The University of Technology Sydney

Doctoral Thesis

Characterizing two dimensional materials and their hybrids

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Declaration of Authorship

I, Kristopher M. Fair, declare that this thesis titled, 'Characterizing two dimensional materials and their hybrids' and the work presented in it are my own. I confirm that:

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"Nature uses only the longest threads to weave her patterns, so that each small piece of her fabric reveals the organization of the entire tapestry."

Richard P. Feynman

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Abbreviations

2D	**T**wo **D**imensional
AE	**A**ll **E**lectron
AFM	**A**omic **F**orce **M**icroscope
BSSE	**B**asis **S**et **S**uperposition **E**rror
CBM	**C**onduction **B**and **M**inimum
CDW	**C**harge **D**ensity **W**ave
CDW	**C**harge **D**ensity **W**ave
CG	**C**onjugate **G**radient
COOP	**C**rystal **O**rbital **O**verlap **P**opulation
CVD	**C**hemical **V**apour **D**eposition
DFT	**D**ensity **F**unctional **T**heory
DOS	**D**tates **O**f **S**tates
DZ	**D**ouble **Z**eta
EELS	**E**lectron **E**nergy **L**oss **S**pectra
EHT	**T**heory **H**uckel energy band **T**heory
FD	**F**inite **D**ifference
GA	**G**enetic **A**lgorithm
GEA	**G**radient **E**xpansion **A**pproximation
GGA	**G**eneralised **G**radient **A**pproximation
HF	**H**artree **F**ock
HOPT	**H**- **O**- **P**orous **T**iS_2
KS	**K**ohn- **S**ham
LCAO	**L**inear **C**ombination of **A**tomic **O**rbitals
LDA	**L**ocal **D**ensity **A**pproximation
LDOS	**L**ocal **D**tates **O**f **S**tates

LSD	**L**ocal **S**pin- **D**ensity
NN	**N**eural **N**etwork
PL	**P**hoto**L**uminescence
PS	**PS**eudopotential
PTMD	**P**ost **T**ransition **M**etal **D**ichalcogenide
PVS	**P**rogrammed **V**acuum **S**tack
RPA	**R**andom **P**hase **A**pproximation
SL	**S**ingle **L**ayer
SOEC	**S**econd **O**rder **E**lastic **C**onstant
SZ	**S**ingle **Z**eta
TISE	**T**ime- **I**independent **S**chrödinger **E**quation
TMD	**T**ransition **M**etal **D**ichalcogenide
TOEC	**T**hird **O**rder **E**lastic **C**onstant
VBM	**V**alence**B**and **M**aximum
VdW	**V**an **D**er **W**aals

THE UNIVERSITY OF TECHNOLOGY SYDNEY

Abstract

Doctor of Philosophy

Characterizing two dimensional materials and their hybrids

by Kristopher M. Fair

Numerous two dimensional materials are investigated namely graphene, as the progenitor of monolayer materials, and the emerging family of transition metal dichalcogenides (TMD)s. This work is conducted predominately using density functional theory (DFT) with calculations carried out to produce over 200 unique monolayer structures. Several of these materials, in particular graphene, molybdenum dichalcogenides and platinum dichalcogenides are studied in depth, focusing on elastic, electronic and optical properties.

Indentation calculations of large graphene sheets are optimised using empirical force fields and then examined using the higher level modelling of DFT. These demonstrate the possibility of pretension existing in the experimental analogs and suggest a compensating behaviour of such pretension in the empirical formula that was originally used to obtain the elastic properties. In addition the first atomistic modelling and characterization for the indented graphene wrinkles phenomena is given for large sheets. The elastic properties of graphene are then compared to that of MoS_2 and PtX_2 where $X = S, Se, Te$ revealing a higher elasticity in the platinum based monolayers. Electronic calculations of the dichalcogenides show a similar responses for PtX_2 to MoS_2 with orbital quantization as the bulk approaches monolayer. Analysis of the PtX_2 band structure allows the determination of effective hole and electron masses. It was observed that the platinum dichalcogenides posses exceptionally large holes and favourably large exciton binding energies with the latter determined by calculating the exciton wave function.

An alternative explanation of the relative phase stability of the TMDs is provided, utilising the crystal orbital overlap (COOP) for all TMDs in trigonal-prismatic and octahedral

coordination. In addition, transition between these phases is investigated with the calculated barrier energies given for several systems including a proposed α phase. Optical calculations of the different phases are included to emphasize the unique properties of each atomic coordination. Phonon calculations are performed and formation energies compared to summarize the entire family of TMDs by their relative and individual stability for the trigonal-prismatic, octahedral and distorted octahedral coordinations. The details of which are used in a custom neural network to ascertain correlations between material parameters. These results show a weak correlation between several properties that can be somewhat improved when considering multiple input properties at once. This can ultimately help guide the selection of hybrid heterostructure constituents.