16%	K'	1	26	2.25%
591	0	27	2.15%	K	1	26	2.25%	649	1	26	2.15%	K	0	27	2.25%
339	0	27	2.15%	K'	1	26	2.24%	281	1	26	2.15%	K'	0	27	2.24%

Table D.29: Most important transitions contributing to optically active excitons 41-44 (peak V) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

69 (1.519 eV)				70 (1.519 eV)				71 (1.519 eV)			
K	3	27	13.86%	K'	3	27	13.86%	K	2	26	13.86%
K'	3	27	13.86%	K	3	27	13.86%	K'	2	26	13.86%
K'	2	26	13.74%	K	2	26	13.74%	K	3	27	13.74%
K	2	26	13.73%	K'	2	26	13.73%	K'	3	27	13.73%
73 (1.526 eV)				75 (1.526 eV)				76 (1.526 eV)			
K	1	24	6.80%	K	0	25	6.80%	K'	0	25	6.80%
K'	1	24	6.80%	K'	0	25	6.80%	K	0	25	6.80%
K'	0	25	4.82%	K'	1	24	4.81%	K	1	24	4.82%
K	0	25	4.82%	K	1	24	4.81%	K'	1	24	4.82%
K	0	24	3.60%	K	1	25	3.61%	K'	1	25	3.60%
K'	0	24	3.60%	K'	1	25	3.61%	K	1	25	3.60%
K'	1	25	2.55%	K'	0	24	2.55%	K	0	24	2.55%
K	1	25	2.55%	K	0	24	2.55%	K'	0	24	2.55%

Table D.30: Most important transitions contributing to optically active excitons 69, 70, 71, 73, 75, 76 (peak VI) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

125 (1.594 eV)				126 (1.594 eV)				127 (1.594 eV)				128 (1.594 eV)			
591	2	27	2.45%	591	3	27	2.39%	281	3	26	2.45%	281	2	26	2.39%
339	2	27	2.45%	339	3	27	2.39%	649	3	26	2.45%	649	2	26	2.39%
281	3	26	2.44%	281	2	26	2.38%	591	2	27	2.44%	591	3	27	2.38%
649	3	26	2.44%	649	2	26	2.38%	339	2	27	2.44%	339	3	27	2.38%
281	2	27	2.40%	281	3	27	2.35%	591	3	26	2.40%	591	2	26	2.35%
649	2	27	2.40%	649	3	27	2.35%	339	3	26	2.40%	339	2	26	2.35%
591	3	26	2.40%	591	2	26	2.35%	281	2	27	2.40%	281	3	27	2.35%
339	3	26	2.40%	339	2	26	2.35%	649	2	27	2.40%	649	3	27	2.35%

Table D.31: Most important transitions contributing to optically active excitons 125-128 (peak VII) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

174 (1.629 eV)				176 (1.629 eV)			
282	0	26	1.40%	369	1	27	1.40%
648	0	26	1.40%	561	1	27	1.40%
369	1	27	1.40%	648	0	26	1.40%
561	1	27	1.40%	282	0	26	1.40%
369	0	26	1.36%	648	1	27	1.36%
561	0	26	1.36%	282	1	27	1.36%
648	1	27	1.36%	369	0	26	1.36%
282	1	27	1.36%	561	0	26	1.36%
182 (1.634 eV)				184 (1.634 eV)			
K	0	24	1.70%	K	1	25	1.70%
K'	0	24	1.70%	K'	1	25	1.70%
K	1	25	1.70%	K	0	24	1.70%
K'	1	25	1.70%	K'	0	24	1.70%
591	0	24	1.48%	649	1	25	1.49%
339	0	24	1.48%	281	1	25	1.49%
649	1	25	1.48%	591	0	24	1.49%
281	1	25	1.48%	339	0	24	1.49%
649	0	24	1.46%	339	1	25	1.47%
281	0	24	1.46%	591	1	25	1.47%
339	1	25	1.46%	649	0	24	1.47%
591	1	25	1.46%	281	0	24	1.47%
186 (1.634 eV)				188 (1.634 eV)			
649	1	24	2.00%	591	0	25	2.00%
281	1	24	2.00%	339	0	25	2.00%
591	0	25	1.99%	281	1	24	1.99%
339	0	25	1.99%	649	1	24	1.99%
591	1	24	1.99%	281	0	25	1.98%
339	1	24	1.99%	649	0	25	1.98%
281	0	25	1.97%	591	1	24	1.98%
649	0	25	1.97%	339	1	24	1.98%

Table D.32: Most important transitions contributing to optically active excitons 174, 176, 182, 184, 186, 188 (peak VIII) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

241 (1.663 eV)				242 (1.663 eV)				244 (1.663 eV)			
K'	1	24	9.17%	K	1	24	9.17%	K'	0	25	9.17%
K	1	24	9.17%	K'	1	24	9.17%	K	0	25	9.17%
K	0	25	9.09%	K'	0	25	9.09%	K	1	24	9.09%
K'	0	25	9.09%	K	0	25	9.09%	K'	1	24	9.09%
K'	0	24	4.86%	K	0	24	4.86%	K'	1	25	4.86%
K	0	24	4.86%	K'	0	24	4.86%	K	1	25	4.86%
K	1	25	4.82%	K'	1	25	4.82%	K	0	24	4.82%
K'	1	25	4.82%	K	1	25	4.82%	K'	0	24	4.82%

Table D.33: Most important transitions contributing to optically active excitons 241, 242, 244 (peak IX) in B^{MM}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

D.1.5 B^{XX}-stacked MoS₂ homobilayers

5 (1.334 eV)				6 (1.334 eV)				7 (1.334 eV)				8 (1.334 eV)			
K'	1	26	7.12%	K	0	26	7.12%	K'	0	27	7.13%	K	1	27	7.13%
K'	0	26	7.12%	K	1	26	7.12%	K'	1	27	7.13%	K	0	27	7.13%
K	1	26	7.11%	K'	1	26	7.11%	K	0	27	7.10%	K'	0	27	7.10%
K	0	26	7.11%	K'	0	26	7.11%	K	1	27	7.10%	K'	1	27	7.10%

Table D.34: Most important transitions contributing to optically active excitons 5-8 (peak I) in B^{XX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

17 (1.472 eV)				18 (1.472 eV)				19 (1.472 eV)				20 (1.472 eV)			
K'	2	25	12.32%	K'	2	25	12.32%	K'	3	24	12.32%	K'	3	24	12.32%
K	2	24	11.87%	K	2	24	11.87%	K	3	25	11.87%	K	3	25	11.87%

Table D.35: Most important transitions contributing to optically active excitons 17-20 (peak II) in B^{XX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

57 (1.505 eV)				58 (1.505 eV)				59 (1.505 eV)				60 (1.505 eV)			
K'	1	26	9.55%	K'	0	26	9.57%	K'	0	27	9.58%	K'	1	27	9.55%
K	1	26	9.52%	K	0	26	9.54%	K	0	27	9.55%	K	1	27	9.52%
K	0	26	9.50%	K	1	26	9.53%	K	1	27	9.53%	K	0	27	9.51%
K'	0	26	9.46%	K'	1	26	9.50%	K'	1	27	9.49%	K'	0	27	9.47%
K'	0	27	6.84%	K'	1	27	6.81%	K'	1	26	6.81%	K'	0	26	6.83%
K	0	27	6.80%	K	1	27	6.78%	K	1	26	6.78%	K	0	26	6.80%
K	1	27	6.79%	K	0	27	6.76%	K	0	26	6.76%	K	1	26	6.79%
K'	1	27	6.75%	K'	0	27	6.73%	K'	0	26	6.72%	K'	1	26	6.75%

Table D.36: Most important transitions contributing to optically active excitons 57-60 (peak III) in B^{XX}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

137 (1.612 eV)				138 (1.612 eV)				139 (1.612 eV)				140 (1.612 eV)			
338	2	27	2.64%	592	3	27	2.95%	251	2	26	2.81%	679	2	26	2.55%
592	2	27	2.64%	338	3	27	2.95%	679	2	26	2.81%	251	2	26	2.55%
338	3	27	2.25%	592	2	27	2.00%	251	3	26	2.15%	592	2	26	2.41%
592	3	27	2.25%	338	2	27	2.00%	679	3	26	2.15%	338	2	26	2.41%
251	3	27	1.91%	679	3	27	1.99%	338	3	26	2.08%	679	3	26	2.32%
679	3	27	1.91%	251	3	27	1.99%	592	3	26	2.08%	251	3	26	2.32%
251	2	27	1.73%	679	2	27	1.72%	338	2	26	1.62%	592	3	26	1.25%
679	2	27	1.73%	251	2	27	1.72%	592	2	26	1.62%	338	3	26	1.25%

Table D.37: Most important transitions contributing to optically active excitons 137-140 (peak IV) in B^{xx}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

213 (1.648 eV)				214 (1.648 eV)				215 (1.648 eV)				216 (1.648 eV)			
K'	3	24	23.53%	K'	3	24	23.54%	K'	2	25	23.54%	K'	2	25	23.53%
K	3	25	22.68%	K	3	25	22.69%	K	2	24	22.68%	K	2	24	22.67%
K'	2	25	9.58%	K'	2	25	9.57%	K'	3	24	9.57%	K'	3	24	9.58%
K	2	24	9.23%	K	2	24	9.22%	K	3	25	9.23%	K	3	25	9.24%

Table D.38: Most important transitions contributing to optically active excitons 213-216 (peak V) in B^{xx}-stacked MoS₂ homobilayers in vacuum. The calculation used a 30×30 k-grid and a cutoff energy of 3.0 eV.

D.2 Twisted systems

D.2.1 21.79° twisted MoS₂ homobilayers

49 (1.331 eV)				54 (1.331 eV)			
60	0	195	44.77%	30	1	194	44.69%
59	1	195	8.19%	29	1	195	8.18%
69	1	195	8.19%	39	1	195	8.18%
52	1	195	7.98%	22	1	195	7.97%
51	3	194	7.31%	21	3	194	7.20%
61	3	194	7.29%	31	3	194	7.19%
68	3	194	7.14%	38	3	194	7.05%

Table D.39: Most important transitions contributing to optically active excitons 49 and 54 (peak I) in 21.79° twisted MoS₂ homobilayers in vacuum. The calculation used a 9×9 k-grid and a cutoff energy of 2.3 eV.

345 (1.472 eV)				346 (1.472 eV)			
30	2	193	21.03%	60	2	193	20.84%
60	2	193	18.25%	30	2	193	18.03%
349 (1.472 eV)							
30	3	192	33.29%				
39	0	193	7.18%				
29	0	193	7.18%				
22	0	193	7.02%				
60	3	192	6.48%				
31	2	192	6.27%				
21	2	192	6.26%				
38	2	192	6.19%				

Table D.40: Most important transitions contributing to optically active excitons 345, 346, 349 (peak II) in 21.79° twisted MoS₂ homobilayers in vacuum. The calculation used a 9×9 k-grid and a cutoff energy of 2.3 eV.

461 (1.495 eV)				463 (1.495 eV)			
60	0	195	51.40%	30	1	194	51.41%
68	3	194	10.09%	38	3	194	10.02%
59	1	195	7.99%	39	1	195	8.03%
69	1	195	7.97%	29	1	195	8.00%

Table D.41: Most important transitions contributing to optically active excitons 461 and 463 (peak III) in 21.79° twisted MoS₂ homobilayers in vacuum. The calculation used a 9×9 k-grid and a cutoff energy of 2.3 eV.

1277 (1.637 eV)				1283 (1.638 eV)			
30	2	193	33.93%	30	3	192	54.68%
60	2	193	22.68%	22	0	193	6.02%
				29	0	193	4.70%
				39	0	193	4.66%
				21	2	192	2.59%
				31	2	192	2.57%

Table D.42: Most important transitions contributing to optically active excitons 1277 and 1283 (peak IV) in 21.79° twisted MoS₂ homobilayers in vacuum. The calculation used a 9×9 k-grid and a cutoff energy of 2.3 eV.

1604 (1.667 eV)				1605 (1.667 eV)			
53	2	195	4.31%	53	2	195	3.69%
77	2	195	3.64%	37	2	195	3.26%
37	2	195	3.03%	77	2	195	3.16%
13	2	195	2.64%	13	2	195	2.89%
44	5	193	2.42%	44	5	193	2.09%
50	2	195	2.03%	46	5	193	1.87%
1622 (1.669 eV)							
77	3	194	5.80%				
53	3	194	4.93%				
13	3	194	4.76%				
37	3	194	3.94%				

Table D.43: Most important transitions contributing to optically active excitons 1604, 1605, 1622 (peak V) in 21.79° twisted MoS₂ homobilayers in vacuum. The calculation used a 9×9 k-grid and a cutoff energy of 2.3 eV.

605 (1.353 eV)				606 (1.353 eV)			
28	0	1029	15.16%	14	0	1029	15.17%
14	1	1028	8.92%	28	1	1028	8.91%
34	2	1029	6.14%	8	2	1029	6.14%
27	2	1029	6.13%	15	2	1029	6.13%
23	2	1029	6.11%	19	2	1029	6.11%
22	3	1028	5.84%	20	3	1028	5.84%
29	3	1028	5.82%	13	3	1028	5.82%
33	3	1028	5.80%	9	3	1028	5.80%
621 (1.354 eV)				622 (1.354 eV)			
14	1	1028	15.38%	28	1	1028	15.39%
28	0	1029	9.13%	14	0	1029	9.13%
13	2	1029	6.14%	29	2	1029	6.14%
20	2	1029	6.13%	22	2	1029	6.13%
9	2	1029	6.10%	33	2	1029	6.11%
15	3	1028	5.86%	27	3	1028	5.87%
8	3	1028	5.84%	34	3	1028	5.85%
19	3	1028	5.82%	23	3	1028	5.82%

Table D.44: Most important transitions contributing to optically active excitons 605, 606, 621 and 622 (peak I) in 9.43° twisted MoS₂ homobilayers in vacuum. The calculation used a 6×6 k-grid and a cutoff energy of 1.85 eV.

3904 (1.520 eV)							
14	0	1029	34.54%				
28	1	1028	26.22%				
3972 (1.523 eV)				3973 (1.523 eV)			
14	1	1028	37.30%	28	1	1028	37.30%
28	0	1029	29.16%	14	0	1029	29.16%

Table D.45: Most important transitions contributing to optically active excitons 3904, 3972 and 3973 (peak II) in 9.43° twisted MoS_2 homobilayers in vacuum. The calculation used a 6×6 k-grid and a cutoff energy of 1.85 eV.

4755 (1.546 eV)			
18	15	1024	4.42%
3	14	1025	4.38%
29	21	1029	4.19%
33	21	1029	3.81%
14	0	1029	3.67%
28	1	1028	3.56%
23	23	1028	3.47%
8	21	1029	3.45%

Table D.46: Most important transitions contributing to optically active excitons 4755 (peak III) in 9.43° twisted MoS_2 homobilayers in vacuum. The calculation used a 6×6 k-grid and a cutoff energy of 1.85 eV.

7332 (1.608 eV)				7337 (1.608 eV)				7350 (1.608 eV)				7353 (1.608 eV)			
29	9	1029	10.31%	29	9	1029	7.38%	19	10	1029	7.31%	16	7	1027	6.07%
33	6	1029	2.98%	16	6	1027	5.31%	33	11	1029	3.56%	10	8	1029	5.96%
32	2	1028	2.92%	19	4	1029	4.58%	23	14	1028	2.77%	15	2	1029	4.02%
30	1	1027	2.76%	24	6	1027	4.12%	34	6	1028	2.45%	17	9	1028	3.99%
16	6	1027	2.58%	25	6	1029	3.47%	10	2	1029	2.14%	24	7	1027	3.68%
9	11	1028	2.26%	33	4	1029	3.10%	29	11	1029	2.05%	2	7	1027	3.60%
22	12	1029	2.05%	2	6	1027	2.80%	8	11	1029	1.91%	7	8	1029	3.05%
19	4	1029	2.00%	10	6	1029	2.58%	9	6	1028	1.84%	22	2	1029	2.72%
7460 (1.610 eV)				7525 (1.612 eV)				7573 (1.612 eV)							
19	2	1029	5.23%	24	7	1027	7.29%	32	9	1028	12.55%				
16	7	1027	5.21%	25	8	1029	5.74%	33	2	1029	11.56%				
17	9	1028	4.96%	19	2	1029	5.30%	25	8	1029	6.04%				
25	8	1029	4.62%	10	8	1029	5.02%	2	7	1027	5.84%				
10	8	1029	4.13%	17	9	1028	4.80%	19	2	1029	5.66%				
33	2	1029	3.87%	2	7	1027	4.40%	2	7	1026	3.32%				
32	9	1028	3.65%	9	3	1028	3.41%	24	7	1026	2.79%				
24	7	1027	3.62%	23	3	1028	2.61%	18	10	1024	2.59%				

Table D.47: Most important transitions contributing to optically active excitons 7332, 7337, 7350, 7353, 7460, 7525, 7573 (peak IV) in 9.43° twisted MoS_2 homobilayers in vacuum. The calculation used a 6×6 k-grid and a cutoff energy of 1.85 eV.

8882 (1.637 eV)			
25	8	1029	6.41%
32	9	1028	6.34%
21	11	1026	4.88%
24	13	1026	4.51%
2	13	1026	3.94%
23	23	1028	3.33%
3	11	1025	2.84%
24	7	1027	2.79%

Table D.48: Most important transitions contributing to optically active excitons 8882 (peak V) in 9.43° twisted MoS₂ homobilayers in vacuum. The calculation used a 6×6 k-grid and a cutoff energy of 1.85 eV.

D.2.2 9.43° twisted MoS₂ homobilayers

D.2.3 7.34° twisted MoS₂ homobilayers

876 (1.360 eV)				899 (1.363 eV)				900 (1.363 eV)			
3	7	1698	13.09%	1	11	1699	9.22%	1	10	1698	9.20%
2	7	1699	11.92%	3	11	1699	9.21%	3	10	1698	9.18%
1	6	1698	11.89%	2	10	1698	9.19%	2	11	1699	9.18%
3	10	1697	8.15%	3	6	1696	8.24%	3	7	1697	8.19%
3	9	1698	7.00%	1	7	1696	6.16%	2	7	1696	6.17%
2	11	1696	6.97%	2	6	1697	6.16%	1	6	1697	6.17%
1	10	1697	6.95%	3	13	1699	4.03%	3	12	1698	4.06%
2	8	1699	5.89%	1	8	1696	3.69%	1	9	1697	3.68%

Table D.49: Most important transitions contributing to optically active excitons 876, 899 and 900 (peak I) in 7.34° twisted MoS₂ homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 2.0 eV.

2069 (1.457 eV)			
1	10	1697	10.73%
2	11	1696	10.27%
3	10	1697	8.67%
1	6	1698	4.72%
3	7	1698	4.71%
2	7	1699	4.47%
3	12	1697	4.33%
1	9	1698	3.11%

Table D.50: Most important transitions contributing to optically active exciton 2069 (peak II) in 7.34° twisted MoS₂ homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 2.0 eV.

2595 (1.493 eV)				2601 (1.493 eV)			
3	7	1697	26.08%	3	9	1697	21.37%
3	12	1698	21.55%	3	10	1698	15.45%
2	8	1696	6.87%	3	10	1697	7.58%
1	10	1698	6.86%	1	12	1698	7.19%
2	11	1699	6.78%	2	13	1699	7.13%
1	9	1697	6.70%	2	7	1696	6.15%
1	6	1697	3.36%	1	6	1697	6.14%
2	7	1696	3.15%	3	9	1698	5.16%

Table D.51: Most important transitions contributing to optically active exciton 2595 and 2601 (peak III) in 7.34° twisted MoS₂ homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 2.0 eV.

3444 (1.532 eV)				3452 (1.532 eV)				3541 (1.535 eV)			
3	7	1694	23.13%	3	9	1694	19.94%	3	10	1694	8.37%
2	8	1695	15.80%	2	7	1695	14.66%	3	11	1695	5.76%
1	9	1694	15.71%	1	6	1694	14.55%	3	9	1689	4.36%
3	12	1689	8.75%	3	10	1689	8.43%	1	12	1694	4.00%
1	10	1689	5.33%	1	9	1694	4.86%	1	6	1689	3.96%
2	11	1688	5.20%	2	8	1695	4.77%	2	13	1695	3.81%
1	6	1694	4.40%	1	12	1689	4.43%	2	11	1695	3.26%
2	7	1695	4.31%	2	13	1688	4.33%	2	7	1688	3.09%
3547 (1.535 eV)				3551 (1.535 eV)				3558 (1.535 eV)			
2	79	1699	6.08%	3	12	1694	11.61%	3	36	1698	13.39%
3	66	1697	4.91%	3	7	1689	7.64%	3	36	1697	9.84%
1	6	1681	4.42%	1	10	1694	7.30%	1	14	1681	7.49%
1	10	1681	3.54%	2	11	1695	6.63%	3	12	1694	3.49%
3	66	1698	3.38%	2	8	1688	4.86%	2	93	1696	1.96%
1	64	1698	2.88%	1	9	1689	4.78%	2	58	1699	1.84%
1	64	1697	2.43%	2	13	1695	3.48%	3	7	1680	1.69%
3	10	1684	2.19%	1	12	1694	2.96%	2	16	1677	1.60%

Table D.52: Most important transitions contributing to optically active exciton 3444, 3452, 3541, 3547, 3551, 3558 (peak IV) in 7.34° twisted MoS₂ homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 2.0 eV.

D.2.4 6.01° twisted MoS₂ homobilayers

2373 (1.368 eV)				2374 (1.368 eV)				2438 (1.371 eV)				2439 (1.371 eV)			
8	4	2535	23.81%	4	4	2535	23.76%	5	24	2544	0.55%	8	4	2535	1.88%
4	7	2534	15.77%	8	7	2534	15.63%	0	50	2546	0.53%	4	4	2535	1.87%
4	3	2534	6.24%	8	3	2534	5.91%	7	12	2542	0.50%	4	7	2534	1.72%
7	9	2535	5.56%	5	9	2535	5.54%	7	24	2544	0.45%	8	7	2534	1.71%
2	9	2535	5.51%	1	9	2535	5.51%	4	24	2546	0.43%	4	3	2534	0.71%
3	9	2535	5.50%	6	9	2535	5.51%	5	9	2543	0.40%	8	3	2534	0.68%
5	12	2532	3.48%	2	12	2532	3.44%	8	35	2545	0.38%	2	24	2544	0.43%
6	12	2532	3.44%	3	12	2532	3.44%	1	24	2544	0.32%	4	38	2545	0.39%
2440 (1.371 eV)				2441 (1.371 eV)				2442 (1.371 eV)				2443 (1.371 eV)			
4	4	2535	9.11%	8	4	2535	8.87%	4	4	2535	1.38%	8	23	2544	0.67%
8	7	2534	8.32%	4	7	2534	8.16%	8	7	2534	1.26%	5	24	2544	0.61%
8	4	2535	8.01%	4	4	2535	7.45%	8	4	2535	1.16%	7	24	2544	0.59%
4	7	2534	7.36%	8	7	2534	6.81%	4	7	2534	1.07%	8	22	2545	0.54%
8	3	2534	3.28%	4	3	2534	3.35%	6	23	2545	0.53%	4	24	2544	0.46%
4	3	2534	3.03%	8	3	2534	2.68%	4	22	2545	0.53%	2	24	2544	0.45%
5	17	2535	1.86%	7	17	2535	1.80%	8	3	2534	0.49%	4	22	2545	0.42%
6	17	2535	1.86%	3	17	2535	1.79%	4	3	2534	0.44%	4	27	2544	0.38%

Table D.53: Most important transitions contributing to optically active excitons 2373, 2374, and 2438-2443 (peak I) in 6.01° twisted MoS₂ homobilayers in vacuum. The calculation used a 3×3 k-grid and a cutoff energy of 1.8 eV.

6007 (1.471 eV)			
8	38	2534	17.54%
4	39	2535	8.63%
5	17	2531	3.81%
5	9	2535	3.72%
7	15	2530	3.66%
1	17	2531	3.43%
6	17	2531	3.35%
7	12	2532	3.24%

Table D.54: Most important transitions contributing to optically active exciton 6007 (peak II) in 6.01° twisted MoS₂ homobilayers in vacuum. The calculation used a 3×3 k-grid and a cutoff energy of 1.8 eV.

D.2.5 5.09° twisted MoS₂ homobilayers

D.2.6 4.41° twisted MoS₂ homobilayers

D.2.7 3.89° twisted MoS₂ homobilayers

9162 (1.528 eV)				9195 (1.529 eV)			
4	4	2535	33.24%	8	7	2534	26.21%
6	9	2535	6.45%	8	3	2534	10.50%
8	7	2534	5.19%	4	4	2535	7.24%
1	9	2535	4.50%	1	9	2531	6.36%
5	9	2535	4.04%	6	9	2531	4.92%
2	15	2530	3.74%	3	12	2530	4.05%
4	5	2535	3.19%	5	9	2531	3.17%
3	15	2530	2.92%	2	12	2530	3.01%

Table D.55: Most important transitions contributing to optically active excitons 9162 and 9195 (peak III) in 6.01° twisted MoS_2 homobilayers in vacuum. The calculation used a 3×3 k-grid and a cutoff energy of 1.8 eV.

2863 (1.378 eV)				2864 (1.378 eV)				2981 (1.382 eV)				2982 (1.382 eV)			
3	6	3535	19.92%	3	7	3534	19.82%	3	6	3535	19.92%	3	10	3534	15.21%
1	6	3535	17.07%	2	6	3535	17.02%	1	6	3535	17.07%	2	11	3535	13.66%
2	7	3534	17.06%	1	7	3534	17.01%	2	7	3534	17.06%	1	10	3534	13.66%
1	11	3532	7.38%	1	10	3533	7.35%	1	11	3532	7.38%	3	7	3533	11.09%
2	10	3533	7.36%	2	11	3532	7.34%	2	10	3533	7.36%	1	7	3533	10.80%
3	11	3532	7.19%	3	10	3533	7.18%	3	11	3532	7.19%	2	6	3532	10.77%
0	26	3540	2.47%	0	27	3541	2.46%	0	26	3540	2.47%	0	51	3541	2.06%
0	28	3536	2.12%	0	29	3537	2.11%	0	28	3536	2.12%	0	29	3535	1.78%

Table D.56: Most important transitions contributing to optically active excitons 2863, 2864, 2981 and 2982 (peak I) in 5.09° twisted MoS_2 homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 1.8 eV.

5602 (1.455 eV)			
3	10	3533	13.61%
3	7	3534	11.07%
1	10	3533	10.88%
2	11	3532	10.65%
3	12	3533	8.88%
1	7	3534	2.71%
2	6	3535	2.59%
0	27	3541	1.83%

Table D.57: Most important transitions contributing to optically active exciton 5602 (peak II) in 5.09° twisted MoS_2 homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 1.8 eV.

8148 (1.509 eV)				8200 (1.510 eV)			
3	7	3533	12.79%	3	10	3533	8.77%
3	10	3534	12.58%	3	7	3534	5.83%
3	10	3533	4.64%	3	9	3533	5.34%
1	39	3534	4.57%	3	12	3534	3.92%
1	7	3533	4.25%	3	10	3534	3.90%
2	6	3532	4.23%	1	7	3534	3.36%
1	10	3534	4.08%	3	9	3534	3.29%
3	7	3534	3.90%	2	11	3532	3.11%

Table D.58: Most important transitions contributing to optically active excitons 8148 and 8200 (peak III) in 5.09° twisted MoS_2 homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 1.8 eV.

13468 (1.599 eV)				13475 (1.599 eV)				13478 (1.599 eV)			
0	24	3539	4.17%	3	124	3533	3.39%	0	29	3539	4.03%
0	13	3537	4.14%	3	124	3534	3.28%	0	27	3533	3.80%
0	13	3533	2.87%	1	171	3533	3.20%	0	23	3537	3.05%
0	23	3533	2.71%	2	154	3532	1.44%	0	23	3533	2.63%
0	24	3533	2.59%	3	130	3534	1.33%	0	21	3533	1.90%
0	24	3537	2.41%	3	130	3533	1.32%	0	27	3541	1.82%
0	12	3537	2.38%	0	57	3531	1.31%	0	24	3537	1.73%
0	13	3531	2.29%	2	123	3532	1.29%	0	29	3535	1.70%

Table D.59: Most important transitions contributing to optically active excitons 13468, 13475 and 13478 (peak IV) in 5.09° twisted MoS_2 homobilayers in vacuum. The calculation used a 2×2 k-grid and a cutoff energy of 1.8 eV.

3237 (1.378 eV)				3238 (1.378 eV)				3384 (1.382 eV)				3385 (1.382 eV)			
0	33	4703	9.87%	0	28	4705	9.18%	0	48	4705	6.66%	0	47	4703	6.67%
0	32	4702	9.87%	0	29	4704	9.18%	0	49	4704	6.66%	0	46	4702	6.67%
0	29	4704	9.19%	0	32	4702	6.80%	0	32	4698	6.01%	0	49	4704	6.66%
0	28	4705	9.19%	0	33	4703	6.80%	0	33	4699	6.01%	0	48	4705	6.66%
0	34	4704	5.31%	0	35	4705	5.31%	0	46	4702	5.52%	0	53	4701	5.69%
0	35	4705	5.31%	0	34	4704	5.31%	0	47	4703	5.52%	0	52	4700	5.69%
0	27	4701	3.71%	0	26	4700	5.26%	0	52	4700	5.41%	0	33	4698	5.56%
0	26	4700	3.71%	0	27	4701	5.26%	0	53	4701	5.41%	0	32	4699	5.56%

Table D.60: Most important transitions contributing to optically active excitons 3237, 3238, 3384 and 3385 (peak I) in 4.41° twisted MoS_2 homobilayers in vacuum. The calculation used a 1×1 k-grid and a cutoff energy of 1.85 eV.

4599 (1.372 eV)				4600 (1.372 eV)				4809 (1.377 eV)				4810 (1.377 eV)			
0	34	6037	12.12%	0	35	6036	11.89%	0	37	6030	8.40%	0	36	6031	8.33%
0	35	6036	12.12%	0	34	6037	11.89%	0	36	6031	8.40%	0	37	6030	8.33%
0	30	6032	10.01%	0	31	6033	10.12%	0	30	6029	7.18%	0	31	6028	7.18%
0	31	6033	10.01%	0	30	6032	10.12%	0	31	6028	7.18%	0	30	6029	7.18%
0	37	6035	9.51%	0	36	6034	9.21%	0	45	6035	7.08%	0	44	6034	7.12%
0	36	6034	9.51%	0	37	6035	9.21%	0	44	6034	7.08%	0	45	6035	7.12%
0	45	6030	4.21%	0	44	6031	4.13%	0	50	6032	6.28%	0	51	6033	6.32%
0	44	6031	4.21%	0	45	6030	4.13%	0	51	6033	6.28%	0	50	6032	6.32%

Table D.61: Most important transitions contributing to optically active excitons 4599, 4699, 4809 and 4810 (peak I) in 3.89° twisted MoS_2 homobilayers in vacuum. The calculation used a 1×1 k-grid and a cutoff energy of 1.85 eV.