TWO DIMENSIONAL LAYERED MATERIALS:
FIRST-PRINCIPLE INVESTIGATION

A Dissertation in
Physics
by
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Abstract

Two-dimensional layered materials have emerged as a fascinating research area due to their unique physical and chemical properties, which differ from those of their bulk counterparts. Some of these unique properties are due to carriers and transport being confined to 2 dimensions, some are due to lattice symmetry, and some arise from their large surface area, gateability, stackability, high mobility, spin transport, or optical accessibility. How to modify the electronic and magnetic properties of two-dimensional layered materials for desirable long-term applications or fundamental physics is the main focus of this thesis. We explored the methods of adsorption, intercalation, and doping as ways to modify two-dimensional layered materials, using density functional theory as the main computational methodology.

Chapter 1 gives a brief review of density functional theory. Due to the difficulty of solving the many-particle Schrödinger equation, density functional theory was developed to find the ground-state properties of many-electron systems through an examination of their charge density, rather than their wavefunction. This method has great application throughout the chemical and material sciences, such as modeling nano-scale systems, analyzing electronic, mechanical, thermal, optical and magnetic properties, and predicting reaction mechanisms.

Graphene and transition metal dichalcogenides are arguably the two most important two-dimensional layered materials in terms of the scope and interest of their physical properties. Thus they are the main focus of this thesis. In chapter 2, the structure and electronic properties of graphene and transition metal dichalcogenides are described. Alkali adsorption onto the surface of bulk graphite and metal intercalation into transition metal dichalcogenides – two methods of modifying properties through the introduction of metallic atoms into layered systems – are described in chapter 2.

Chapter 3 presents a new method of tuning the electronic properties of 2D materials: resonant physisorption. An example is given for adsorption of polycyclic aromatic hydrocarbon molecules onto graphene. The energy levels of these molecules were fine tuned to make them resonate with the graphene Fermi level, thus enhancing
the strength of their effect on the graphene electronic structure.

Chapter 4 develops the idea of coupling two distinct surface adsorption systems across a suspended atomically thin membrane. We examine a system of dual-sided adsorption of potassium onto a graphene membrane. The sequence of adsorption patterns predicted undergoes a striking devil’s staircase of intermediate coverage fractions as the difference in adsorbate chemical potential between the two sides of the membrane varies.

Chapter 5 is devoted to magnetic and band structure engineering of transition metal dichalcogenides through introduction of magnetic atoms into the lattice. Semiconducting transition metal dichalcogenide systems such as MoS$_2$ and WS$_2$ have band gaps suitable for electronic and optoelectronic applications, but are not magnetic. By intercalating and doping in a carefully designed stoichiometric ratio that precisely controls the occupation and relative placement of the dopant and host levels, we can convert a semiconducting transition metal dichalcogenide system into a half-metal or – more surprisingly – a half-semiconductor, where the conduction band is fully spin polarized and the energy scale for magnetism is the band gap.
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List of Symbols

DFT  Density functional theory
LDA  Local density approximation
GGA  Generalized gradient approximation
PBE  Perdew, Burke, and Ernzerhof functional
PAW  Projector augmented wave
TMD  Transition metal dichalcogenide
LUMO lowest unoccupied molecular orbital
HOMO Highest occupied molecular orbital
VASP Vienna \textit{ab initio} Simulation Package
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Dedication

To my family.
Chapter 1  Density Functional Theory

1.1 Introduction

Solving the Schrödinger equation exactly is essentially impossible for typical solid-state systems that have very large numbers of interacting electrons. Density functional theory (DFT) is a computational method to investigate the properties of many-body systems without solving the Schrödinger equation directly, but instead focusing on the ground-state charge density, a much simpler physical quantity than the wavefunction. DFT is based on the Hohenberg-Kohn theorem, which states that the external potential of a many-electron system is uniquely determined (up to a constant) by the electronic ground-state charge density $n_0(\mathbf{r})$. In other words, ground-state charge density formally determines everything about the many-body system’s ground state. To prove this theorem, we start from the many-electron problem

$$\hat{H} = \left[ \sum_i^N \left( -\frac{\hbar^2 \nabla_i^2}{2m} \right) + \hat{V}(\mathbf{r}_i) \right] + \hat{U}$$

(1.1)

$$\hat{U} = \sum_{i<j} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

(1.2)

$$\hat{H} \Phi = E \Phi$$

(1.3)

where $\hat{U}$ is the electron-electron interaction operator, $\hat{V}$ is the external potential, and $q$ is electron charge (here set to $q = 1$ for convenience). The system has a ground state $\Phi$ with density $n_0(\mathbf{r})$. If the Hohenberg-Kohn theorem is not true, then there exists another external potential $\hat{V}'$ and Hamiltonian $H' = -\hat{P}^2/2m + \hat{V}' + \hat{U}$ with ground-state $\Psi$ and a ground-state energy $E'$ which has the same charge.
density $n_0(r)$. Because $\Phi$ is not the ground state of $\hat{H}'$ while $\Psi$ is not the ground state of $\hat{H}$

$$\langle \Phi | \hat{H}' | \Phi \rangle + \langle \Psi | \hat{H} | \Psi \rangle > \langle \Phi | \hat{H} | \Phi \rangle + \langle \Psi | \hat{H}' | \Psi \rangle = E + E'. \quad (1.4)$$

On the other hand, we can also relate the expectation values of these two Hamiltonians by simply adding and subtracting the corresponding external potentials:

$$\langle \Phi | \hat{H}' | \Phi \rangle = \langle \Phi | \hat{H} - \hat{H}' | \Phi \rangle + \langle \Phi | \hat{H} | \Phi \rangle = \langle \Phi | \hat{V} - \hat{V}' | \Phi \rangle + E \quad (1.5)$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{H} - \hat{H}' | \Psi \rangle + \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{V} - \hat{V}' | \Psi \rangle + E'. \quad (1.6)$$

Adding equations 1.5 and 1.6, we obtain

$$\langle \Phi | \hat{H}' | \Phi \rangle + \langle \Psi | \hat{H} | \Psi \rangle = \langle \Phi | \hat{V} - \hat{V}' | \Phi \rangle + E + \langle \Psi | \hat{V} - \hat{V}' | \Psi \rangle + E' = E + E'. \quad (1.7)$$

Now comparing 1.4 and 1.7, we obtain a contradiction. Namely,

$$E + E' > E + E'. \quad (1.8)$$

Therefore, the external potential of a many electron system must be uniquely determined up to a constant by the electron ground-state charge density.

From the theorem, a given density $n_0(r)$ uniquely determines the kinetic energy and electron-electron interaction energy of the system. There are one-to-one mapping between $n_0(r)$ & $T$ and $n_0(r)$ & $U$. Based on that, we can define the kinetic energy functional $T[n]$ and electron-electron interaction energy $U[n]$ functional. To introduce the second Hohenberg-Kohn theorem, We also define $F[n]$ and $V[n]$

$$F[n] = T[n] + U[n] \quad (1.9)$$

$$V[n] = \int dr^3 n(r)V(r) \quad (1.10)$$

The ground state energy of this system in an external potential $V$ can thus be written as a functional of both $V$ and $n$:

$$E[V, n] = \int dr^3 n(r)V(r) + \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle$$
\[
\begin{align*}
\int dr^3 n(r)V(r) + F[n] &= \int dr^3 n(r)V(r) + F[n] \\
V[n] + F[n] &= \int dr^3 n(r)V(r) + F[n] 
\end{align*}
\] (1.11)
(1.12)

Here the \( \Phi \rightarrow n \) means any wave function that have electron density equal to \( n \). \( \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle \) means search over all wave functions that have electron density equal to \( n \) for the minimum of \( \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle \). \( F[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle \) is independent of \( V \). The ground-state energy can be obtained variationally: the density that minimizes the \( E[V,n] \) is the exact ground-state density. This is the second Hohenberg-Kohn theorem: the functional \( F[n] \)'s output is the lowest energy (ground state energy) of the system if and only if the input density is the true ground state density.

The \( F[n] \) and \( E[V,n] \) is defined for ground state density. A density is said to be \( v \)-representable if it is associated with an antisymmetric ground state wave function of a Hamiltonian. There is no known general procedure to determine whether or not a given density is \( v \)-representable. One would reasonably expect that a physical charge density should satisfy the following conditions:

\[
\int dr^3 n(r) = N, \quad n \geq 0, \quad \int dr^3 |\nabla n(r)|^{1/2} < +\infty
\]

Related to this, we note that there are many examples of reasonable densities (i.e. satisfying the conditions given above) are not \( v \)-representable. This will cause problem if we don’t know weather an input density is a ground state density. To solve the issue, we need to introduce \( N \)-representable. Most reasonable densities can be obtained from some antisymmetric eigenstate of a Hamiltonian, although not necessarily a ground state. Such a density is called \( N \)-representable. The condition on \( N \)-representability is well established [1].

The first Hohenberg-Kohn theorem demonstrates that their is a one-to-one mapping between ground state density and kinetic/potential energy of a system. The second theorem contains a functional \( F[n] \) that is defined only for \( v \)-representable densities. The variational formula 1.11 is not for a non \( v \)-representable trial density. Since the condition for a density be \( v \)-representable is still unknown, the \( v \)-representable requirement of the density need be bypassed. Levy and Lieb developed a constrained search formulation [2–4] that only requires a density to
be N-representable:

\[ E_0[V] = \min_n \left[ \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle \right] + \int dr^3 n(r)V(r) \quad (1.13) \]

This scheme searches all antisymmetric wave functions that yield the density \( n \). There is no longer a need that \( n \) is \( v \)-representable so long as it comes from an antisymmetric wave function. In another word, \( n \) only need be N-representable. The Levy and Lieb search scheme not only leads to same ground state energy and density as the Hohenberg-Kohn analysis, but also provide a formal procedure for \( F[n] \) functional. However, to find a practical procedure for obtaining a reasonable approximation to \( F[n] \) requires further work.

### 1.2 Exchange-Correlation energy

For an interacting system, to get a practical way for computation, Kohn and Sham invoked an auxiliary non-interacting system that is designed to have the same charge density as the interacting system \( (n(r) = n_s(r)) \):

\[ \hat{H}_s = \hat{T}_s + \hat{V}_s \quad (1.14) \]

Here \( \hat{H}_s \), \( \hat{T}_s \) and \( \hat{V}_s \) are the Hamiltonian, kinetic energy operator and potential energy operator of the auxiliary non-interacting system. The kinetic energy of the interacting system \( T \) can be divided into two terms:

\[ T = T_s + T_c \quad (1.15) \]

\( T_c \) is the difference of kinetic energy between the interacting and non-interacting systems. \( T_s \) is usually treated in terms of non-interacting system’s orbitals. This leaves the \( T_c \) yet to be treated. Define the Hartree energy as:

\[ U_H[n] = \frac{1}{2} \int dr^3 \int dr^3 n(r)n(r')/|\mathbf{r} - \mathbf{r}'| \quad (1.16) \]

Then

\[ E[n] = T_s[n] + V[n] + U_H[n] + E_{xc}[n] \quad (1.17) \]
where
\[ E_{xc}[n] = T[n] - T_s[n] + U[n] - U_H[n] \] (1.18)

\( E_{xc}[n] \) is called the exchange-correlation energy. It is the difference between the kinetic energies of the interacting and non-interacting systems plus the non-classical part of the electron-electron interaction energy. The \( T_s, V, U_H \) term can be expressed in terms non-interacting system’s orbitals and the leftover \( E_{xc} \) is yet to be treated.

The Thomas-Fermi model, introduced in 1927, is the best known simple model of DFT. The essence of Thomas-Fermi model is to apply the homogeneous non-interacting system’s kinetic energy formula to slowly varying system. For the ground state of a homogeneous non-interacting system with charge density \( n_h \), the electrons’ momenta occupy a sphere centered at \( k = 0 \), so that the kinetic energy \( T_h \) of the system is

\[ T_h[n_h(r)] = \int dr^3 \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n_h(r)^{5/3} \] (1.19)

Since the system has equal local density everywhere, the ground state has a kinetic energy density of

\[ t_h[n_h(r)] = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n_h(r)^{5/3} \] (1.20)

In the Thomas-Fermi model, the kinetic energy at any point is a function of the charge density at that point. This function is a direct extension of the kinetic energy functional for a homogeneous non-interacting system to a system that varies very slowly in space.

\[ T_s[n] = \int dr^3 t_s[n] \] (1.21)

\( t_s[n] \) is the density of \( T_s[n] \). The \( t_s[n] \) is approximated as

\[ t_s[n(r)] \approx \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n(r)^{5/3}. \] (1.22)

Hence

\[ T_s[n] = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} \int dr^3 n(r)^{5/3} \] (1.23)

Classical Thomas-Fermi model does not have exchange energy term. Later a exchange energy \( E_{x}[n] \) term was proposed by Dirac [7] which resulted in Thomas-
Fermi-Dirac theory.

\[
\epsilon_x[n] = -\frac{3q^2}{4}\left(\frac{3}{\pi}\right)^{1/3}n^{4/3}
\]

\[
E_x[n] = -\frac{3q^2}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r n(r)^{4/3}
\]

(1.24)

(1.25)

The Thomas-Fermi-Dirac theory can be written as:

\[
E_{TF}[n] = \frac{3\hbar^2}{10m}(3\pi^2)^{2/3} \int dr^3 n(r)^{5/3} - \frac{3q^2}{4}\left(\frac{3}{\pi}\right)^{1/3}\int d^3r n(r)^{4/3} + \frac{1}{2} \int dr^3 \int dr' n(r)n(r')/|r-r'|
\]

(1.26)

There is no correlation energy in the Thomas-Fermi model. In Thomas-Fermi model, electronic properties of a system are expressed as functionals of electron density which is the most important idea in modern DFT.

### 1.3 Kohn-Sham equation

As mentioned previously, \( T_s \) is the non-interacting system kinetic energy.

\[
T_s = \langle \Phi_s | \hat{T} | \Phi_s \rangle = -\frac{\hbar^2}{2m} \sum_i \int d^3r \phi_i^* \nabla_i^2 \phi_i
\]

(1.27)

\[
\Phi_s = <\phi_1, \phi_2, \phi_3, \cdots \phi_N>
\]

(1.28)

\[
n(r) = n_s(r) = \sum_i \phi_i^* \phi_i
\]

(1.29)

\( \Phi_s \) is the wave-function of the non-interacting system and \( \phi_i \) is the single electron wave-function of the non-interacting system. The interacting system and the non-interacting system have the same electron density. Define

\[
V_{eff}(r) = V(r) + \delta U_H[n]/\delta n(r) + \delta E_{xc}[n]/\delta n(r)
\]

(1.30)

\[
V_{eff}(r) = V(r) + \int dr^3 n(r')/|r-r'| + V_{xc}(r)
\]

(1.31)

Where \( V_{xc}(r) = \delta E_{xc}[n]/\delta n(r) \) is the exchange-correlation potential.

\[
E[n] = -\frac{\hbar^2}{2m} \sum_i \int d^3r \phi_i^* \nabla_i^2 \phi_i + \int d^3r n(r)V(r)
\]

\[
+ \frac{1}{2} \int dr^3 \int dr' n(r)n(r')/|r-r'| + E_{xc}[n]
\]

(1.32)
Finding the ground state energy of Hamiltonian $H$ is equivalent to

$$\min_{\Phi \to \mathbb{R}^n} \left[ -\frac{\hbar^2}{2m} \sum_i \int dr^3 \phi_i^* \nabla_i^2 \phi_i + \int dr^3 n(r)V(r) + \frac{1}{2} \int dr^1 \int dr^3 n(r)n(r')/|r-r'| + E_{xc}[n] \right]$$

(1.33)

with the constraint of

$$\int dr^3 \phi_i^* \phi_i = \delta_{ij}$$

(1.34)

and

$$\int dr^3 n_s(r) = \int dr^3 \sum_i \phi_i^* \phi_i = N$$

(1.35)

Define the functional of orbits:

$$\Omega[(\phi_i)] = E[n] - \sum_{i,j} \varepsilon_{ij} \int dr^3 \phi_i^* \phi_i$$

(1.36)

where $\varepsilon_{ij}$ are Lagrange multipliers. The constrained search results in the following equation set.

$$\left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(r) \right) \phi_i = \sum_j \varepsilon_{ij} \phi_j$$

(1.37)

here $\varepsilon_{ij}$ is Hermitian and can be diagonalized, and leading to the Kohn-Sham equation [9].

$$\left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(r) \right) \tilde{\phi}_i = \varepsilon_i \tilde{\phi}_i$$

(1.38)

This equation is nonlinear and can be solved iteratively. The total energy of the system is thus

$$E_0 = \sum_i \varepsilon_i - \frac{q^2}{2} \int d^3r \int d^3r' \frac{n_s(r)n_s(r')}{|r-r'|} - \int d^3r v_{xc}(r)n_s(r) + E_{xc}(n_s)$$

(1.39)

The Kohn-Sham equation treats $T_s$, the majority of the kinetic energy of the system specifically in terms of auxiliary orbitals. The Kohn-Sham scheme replaces the many-electron systems with an auxiliary non-interacting system. Hence the properties of a many electron system can be calculated with independent-particle methods [10]. The Kohn-Sham equation are the basis of most first principle calculations.
1.4 Exchange-Correlation function approximation

In the Kohn-sham equation the only thing yet to define is $E_{xc}[n]$ which is the most important quantity for determining the accuracy of a many electron system solution. Two main types of approximation are the local density approximation (LDA) and the generalized gradient approximation (GGA). The LDA treats $E_{xc}[n]$ on the density at the coordinate where $E_{xc}[n]$ is evaluated.

$$E_{xc}^{LDA}[n] = \int dr^3 n(r) \varepsilon_{xc}[n]$$ (1.40)

where $\varepsilon_{xc}[n]$ is the Exchange-Correlation density functional $\varepsilon_{xc}[n]$ can further be written as

$$\varepsilon_{xc}[n] = \varepsilon_x[n] + \varepsilon_c[n]$$ (1.41)

The Thomas Fermi model is an especially simple form of LDA. LDA usually underestimates $\varepsilon_c[n]$ while overestimates $\varepsilon_x[n]$. LDA also usually leads to over-bonding and underestimation of the band gap. GGA improves the exchange-correlation energy by including the gradient of the density.

$$E_{xc}^{GGA}[n] = \int dr^3 n(r) \varepsilon_{xc}[n(r), \nabla n(r)]$$ (1.42)

The GGA is still local and usually lead to under-binding. Two most common versions of GGA are PBE [11] and BLYP [12,13]. PBE is a parameter-free GGA proposed by John P. Perdew, Kieron Burke and Matthias Ernzerhof. Its parameters are fundamental constants which don’t depend on experimental data. BLYP is proposed by A. D. Becke. BLYP fits the exact Hartree-Fock exchange energies of a wide variety of atomic systems and reproduces the correct $\frac{1}{r}$ asymptotic behavior of the exchange-energy density. GGA give much better results than LDA on binding energy of molecules and solids. Both LDA and GGA fail for many strongly correlated systems such as copper oxide planar materials [10]. Neither LDA nor GGA are able to describe van der Waals interactions. Van der Waals force is a long-range correlation which is lacking in most standard Exchange-Correlation function approximation. Many approximations [14–34] emerged to treat van der Waals interactions. Some of these approximations [18–22] are empirical methods which use fitted data set to obtain long rang dispersion interactions. Some
methods [23–34] calculate the dispersion interaction directly by adding a non-local correlation functionals. These methods add a van der Waals dispersion directly within a DFT functional.

1.5 Spin density functional theory

When a magnet field is present in a system, more information than just the charge density is needed to characterize the system. In the same way as proving Hohenberg-Kohn theorem, it can be shown that both α (spin up) and β (spin down) electron densities are needed now and the theory becomes spin-density-functional-theory. The spin density is now reflected in the exchange correlation functional.

In the presence of magnetic field \( B(r) \), the Hamiltonian is:

\[
\hat{H} = \sum_i^N \left( -\frac{\hbar^2 \nabla_i^2}{2m} \right) + \hat{V}(r) + \hat{U}(r) + 2 \sum_i^N B(r) \cdot \mathbf{s}_i
\]  

(1.43)

\( \mathbf{s}_i \) is the electron spin. The constrained searching formula now becomes

\[
E_0[V] = \min_{n_\alpha, n_\beta} \left[ \min_{\Phi \rightarrow n_\alpha, n_\beta} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle + \int dr^3 n(r)V(r) + \int dr^3 (n_\alpha - n_\beta)B_z(r) \right]
\]  

(1.44)

Where \( n_\alpha \) and \( n_\beta \) are α and β spin electron densities respectively. Define

\[
F[n_\alpha, n_\beta] = \min_{\Phi \rightarrow n_\alpha, n_\beta} \langle \Phi | \hat{T} + \hat{U} | \Phi \rangle
\]  

(1.45)

\( F[n_\alpha, n_\beta] \) is independent of \( V \) and \( B(r) \). It searches all \( \Phi(r) \) which give the \( (n_\alpha, n_\beta) \) electron density. \( F[n_\alpha, n_\beta] \) can be separated into kinetic energy and electron-electron interaction energy

\[
F[n_\alpha, n_\beta] = T[n_\alpha, n_\beta] + U[n_\alpha, n_\beta] + E_{xc}[n_\alpha, n_\beta]
\]  

(1.46)

Following the Kohn-Sham method,

\[
F[n_\alpha, n_\beta] = T_s[n_\alpha, n_\beta] + J[n_\alpha, n_\beta] + E_{xc}[n_\alpha, n_\beta]
\]  

(1.47)

\( T_s \) is the Kohn-Sham kinetic energy corresponding to the non-interacting system with \( [n_\alpha, n_\beta] \) density. \( E_{xc}[n_\alpha, n_\beta] \) is the exchange-correlation energy. \( T_s[n_\alpha, n_\beta] \)
follows the constrained search of:

$$T_s[n_\alpha, n_\beta] = -\frac{\hbar^2}{2m} \min \left[ \sum_{i,\sigma} \lambda_{i,\sigma} \int dr^3 \phi_{i,\sigma}^* \nabla_i^2 \phi_{i,\sigma} \right]$$  (1.48)

with the constraint of

$$n_\alpha = \sum_{i,\alpha} \lambda_{i,\alpha} \phi_{i,\alpha}^* \phi_{i,\alpha}$$  (1.49)

$$n_\beta = \sum_{i,\beta} \lambda_{i,\beta} \phi_{i,\beta}^* \phi_{i,\beta}$$  (1.50)

The Kohn-Sham equations can now be written as:

$$\left( -\frac{\hbar^2 \nabla_{i,\alpha}^2}{2m} + V_{\alpha \text{eff}}(r) \right) \phi_{i,\alpha} = \varepsilon_{i,\alpha} \phi_{i,\alpha}$$  (1.51)

$$\left( -\frac{\hbar^2 \nabla_{i,\beta}^2}{2m} + V_{\beta \text{eff}}(r) \right) \phi_{i,\beta} = \varepsilon_{i,\beta} \phi_{i,\beta}$$  (1.52)

The Spin effective potentials are

$$V_{\alpha \text{eff}}(r) = V(r) + \int dr^3 n(r')/|r - r'| + V_{\alpha x\text{c}}(r) + B_z(r)$$  (1.53)

$$V_{\beta \text{eff}}(r) = V(r) + \int dr^3 n(r')/|r - r'| + V_{\beta x\text{c}}(r) - B_z(r)$$  (1.54)

$$V_{\alpha x\text{c}}(r) = \delta E_{xc}[n_\alpha, n_\beta]/\delta n_\alpha(r)$$  (1.55)

$$V_{\beta x\text{c}}(r) = \delta E_{xc}[n_\alpha, n_\beta]/\delta n_\beta(r)$$  (1.56)

The spin density functional theory is used when a system is in the presence of a magnetic field, or try to calculate the magnetic properties of a system.

### 1.6 Pseudopotential

Most solid-state DFT calculations use plane wave basis sets to describe the electronic wave functions. The wave functions close to the nucleus oscillate rapidly in space and require large basis sets to describe. The idea of pseudopotentials is replacing the atomic all-electron Coulombic potential by an effective potential acting on valence electrons. Core electrons usually change very little in all bonding situations and
thus may be treated as unchanged in calculations. Pseudopotentials replace the motion of the core electrons and the nucleus with an effective potential with core electrons are removed. Atom Coulomb potential closed to nucleus are replaced with smooth potential so that the the valence electrons are described by pseudowavefunctions with much fewer plane wave basis sets. The pseudopotential have the following advantages: reduction of basis set size, reduction of number of electrons. Two common pseudopotentials are norm-conserving [35,36] and ultrasoft pseudopotential [37]. Norm-conserving pseudopotential require the norm of the pseudo-wavefunction be identical to that of its corresponding wavefunction inside the cut off radius. Outside of the cutoff radius pseudo-wavefunction is the same as the corresponding all electron wavefunction. Norm-conserving pseudopotentials are generated by self-consistent DFT calculation of an atom with a given reference state. Ultrasoft pseudopotentials forgo the norm-conserving constraint and hence further reduce the basis-set size. The strategy is to makes the pseudopotential fully non-local and takes the form of a sum of separable terms. Ultrasoft pseudopotentials minimize the Fourier components needed to describe valence electrons. Typically, using ultrasoft pseudopotential for calculation requires only half of the cutoff energy of that of norm-conserving pseudopotentials. Ultrasoft pseudopotentials are related to the technique of projector augmented wave [38] (PAW).

1.7 Projector augmented wave method

In 1937, Slater constructed a set of basis functions which was called augmented plane wave. It consists of plane waves outside of core region while transform to atom wave function like functions inside the core region. Wave functions near the nucleus oscillate rapidly, hence requires many Fourier components to describe. PAW transforms wave functions near the nucleus to smooth wave functions to increase computational efficiency. The PAW introduces a linear transformation operator $\mathcal{T}$ which transforms the pseudo-wavefunction $|\tilde{\Phi}\rangle$ to Kohn-Sham single particle wavefunction $|\Phi\rangle$.

$$|\Phi\rangle = \mathcal{T}|\tilde{\Phi}\rangle$$ (1.57)

$$\mathcal{T} = 1 + \sum_R \hat{T}_R$$ (1.58)
The $|\tilde{\Phi}\rangle$ and $|\Phi\rangle$ differ only in a spherical region around the nucleus. $\hat{T}_R$ is non-zero in the spherical augmentation region around atom $R$ and is zero outside the sphere. In spherical augmentation region, pseudo-wavefunction can be written in terms of pseudo-partial waves. The partial waves are radial functions multiplied with spherical harmonics.

$$|\Phi\rangle = \sum_i |\tilde{\Phi}_i\rangle c_i$$ (1.59)

Define projector functions as

$$\langle p_i | \tilde{\Phi}_i \rangle = \delta_{ij}$$ (1.60)

$$|\tilde{\Phi}_i\rangle \langle p_i| = 1$$ (1.61)

Then $c_i$ can be expressed as:

$$c_i = \langle p_i | \Phi \rangle$$ (1.62)

Hence by specifying $|\tilde{\Phi}_i\rangle$, $\langle p_i |$ and $|\Phi\rangle$, $\mathcal{T}$ can be completely defined

$$\mathcal{T} = 1 + \sum_i (|\Phi_i\rangle - |\tilde{\Phi}_i\rangle) \langle p_i |$$ (1.63)

The $\mathcal{T}$ operators are also calculated as a radial functions multiplied with spherical harmonics. And then transformed into plane-wave representation since pseudo wave functions are in plane-wave representation in most DFT calculations. The PAW greatly increased the density functional theory calculations efficiency while keeping the high accuracy of first principle calculation. The PAW can be easily incorporated into pseudopotential based DFT calculation.
Chapter 2
Two Dimensional Layered materials: An introduction

2.1 Graphene

Two Dimensional (2D) Layered materials have been a hot topic of study because of their many unusual physics properties and application potentials. Among these 2D materials, graphene is the most popular 2D material and was most extensively studied. It has the most simple structure and contain only one type of element. Because of its \([\text{He}]2s^22p^2\) electronic configuration, carbon has many allotropes, such as diamond, graphite, fullerenes, armorphous carbons and graphene. Graphene is one-atom-thick sheet of \(sp^2\)-bonded carbon atoms arranged in a honeycomb lattice, first isolated by micro-mechanical cleavage of graphite. Novoselov and Geim obtained an isolated graphene layer with sticky tape [39, 40]. In October 2010, Novoselov and Geim were awarded the 2010 Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". Graphene is the building block of graphite, when rolled, nanotubes and when wrapped, 0D fullerenes. Graphene shows much interesting physics such as extremely high carrier mobility [41–43] (about 15000 \(cm^2V^{-1}s^{-1}\) at room temperature) due to zero effective mass, ballistic transport [41–43], spin transport [44–46], an unusual half-integer quantum Hall effect [47, 50, 84, 85] and coherent nonlinear optical response [51]. Graphene’s most striking property is the linear band dispersion at the point-like crossings of the conduction and valence bands at the corners of the hexagonal Brillouin zone. These so-called Dirac points support massless
Figure 2.1. Upper left panel: Graphene structure. Bottom left panel: Graphene lattice and unit vector. Upper right panel: Graphene Brillouin zone and reciprocal vectors. Bottom right panel: Graphene band structure based on DFT. The cross point at the Fermi energy is called Dirac point. The degeneracy of energy at Dirac point is due to the graphene $D_{6h}$ point group symmetry and the equivalency of A and B sub-lattice sites.

(i.e. relativistic) Dirac fermions which exhibit unusual physics such as Klein tunneling [53–55] and super-collimation [56].

2.1.1 Graphene Structure

In graphene, carbon atoms form honeycomb lattice with $D_{6h}$ point group symmetry. The C-C atom distance is $a = 1.42\,\text{Å}$, somewhat shorter than the bond length in diamond. This is because of graphene is $sp^2$ bonded while diamond is $sp^3$
bonded.

Each graphene unit cell contains 2 carbon atoms, A and B (Fig. 2.1 bottom left panel). The lattice vectors and reciprocal vectors are

\[
a_1 = (3, -\sqrt{3})a/2 \quad (2.1)
\]

\[
a_2 = (3, \sqrt{3})a/2 \quad (2.2)
\]

\[
b_1 = 2\pi(1, \sqrt{3})/3a \quad (2.3)
\]

\[
b_2 = 2\pi(1, -\sqrt{3})/3a \quad (2.4)
\]

### 2.1.2 Band Structure of Graphene

Each carbon atom in graphene is in an \(sp^2\) hybridization state with one 2s orbital and two 2p orbitals hybridized to create three hybridized \(sp^2\) orbitals. These hybridized orbitals are all in the graphene plane and are separated \(\pi/3\). The remaining occupied carbon p orbital is perpendicular to the graphene plane. These perpendicular p orbitals form graphene \(\pi\) band while the hybridized orbitals form \(\sigma\) bands. Since the \(\sigma\) band is lower in energy than \(\pi\) band, one can consider only \(\pi\) orbitals when studying graphene’s near fermi energy band structure in tight binding models. Each graphene unit cell contains two carbon atoms and graphene is comprised of two sub-lattices, called the A and B sub-lattice. Graphene can be described in the simplest approximation with a nearest neighbor tight binding model:

\[
H = \sum_{m,n,\sigma} -tC_{m\sigma}^+ C_{n\sigma}^- + h.c. \quad (2.5)
\]

where \(t\) is the nearest neighbor hopping energy (\(t=2.8\) eV). \(m\) denotes a site on sub-lattice A and \(n\) denotes a site on sub-lattice B.

\[
|A, k\rangle = (1/\sqrt{N}) \sum_m \exp(ikx_m)|m\rangle \quad (2.6)
\]

\[
|B, k\rangle = (1/\sqrt{N}) \sum_n \exp(ikx_n)|n\rangle \quad (2.7)
\]

Where \(|A, k\rangle\) and \(|B, k\rangle\) are the A and B sub-lattice wave function with crystal momentum \(k\). \(N\) is total number of unit cells. Solving the Hamiltonian gives the
band energy:

\[
E(k) = \pm t \sqrt{1 + 4\cos^2 \left( \frac{\sqrt{3}k_y a}{2} \right) + 4\cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right) + 4\cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right)}
\] (2.8)

The nearest neighbor tight binding approximation band energy shows electron-hole symmetry. Around the Dirac point, \( k = K + q \), the band structure can be expanded as \( E(q) = \pm v_F q \), \( v_F \approx 10^6 \text{m/s} \) is Fermi velocity. The Fermi velocity around Dirac point does not depend on the energy or momentum in the nearest neighbor tight binding approximation. Graphene is a semi-metal because its fermi surface is just \( K \) and \( K' \) points where the band structure shows linear dispersion. The degeneracy of energy at Dirac point is due to the graphene \( D_{6h} \) point group symmetry and the equivalency of \( A \) and \( B \) sub-lattice sites. When including the next nearest neighbor hopping of energy \( t_2 \) \( (t_2=0.1 \text{ eV}) \), one obtains:

\[
E(k) = \pm t \sqrt{1 + 4\cos^2 \left( \frac{\sqrt{3}k_y a}{2} \right) + 4\cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right) + 4\cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right) - t_2 \left(2\cos \left( \sqrt{3}k_y a \right) + 4\cos \left( \frac{3k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right)\right)}
\] (2.9)

There is a second order term added to the nearest neighbor tight binding approximation result:

\[
E(q) = \pm v_F q + O[(q/K)^2]
\] (2.10)

The electron-hole symmetry is broken. The second order term has a three fold symmetry in \( K \) space and this leads to trigonal warping of the electronic structure [57].

### 2.1.3 Potassium adsorption onto graphite

In chapter 4, dual sided adsorption of potassium on graphene is studied within first principle calculation. Here we would like to give a brief introduction of potassium adsorption onto graphite first. Experimental [60,61] and theoretical [62–64] works have been performed on akali atom adsorption on graphite for 30 years. Both theoretical and experimental works have confirmed that alkali atoms prefer the hexagonal center site regardless of adsorption density. Although there is no
Figure 2.2. Upper left panel: K adsorption on Graphene with $2 \times 2$ and $7 \times 7$ adsorption pattern [59]. Upper right panel: Band structure of K adsorption on Graphene with $2 \times 2$ pattern [58]. Bottom panel: adsorption pattern evolution at 50K and 90K. [59]

experimental works on alkali atom adsorption on graphene, theoretical works on this topic have rise up in recently a few years. These works are mainly focused on the nature of the bonding, the charge transfer between graphene and alkali and the phase transition of adsorption pattern.

The phases of K on graphite has been studied the most among all alkali metals. The K atoms sit in the hexagonal center sites of the graphite layer. The K-graphite layer perpendicular distance is about 2.79 Å and the C-K distance is about 3.13 Å. Low-energy electron diffraction and electron energy loss spectroscopy studies [60,61] have been performed to show the adsorption patterns. Low coverage supports a dispersed phase with a large K-K separation (up to 60 Å) due to a repulsive long-range interaction. The repulsive interaction mainly comes from band filling effect and the dipole-dipole interaction. The K-K distance is well-defined, although long-range crystalline order is lacking. As the coverage increases, the K-K distance decreases to about 14 Å (corresponding roughly to a $7 \times 7$ super-lattice) below which
point a dense, metallically bonded $2 \times 2$ phase appears [60].

### 2.2 Transition metal dichalcogenide

Transition metal dichalcogenide (TMD) monolayers have been isolated and characterized recently. Some semiconducting TMDs have great potential in electronic [65–69] and optoelectronic [70–72] applications because their bandgaps [65–69] are in the visible portion of the spectrum. There have already been several reports of MoS$_2$ based transistors [75,76]. The TMDs also show many fascinating phenomena such as superconductivity [77–79], charge density wave [77,80,81] and Mott transition [82].

Two common TMD monolayer structures are the honeycomb [73] (H) structure and centered honeycomb [73] (T) structure. In both type of structures, transition metal (TM) ions form a triangular lattice that is sandwiched between 2 layers of S, Se or Te atoms. For the H structure, each TM ion is trigonal prismatic coordinated by 6 S atoms and each sulfur is connected to 3 TM atoms. The H structure has a $D_{3h}$ point group symmetry. For the T structure, the upper S layer, the TM ion layer and the bottom S layer have a ABC close packing. Hence the point group symmetry is $S_6$.

Here we will focus on H-structure compounds. Typical H-structure TMDs are MoS$_2$, TaS$_2$, WS$_2$, NbS$_2$ and CrS$_2$. In these TMDs, each S ion receives 2 electrons while each transition metal ion gives 2 electrons from outer-shell d orbital. The transition metals outer shell d orbitals with different symmetry are gapped from each other by 1-2 eV due to ligand fields. These 1-2 eV gaps may not coincide with the Fermi level. For MoS$_2$ mono-layers, Mo’s 4$d_{z^2}$ orbitals are about 1.9 eV below Mo’s other 4d orbitals. The 1.9 eV gap between them corresponds to the semi-conducting gap. Since Ta has one less valence electron than Mo, TaS$_2$ is metallic. The Fermi level is below the gap between Ta’s 5$d_{z^2}$ and other 5d orbitals. The Fermi level cut the Ta’s 5$d_{z^2}$ bands which are half filled. To distinguish from the semi-conducting gap, we define these gaps within d bands as d-gaps.

MoS$_2$ monolayer is semi-conducting with a direct band gap of 1.9 eV. The conduction band minimum and valence band maximum are both at the $\Gamma$ point. This is different compared to bulk MoS$_2$. Bulk MoS$_2$ has a indirect band gap of 1.3 eV. In MoS$_2$ monolayer, all sulfur’s 3p orbitals are filled. Mo’s 4$d_{z^2}$ orbital has 2
Figure 2.3. H structure and T structure of TMD [73].

Figure 2.4. DFT calculated band structure of MoS$_2$ and TaS$_2$. $d_{z^2}$ bands are in light blue background. Other $d$ bands are back-grounded with yellow green. MoS$_2$ is semiconducting while TaS$_2$ is metallic.

electrons while other 4$d$ and 5$p$ orbitals are empty. Hence each Mo lost 4 electrons to S. In contrast, TaS$_2$ monlayer has one less electron, so Ta’s 5$d_{z^2}$ orbital has 1 electron while its other 4$d$ and 5$p$ orbitals are empty. Hence TaS$_2$ is metallic. The band structure of NbS$_2$ are very similar to that of TaS$_2$.

For bulk MoS$_2$ (or TaS$_2$), MoS$_2$ (or TaS$_2$) layers stack together with a periodicity of two layers. Each MoS$_2$ (or TaS$_2$) primitive cell contain 2 Mo (or Ta) and 4S ions. However, bulk TaS$_2$ and MoS$_2$ have different stacking sequences. In a primitive cell of MoS$_2$, the Mo ion in one layer is exactly above (or under) the S ion of the other
Figure 2.5. Lattice structure of $\text{Mn}_{1/4}\text{TaS}_2$ [224], Mn is at the mid point of two Ta1 atoms. S1 atoms has no Mn neighbor while S2 atoms has one Mn neighbor.

Figure 2.6. DFT calculated $\text{Mn}_{1/4}\text{TaS}_2$ band structure. Spin up bands are in blue while spin down are in red.
Figure 2.7. DFT calculated Mn$_{1/9}$TaS$_2$ band structure. Spin up bands are in blue while spin down are in red.

layer. The space group of bulk MoS$_2$ is $P6_3/mmc$. In a primitive cell of TaS$_2$, the Ta ion in one layer is exactly above (or under) the Ta ion of the other layer and the reversion symmetry center is the mid of these two Ta-Ta ions.

Bulk TaS$_2$ and NbS$_2$ are able to intercalate different metal atoms. Most common intercalated atoms are simple metals such as Cu, Li and 3$d$ transition metals such as Mn. In Mn$_{1/4}$TaS$_2$ compound, each Mn ion is located in one of every 4 octahedral holes sandwiched between two layers of TaS$_2$. In both Mn$_{1/9}$TaS$_2$ and Mn$_{1/4}$TaS$_2$, Mn donates electrons to TaS$_2$. Both Mn$_{1/9}$TaS$_2$ and Mn$_{1/4}$TaS$_2$ alloys show spin polarization and magnetization. The magnetization is found mostly on Mn. Mn can be intercalated in TaS$_2$ because its 5$d_{z^2}$ below the $d$-gap is partially filled. Mn intercalation in MoS$_2$ is not themaldynamic prefered because MoS$_2$’s bands below the d-gap are fully filled and there is a penalty in energy to accommodate Mn’s extra electrons.
Chapter 3

Theory of tuning the electronic properties of 2D materials through resonant physisorption

3.1 Introduction

Resonant interaction between the electronic states of an atomically thin two-dimensional material and the molecular orbitals of a monolayer of physically adsorbed aromatic molecules provides a general scheme for controlling the near-Fermi-level electronic structure of the combined system. Here we design a molecular adlayer whose electron-withdrawing groups bring its lowest occupied molecular orbital into resonance with the Fermi level of a semimetallic sp² hybridized sheet. The resulting resonance opens a gap of ~0.37 eV between the sheet-derived valence and conduction bands, with an empty molecular level interposed. This method of property tuning through resonant physisorption is gentle, patternable, and reversible. The free boundary condition at the edge of a planar aromatic molecule affords a large design space, which suggests that this strategy could be applied to control multiple material properties across a range of atomically thin two-dimensional systems, assuming requisite control over the packing geometry and electronic structure of the adsorbate.

Atomically thin two-dimensional materials [47,50,83] provide unique capabilities, some deriving directly from the reduced dimensionality and sublattice symmetry [47, 50,53–56,84,85] and others from their large surface area, gateability [83,86–88],
Stackability, high mobility [41–43], spin transport [44–46], or optical accessibility [51]. Stackability has been recognized as a potential defining strength of these systems, since it incorporates the architectural strengths of semiconductor heterostructures without the stringent synthetic requirements of bulk epitaxy [89]. For example, stacking of 2D layers provides a means to minimize substrate effects [90] or generate electronic or optical properties absent from the individual constituents [91,92]. “Stacking” does not require that every layer be a continuous covalent lattice, but only that the electronic properties of two layers interact in a desirable way. Here we consider stacking between one continuous, atomically thin 2D layer and an ordered adlayer of molecular adsorbates. When appropriately designed, these hybrid systems can resonantly couple the electronic properties of the continuous layer to those of the non-continuous layer. The release of the requirement for covalent lattice periodicity in the second layer greatly expands the design space, with prospects for rational tuning of the near-Fermi-level electronic structure of the continuous layer.

As an initial example, we consider the induction of a band gap in carbon-based sp² sheets. Although the gapless nature of single-layered carbon-based sp² systems generates much novel physics, the lack of a bandgap is a drawback in applications that require confinement within or switching across a gap. Many strategies have been applied to solve this problem, each with unique strengths and drawbacks. Quantum confinement into ribbons [93,94] requires precise and scalable nanoscale patterning. Fascinating advances in self-assembly along these lines have been reported [95–97], and these systems also promise interesting edge-state physics [98–116]. Covalent modification through hydrogenation [117,118], fluorination [119], SiC-underlayers [120], or attachment of more complex polyatomic ligands [117,121,122] introduces sp³ character to the sheet – the resulting gapping is robust, but the disruption of the sp² complex is locally strong. The gap of the fully saturated system is too large for most applications, so the degree of structural order in the distribution of a low-density sp³ component [83,87] must be closely controlled, which is difficult in a system [123] not known for the facile reversibility that facilitates equilibration of long-range structural order. Peierls-like effects may facilitate this control, but clustering of ligands could also be important [124]. The weaker interactions during non-covalent adsorption of closed-shell species [125–129] provides much better reversibility, but these interactions are typically too weak to generate band gaps large enough to sustain room-temperature device operation.
More strongly interacting species such as metals can generate larger gaps, [130–132] but typically at the expense of strong doping that moves the Fermi level away from the gap. For those cases otherwise [133], stability upon air exposure remains a serious concern. Stacking of graphene into a bilayer provides strong resonant $\pi-\pi$ interactions, although an external field is needed to break the equivalence of the two layers [132,134–137]. Certain adsorbates such as CrO$_3$ can induce states of only partial sp$^3$ character, with the underlying carbon atoms just slightly puckered [138]. These are intriguing as possible agents for inducing usefully moderate bandgaps, although the intermediate character of the hybridization may foreshadow difficulties with long-term stability and the unique nature of these adsorbates complicates generalization of the effect.

Physical adsorption provides good reversibility and thus relatively easy equilibration into high-quality structures with long-range order, as has already been demonstrated for organic molecules adsorbed onto the surface of graphite [139]. For modest-sized aromatic molecules, the adsorption energies can be sufficiently large to ensure reasonable thermal stability [140]. Although – as discussed above – the near-Fermi-level electronic perturbations induced by small closed-shell molecules adsorbed onto graphene are generally weak, the planar $\pi$ complex of an aromatic species often rests parallel to the layer onto which it is adsorbed, providing a large interfacial area for interaction of the sheet with the highest occupied and lowest unoccupied molecular orbitals of the adsorbate. An enormous synthetic effort over past decades in organic electronics and photovoltaics provides a large body of knowledge in tuning the electronic energy levels of small aromatic organic molecules [141], so it should be possible to design adsorbate molecules that align molecular orbitals with desired features in the electronic structure of the 2D layer.

As noted earlier, the interlayer stacking in a graphene bilayer can break the A-B sublattice symmetry of a single layer, but the residual symmetry of the bilayer preserves the Dirac-point degeneracy [142,143], so an additional perturbation that breaks the equivalence of the two constituent layers is necessary to generate a gap. Only two of the the four bands near the Fermi level of an AB-stacked bilayer are degenerate at K; the remaining pair split off by about $\sim$0.7 eV [127,144,145], an energy scale characteristic of the interlayer electronic overlap integrals. Hence the $\pi$-stacking interaction is strong enough to generate useable gaps, but only if it can be applied in a low-symmetry geometry that breaks the A-B sublattice symmetry.
of a graphene sheet. One way to break symmetry is through an out-of-plane electric field, but it is also possible to break the bilayer reflection symmetry by changing the structure of one of the layers, as described below.

### 3.2 Computation details

Consider a Gedanken experiment that starts with a full graphene bilayer, AB stacked, and then removes some fraction of the carbon atoms in the upper layer, capping the resulting dangling bonds with hydrogen to form a periodic array of very small graphene patches above a intact second sheet, as shown in Fig. 3.1. The resulting molecular adsorbate is a polyaromatic, pyrene. It has the chemical formula C$_{16}$H$_{10}$ and is arrayed in a $4 \times 4$ supercell atop the lower graphene layer. We have performed ab initio calculations of such systems, using the projector augmented wave method within local density approximation [146]. The calculations were performed with the Vienna Ab-initio Simulation Package [147–151], using a 400-eV plane-wave energy cutoff, a $6 \times 6 \times 1$ reciprocal-space grid, converging ionic relaxations to less than 0.005eV/Å and converging the self-consistent electronic minimization to a tolerance of $5 \times 10^{-7}$eV. Although this system does generate a band gap in the lower intact graphene layer, it is very small, only 0.04 eV, because the highest occupied and lowest unoccupied orbitals of the adsorbate molecule fall far from the Fermi level of the intact graphene sheet. This is to be expected, since these small aromatic molecules are highly quantum confined.

This difficulty can be solved by modifying the adsorbates so as to lower the lowest unoccupied molecular orbital (LUMO) into energetic alignment with the Fermi level of the sheet below. Hence we replace a number of -CH units of the molecule with isoelectronic (but more electronegative) nitrogen atoms, and also replace some hydrogen with fluorine. A stoichiometry of C$_{10}$N$_6$H$_3$F, with six N/CH substitutions and one F/H substitution, brings the LUMO into alignment with the Dirac point. This solution is not unique: many other substitution patterns and choices of ring structure yield similar effects, and additional adjustments in the number and type of substituent could fine-tune to compensate for quasiparticle effects, etc. We compared the total energies of AA, AB and mid-bond stackings (for the relative registry of the carbon rings), obtaining adsorption energies of 0.48, 0.65, and 0.57 eV respectively. The desired AB stacking geometry is preferred.
Figure 3.1. (color online) Structures of AB-stacked monolayers of the aromatic molecule C_{16}H_{10} / C_{10}N_{6}H_{3}F on graphene. Carbon, nitrogen, fluorine and hydrogen atoms are green, blue, yellow and white respectively.

Although standard implementations of density functional theory do not describe the van der Waals interaction well, the corrugation in the adsorbate/substrate interaction is largely determined by $\pi$-stacking interactions, and these are adequately described by density functional theory. Note also that even AA stacking breaks the sublattice symmetry for a low-symmetry adsorbate such as C_{10}N_{6}H_{3}F. The equilibrium distance between adsorbate layer and underlying graphene sheet is 0.31 nanometers, slightly less than the interlayer stacking in graphite and consistent with physical (not chemical) adsorption.

3.3 Results and discussion

Fig. 3.2 shows the resulting bandstructure. The molecular adsorbate’s LUMO sits in the former location of the Dirac point, thereby strongly breaking the K-point degeneracy and opening a gap of $\sim$0.37 eV between the $\pi$ and $\pi^*$ levels graphene. The new valence band remains $\pi$-like, sitting primarily on the graphene layer, while the new conduction band is molecular in origin and sits on the adsorbate. The gap between these two states is significant, about 0.14 eV. The conduction band is very flat and hence susceptible to localization: it is essentially an impurity level within the gap of the semiconducting 2D sheet.
Figure 3.2. Band-structures for various polyaromatics commensurately adsorbed to graphene. The density is one adsorbate per $5 \times 5$ graphene super cell. The pure-carbon aromatic $C_{16}H_{10}$ generates only a modest gap, 0.04 eV due to the large energy separation between the adsorbate levels and the graphene Fermi level. The LUMO of the more electronegative adsorbate $C_{10}N_{6}H_{3}F$ aligns better to the original graphene Fermi level, thereby strongly hybridizing with graphene and generating a large gap: 0.14 eV between the graphene valence band and the molecular conduction band and 0.37 eV between the graphene $\pi$ and $\pi^*$ bands. The dashed line marks the Fermi energy in the gap between these levels. Adsorbing the same molecule on both sides of a suspended graphene sheet (with ABA stacking) produces an even larger gap: 0.16 eV. Finally, reducing the $C_{10}N_{6}H_{3}F$/graphene distance by 0.04 nm through $c$-axis compression further increases the gap, to 0.22 eV.

The $C_{10}N_{6}H_{3}F$ molecule contains four six-fold rings, and represents a compromise between two competing effects. Smaller adsorbates have larger HOMO-LUMO gaps, and so are more difficult to bring into alignment with the graphene Fermi level. Also, the increased perimeter/area ratio of a smaller adsorbate molecule implies that the total $\pi$-stacking interaction across the monolayer is weaker, since the perimeter terminations create non-$\pi$ buffers between the adsorbates. Larger polyaromatics enhance the overall $\pi$-stacking interaction, but their HOMO-LUMO
Figure 3.3. C_{10}N_{6}H_{3}F adsorbed on graphene with one adsorbate per 5 × 5 graphene super cell. The band gap is 0.10 eV, less than that of one adsorbate per 4 × 4 graphene super cell which is 0.14 eV.

gap shrinks with increasing size, and this molecular gap limits the maximum size possible for the gap of the overall graphene/adsorbate system. Also, the distinction between the adsorbate and graphene layers becomes less pronounced for larger poly-aromatic adsorbates, since the adsorbates begin to look more and more like a second full layer of graphene.

The band calculations reveal no band-overlap charge transfer between C_{10}N_{6}H_{3}F and graphene, so one expects at most weak charge-transfer doping in the real system, small enough to be compensated by standard electrostatic gates. The adsorption energy per C_{10}N_{6}H_{3}F molecule is likely to be reasonably high. The local density approximation yields ≈0.65 eV; although subject to the deficiencies of the LDA in non-bonded interactions, this value is in the ballpark of experimental expectations for aromatic molecules of similar size. This suggests reasonable thermal stability, especially if a capping layer is applied, similar to those used in organic electronics.

Several strategies are available to increase the magnitude of the graphene gap. Pressing the adsorbate layer towards the graphene increases the π stacking interaction. Reducing the equilibrium separation by 0.01, 0.02, 0.03 or 0.04 nm yields gaps of 0.16, 0.18, 0.20 and 0.22 eV. The pressures required to obtain these separations are 1.18, 2.80, 5.05 and 8.18 GPa. Intuitively, one suspects that dual-
Figure 3.4. $C_{24}N_6H_8$ adsorbate structure

Figure 3.5. Band structure of $C_{24}N_6H_8$ adsorbed on graphene with one adsorbate per $5 \times 5$ graphene super cell. $C_{24}N_6H_8$’s LUMO is aligned with graphene Dirac point. The band gap is 0.12 eV.

sided adsorption onto suspected graphene would also increase the gap, and this suspicion is confirmed: stacking $C_{10}N_6H_3F$ molecules in ABA registry to both side of graphene yields a band gap of 0.16 eV.

The adsorbate density affects the band gap size substantially. Larger adsorbate density leads to larger coupling between adsorbates and graphene and hence larger gap. Decreasing the $C_{10}N_6H_3F$ density form one adsorbate per $4 \times 4$ super cell to one adsorbate per $5 \times 5$ super cell results in the band gap decreasing from 0.14 eV to 0.10 eV. $C_{10}N_6H_3F$ is not the only choice of polyaromatic molecules. The size of the polyaromatic molecules can also be modulated. For example, $C_{24}N_6H_8$’s LUMO can be aligned (Fig. 3.5) with graphene Dirac point when the density is one
Figure 3.6. $C_{25}N_5H_9$ adsorbate structure

Figure 3.7. Band structure of $C_{25}N_5H_9$ adsorbed on graphene with one adsorbate per $5 \times 5$ graphene super cell. The LUMO of $C_{24}N_5H_9$ is about 0.2 eV above the Dirac point and there is no mid-gap level in the band structure.

adsorbate per $5 \times 5$ graphene super cell. The resulted band gap is 0.12 eV. The adsorbate’s LUMO is a quasi-mid-gap level and this could be avoid if we raise the LUMO a bit. By decreasing the nitrogen number in $C_{24}N_6H_8$ molecule from 6 to 5, we have successfully raise the LUMO 0.2 eV above (Fig. 3.7) the Dirac point. There is no mid-gap level for $C_{25}N_5H_9$ adsorption on graphene and the band gap is 0.10 eV, only 0.02 eV less than the $C_{24}N_6H_8$ case.

These gaps are large enough to produce quantum confined structures for low-temperature fundamental studies, and may also be sufficient to support applications such as high-speed analog transistors [152]. Keep in mind that the energy gap between dispersive *graphenic* states is larger than this: 0.3 to 0.4 eV, since the
molecular LUMO that forms the conduction band is effectively an mid-gap level within the \( \pi - \pi^* \) gap. This quasi-mid-gap level could be problematic for some device applications, but it may be exploitable in novel device modalities. The typical underestimation of the band-gap in density functional theory suggests that the actual experimental gaps could be larger, although care must also be taken in assessing the accuracy of the local density approximation in computing the strength of the relatively weak \( \pi \)-stacking interactions (e.g. if the true distance between the molecule and the graphene is less (more) than that in the computation, then the real induced gap will be larger (smaller) than anticipated).

In order to obtain consistent sublattice symmetry breaking and strong coherent electronic overlap, the molecular adsorbate layer must be commensurate to the graphene underneath. Experimentally, a large body of research on organic molecules adsorbed onto the surface of graphite – expected to be very similar to graphene – reveals both commensurate and incommensurate registries. For example, alkanes adsorb on graphite commensurately [153] while chrysene is incommensurate [154], since an incommensurate packing maximizes the areal density of adsorbates. The large design space of organic chemistry, including the ability to exploit several distinct level-shifting substitutions (-N for -CH, -F for -H, etc.) strongly suggests that LUMO-aligned aromatic adsorbates of the proper size and shape to pack commensurately on graphene at high areal density can be found. Yet further design flexibility is available, since the Dirac point can also be split by the highest occupied level of an adsorbed polyaromatic. The broad knowledge-base of organic electronics provides numerous other substituents that can tune the HOMO and LUMO levels of polyaromatics. Gap control via \( \pi \)-stacking interactions with level-tuned aromatic physical adsorbates is patternable, reversible, scalable, and tunable. The general strategy should also be applicable to other atomically thin 2D systems.

### 3.4 $\text{SO}_3$ adsorption on graphene

The graphene \( \pi \) and \( \pi^* \) band degeneracy at Dirac point is due to the graphene \( D_{6h} \) point group symmetry and the equivalency of A and B sub-lattice sites. Another method to create a gap in graphene is to break the equivalency of A and B sub-lattice sites. $\text{SO}_3$ molecule has 3 fold symmetry and the S-O distance is 1.42Å which is almost the same as the C-C distance in graphene. The S atom donate
Figure 3.8. SO$_3$ adsorbed on graphene with one adsorbate per 2 × 2 graphene super cell.

Figure 3.9. Band structure of SO$_3$ adsorbed on graphene with one adsorbate per 2 × 2 graphene super cell. The 0.07 eV band gap is due to the disruption of A and B sub-lattice equivalency.

partial of its 3p electrons to O atoms. As a result, S is positively charged while O is negatively charged. Since S is covalently bonded to 3 O atoms, the S atom is substantially charged. If we have SO$_3$ adsorbed on graphene with S on A site and O on B site of graphene (Fig. 3.8). The equivalency of A and B sub-lattice sites can be disrupt. We test the adsorption of one SO$_3$ per 4 graphene cell as shown in Fig. 3.8. We are able to achieve 0.07eV gap (Fig. 3.9). The equivalency of A and B sub-lattice sites can be further disrupt with Dual-sided adsorption. The dual-sided adsorption creates a band gap of 0.13 eV (Fig. 3.10) which is almost twice as that of single-sided adsorption.
Figure 3.10. Band structure of dual-sided adsorption of SO$_3$ onto graphene. The band gap, 0.13 eV is much bigger than that of single-sided adsorption since dual-sided adsorption break the equivalency of A and B sub-lattice much more drastically than that of single-side adsorption.
Chapter 4  
Dual-sided Adsorption: A Devil’s Staircase of Coverage Fractions

4.1 Introduction

By adsorbing the same species onto both sides of a suspended, atomically thin membrane, it is possible to couple together two distinct surface adsorption systems. This new system, with reflection symmetry about the membrane, is described by a phase diagram with two axes, both representing the chemical potential of the same element, but in distinct half-spaces. For the case of potassium adsorption onto a graphene membrane, the result is a devil’s staircase of fractions for the proportion of adsorbates adhered to one side. Fractions with simpler denominators are favored across wider regions of chemical potential, a pattern reminiscent of the structure of other fractional systems across a wide range of physics. This geometry provides a general means to expand the domain of surface science to pairs of weakly coupled surfaces.

The concept of two identical coupled two-dimensional electronic subsystems has been explored in, for example, bilayer graphene [155,156] and the quantum Hall bilayers [157]. In both cases, the interesting degrees of freedom are electronic: the restructuring of the Dirac point in bilayer graphene and the interlayer Coulomb coupling (plus tunneling) in the quantum Hall system. Here we explore the theory of a distinct bilayer system in which the important degrees of freedom correspond to atoms – an adsorption bilayer. In symmetric dual-sided adsorption, identical species adsorb to opposite surfaces of a very thin suspended membrane, such as
graphene [158, 159], hexagonal boron nitride, or transition metal dichalcogenide. In this way, two familiar (i.e. single-sided) surface-physics systems can be coupled together, and through this coupling hopefully generate new physics. The structural phase diagram of dual-sided adsorption has the same variable – the chemical potential of the adsorbate species – on both axes, but referred to different half-spaces, $\mu_{\text{top}}$ and $\mu_{\text{bottom}}$.

4.2 Computation details

We study this geometry first for a prototypical adsorbate system: alkali atoms on sp$^2$ carbon. The strong charge transfer supports substantial cross-layer interactions; the simplicity of the system facilitates detailed analysis, and the principles gleaned will have broader application across other barriers and adsorbates. The adsorption of alkali metal on graphite surfaces is a well-known phenomenon [60–64, 160–164], including extensions to adsorption onto graphene [156, 165–170]. The phase diagram for potassium adsorption onto graphite has been studied extensively both experimentally [60, 61] and theoretically [62–64]. Low coverage supports a dispersed phase with a large K-K separation (up to 60 Å [60]) due to a repulsive long-range interaction. The K-K distance is well-defined, although long-range crystalline order is lacking. As the coverage increases, the K-K distance decreases to about 14 Å (corresponding roughly to a 7 × 7 superlattice) below which a dense, metallically bonded 2 × 2 phase appears [60].

We study dual-sided adsorption of potassium to suspended graphene, first within first principles density functional theory and then using these results to parameterize an empirical treatment that enables a more complete exploration of the structural phase diagram. Density functional calculations use projector augmented waves within the local density approximation [146] at 400-eV plane-wave energy cutoff, as implemented within the Vienna Ab-initio Simulation Package [147–151] (VASP). Ionic relaxations were converged to less than 0.01 eV/Å, and all in-plane lattice constants were relaxed. The out-of-plane periodicity is fixed at 20 Å, with dipole corrections applied to neutralize any spurious c-axis interactions (although at this large separation the inter-sheet dipolar interaction is weak in any case). Previous calculations [63] for adsorption of potassium onto a graphite surface showed a strong preference for the hexagonal center. Potassium preserves this preference in
Figure 4.1. Examples of structures considered in our density functional theory calculations. Solid dots represent upper-side potassium and hollow dots represent bottom-side potassium. Where several solid circles occur in close proximity, the largest one is the lowest-energy location and the others are alternative registries considered. For the $2 \times 2/6 \times 6$ case we also examined a structure with the two lattices coincident. In general, the system prefers for the adsorbate lattices on opposite sides to be maximally offset from each other. Notation for lattices is described in the main text.

dual-sided adsorption. For example, a $3 \times 3$ potassium superlattice bilayer prefers hexagonal centers for both sets of adsorbates, with alternative bond-center and atom-top sites being 0.05 to 0.1 eV per K atom higher in energy; (the full set of atom/sheet registries considered in this case is depicted in Fig. 4.1). We consider only hexagon-centered adsorption sites hereafter.

The system prefers opposing adsorbate lattices that are far-separated from each other, with the atoms on one side centered on the empty centers of the triangles of the lattice opposite. Competing lattice registries, also hexagon-centered on both sides but shifted as indicated in the two left-hand images of Fig. 5.1, are a few tens of meV (0.01 – 0.16 eV) higher in energy. We consider two classes of dual-sided structures, both extensions of familiar single-sided adsorbate superlattices. First, structures with an $a \times a$ superlattice on one side and a $b \times b$ superlattice on the other, written as $a \times a/b \times b$ (and optimized for the best inter-lattice registry).
Table 4.1. The complete set of adsorbate structures considered within density functional theory, as shaded boxes. The integers or simple multiples of $\sqrt{3}$ refer to superlattice vectors for the adsorbate superlattices on opposite sides of the barrier. In the main text, these are written $a \times a/b \times b$ for integers $a, b$. $a, b = \infty$ describes an empty side. The fractions 0.25 and 0.5 describe an overall $n \times n$ superlattice in projection, with the given fraction of the atoms residing on the opposite side of the barrier, as described in the main text.

A empty/bare side is represented by $a$ or $b$ equal to $\infty$. Second, an overall $n \times n$ lattice in projection (i.e. counting adsorbates on both sides), but with a fraction $\alpha$ of the atoms on one side and $1 - \alpha$ on the other (with the specific top/bottom pattern requiring further specification). We denote this second case as $n \times n : \alpha$.

The structures that we have calculated at the density functional level are shown in Table 4.1. For completeness, we also tested several rectangular lattices with the superlattice unit vectors in a $1:\sqrt{3}/2$ ratio (with the same cell areas as $4 \times 4$ and $8 \times 8$); these are not favored in phase diagram, either single or dual-sided. Many different relative registries of the top and bottom superlattices were tested, and in all cases the adsorbed lattice on one side avoids the adsorbed lattice on the other side. This adsorbate-adsorbate repulsion is not simply a direct Coulombic repulsion of the positively-charged alkali atoms, but also includes the Pauli repulsion of the electron clouds that the alkali atoms donate to the graphene sheet below, as previously observed for adsorption onto graphite [164].
### 4.3 DFT phase diagram

Following a standard convex-hull construction, we obtain the phase diagram of the right panel of Fig. 4.2. For comparison, the left panel shows what would result if the adsorbates on opposite sides did not interact, constructed by superposing two orthogonal single-sided phase diagrams derived from a similar density functional theory methodology. The transition from sparse, repulsion-dominated phases at low density to short-ranged metallic bonding at high density is consistent with experimental results for potassium on graphite [60, 61].

The diagram is symmetric across the diagonal, as expected for a system with identical species adsorbed to both sides. The exterior edges of the interacting phase diagram at both high and low chemical potential retain the horizontal or vertical phase boundaries of the non-interacting case: because the adsorbate phase on one surface of the membrane is the same on either side of these phase boundaries, the competition between the phases on the other surface is independent of the chemical potential above the first surface (which is either empty or in the metallic state).
2 × 2 phase). The interaction-driven expansion of the phases with ∞ × ∞ on one side shows that the presence of potassium on one side of the membrane repels potassium from the other side. The interior of the phase diagram deviates markedly from the non-interacting case. Along the diagonal dashed lines in Fig. 4.2 the average chemical potential \( \bar{\mu} \equiv \frac{1}{2}(\mu_{\text{top}} + \mu_{\text{bottom}}) \) is constant while the difference in chemical potentials \( \delta \mu \equiv \mu_{\text{top}} - \mu_{\text{bottom}} \) varies. The adsorption pattern undergoes an interesting evolution along such a path: along the lower dashed line, it retains an overall 5 × 5 lattice when viewed in projection, but with the fraction \( \alpha \) of the adsorbates on one side changing from 0 → 0.25 → 0.5 → 0.75 → 1.0 as \( \delta \mu \) increases. Potassium progressively leaves one side and attaches to the other at a constant overall areal density consistent with the constant \( \bar{\mu} \). Treating the top/bottom degree of freedom as an effective Ising spin, the chemical potential difference \( \delta \mu \) acts as a symmetry-breaking magnetic field. The same evolution with \( \delta \mu \) seems to occur for the 6 × 6 and 8 × 8 structures, although computational limitations reduce the number of intermediate values of \( \alpha \) accessible for these larger lattices.

4.4 DFT limitation and introduction of classical simulation

The investigation of fractional occupations \( \alpha \) is limited by the inability to perform an exhaustive search of complex intermediate fractions \( \alpha \) within first-principles methods. Fractions \( \alpha \) with large denominators have very large unit cells – they are super-cells of a super-cell – and also complex combinatoric choices for which atoms reside on which side. However, a simple empirical electrostatic model can provide a surprisingly accurate treatment, so long as one restricts oneself to comparing \( n \times n : \alpha \) structures of the same \( n \) but different \( \alpha \). The long-ranged repulsive interactions between potassium atoms adsorbed onto a graphite surface at low areal density (or large \( n \)) are dominated by the band energy of the graphene sheet, due to level filling by charge-transferred electrons [164]. For a suspended graphene membrane, this level-filling effect is almost independent of which side each potassium atom adheres to. The large energy scale of this level-filling effect thus determines the \( n \) in \( n \times n : \alpha \), i.e. the overall areal density, but not \( \alpha \).

The remaining Ising-like “which side” degree of freedom for each adsorbate atom
Figure 4.3. Examples of the lowest energy conformations for $6 \times 6:0.6$ with Monte Carlo simulation. Solid dots represent top-side potassium and hollow dots represent bottom-side potassium. The Monte Carlo simulation is performed within a super-cells of a super-cell. After relaxation, the primitive cells of the relaxed structure are shown here. These primitive cells are smaller than the simulation cells. Large panel shows the simulation cell and small panel shows how K atoms are arranged on graphene without showing graphene atoms.

is then governed by the weaker, long-ranged electrostatic dipole-dipole interaction between adsorbates. Thus, although the total energy of any specific adsorbate structure depends on subtle quantum mechanical effects due to indirect adsorbate-adsorbate interactions mediated by charge transferred to the barrier, the energy differences upon flipping an adsorbate from one side to another arise almost entirely from long-ranged electrostatic dipole-dipole interactions that can be accurately described within a classical empirical model. The band-filling energy ($\frac{1}{n}$) varies with $n$ more rapidly than does the electrostatic dipole-dipole interaction ($\frac{1}{n^3}$), thus it dominates at low areal densities [164].

In this empirical model, each adsorbed alkali ion (plus the transferred charge resident in the membrane nearby) is modeled as an electrostatic dipole whose magnitude is extracted from first-principles calculations. Within density functional
theory, the $8 \times 8 : 0, 7 \times 7 : 0, 6 \times 6 : 0$ and $5 \times 5 : 0$ lattices have nearly identical dipole moments of 1.54, 1.53, 1.51, and 1.48 eÅ per adsorbate respectively, since the charge transfer saturates at one electron per adsorbate with nearly-constant $c$-axis relaxation. Switching K atoms from one side to another also leaves the charge transfer and the $c$-axis separation almost unchanged. However, the $6 \times 6 : 0$ and $6 \times 6 : 0.5$ lattices differ in total energy by 59.7 meV per potassium atom. If we fit the dipole moment of a classical electrostatic model to reproduce this result, we obtain a moment of 1.46 eÅ, in excellent agreement with the first-principles moments quoted above. A similar comparison for $8 \times 8 : 0$ versus $8 \times 8 : 0.5$ and $5 \times 5 : 0$ versus $5 \times 5 : 0.5$ yield classical moments of 1.51 eÅ and 1.42 eÅ respectively; (the $5 \times 5$ lattice is the more challenging test, since its higher areal density accentuates structural and charge relaxations that are absent in the simple electrostatic treatment). A reasonable level of agreement can also be obtained for a different choice of exchange-correlation potential: the $7 \times 7, 6 \times 6$ and $5 \times 5$ systems have dipole moments of 1.68, 1.66, and 1.62 eÅ for the Perdew-Burke-Ernzerhof functional. We anticipate that the main results will be insensitive to the detailed choice of exchange-correlation functional, with mainly a slight overall shift in energy scale.

We focus on the $6 \times 6 : \alpha$ family of structures for detailed mapping of the phase diagram along a line of fixed $\bar{\mu}$ and variable $\delta\mu$, i.e. the upper dotted line in Fig.4.2. For a given $\alpha$ one must also optimize the choice of which potassium atoms to place on which side; for a cell containing $N$ adsorbates there are $\binom{N}{M}$ possibilities for $\alpha = M/N$. We perform this optimization with Monte Carlo-based simulated annealing. To obtain arbitrarily fractions, one must simulate supercells of the $6 \times 6$ structure, i.e. supercells of a supercell. We write the $i \times j$ supercell of the $6 \times 6$ base cell using square brackets, as $[i \times j]$. The most energetically favorable such super-supercells are close to square; we have examined $[3 \times 3], [4 \times 4], [4 \times 5], [4 \times 6], [5 \times 5], [5 \times 6], [5 \times 7], [6 \times 6], \text{and} \ [6 \times 8]$. Fig. 4.4 inset shows the resulting lattice energies. The reflection symmetric $\alpha = \frac{1}{2}$ phase is lowest in energy, but is favored only around $\delta(\mu_{\text{top}}-\mu_{\text{down}}) \approx 0$. The convex hull of this distribution yields the phase sequence depicted in Fig. 4.4. We find that simpler fractions are favored across wider regions of chemical potential. The striking step-wise character of this plot follows from general geometrical considerations: Nature typically prefers relatively small unit cells – “when you find a good thing, repeat it often” – especially for
Figure 4.4. Fraction of potassium on upper side of graphene versus $\delta\mu$ for $6 \times 6$: $\alpha$. Some fractions are extended with dash line as the fraction are shown on top of the line. A complete list of all fraction appear on this plot is shown in supplemental material. Inset: Energy per K versus $\alpha$ for $6 \times 6$: $\alpha$. Each point in the plot represents an $\alpha$ with an specific modelling cell size and shape. Red plot is the convex hull of these points. The plot is symmetric around $\alpha = 0.5$.

uniform particles with smooth, non-directional (e.g. Coulombic) interactions.

4.5 Result and discussion

Do these fraction sequences follow any simple patterns? The low density limit clearly does, since it can be expressed as an expanding series of near-square cells: $(3 \times 3)^{-1}, (3 \times 4)^{-1}, (4 \times 4)^{-1}, (4 \times 5)^{-1}, (5 \times 5)^{-1}, \ldots$. Our intuitions deeper into the phase diagram can be best developed by first considering a simplified one-dimensional case, where classical particles are arrayed on a line with one of two
Figure 4.5. Phase diagram for dual-sided adsorption of potassium onto a suspended graphene barrier with the combined result of density functional theory and classical dipole-dipole interaction simulation. $a \times a/b \times b$ and $n \times n: \alpha$. ($\alpha = 0, 1/2$ or 1) structure energy are from DFT. $n \times n: \alpha$ ($n = 5, 6, 8$ and $\alpha = \frac{1}{12}, \frac{1}{9}, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{5}{6}$) structure energy are based on DFT energy of $n \times n: \alpha$. ($\alpha = 0, 1/2$ or 1) plus considering the difference on classical dipole-dipole interaction. Two circles in the phase diagram show examples of four phases almost co-exist at one point in the phase diagram.

configurations and long-ranged interactions. This model has been solved in the context of conductive polymers by Hubbard [171] and Bak and Bruinsma [172] for particles at fixed separation under an infinite-range convex electrostatic repulsion (i.e. a positively curved with respect to interparticle separation) and no on-site interaction. Define $\Delta \mu(\alpha)$ to be the range of relative chemical potential occupied by a given fraction and define $L(\alpha)$, the size of the unit cell for this fraction (or the denominator of this fraction). For dipolar particles, if we take the interaction energy of two neighboring same direction dipole as 1, we obtain

$$\Delta \mu(\alpha) = \frac{4\pi^2}{L^2} \left( \frac{1}{\sin^2(\frac{\pi}{L})} - \frac{\pi \cos(\frac{\pi}{L})}{L \sin^3(\frac{\pi}{L})} - \frac{1}{3} \right)$$

(4.1)
Figure 4.6. Fraction of up dipoles Versus $\delta \mu_{\text{top-down}}$ for one dimension case. Dipoles are arrayed on a line with either up or down conformation and fixed distance. Some fraction are extended with dash line as the fraction are shown on top of the line. Upper inset shows the energy per dipole versus the fraction of up dipoles. The energy are calculated from the states indicated in Hubbard’s [171] work. The $\alpha$ Versus $\delta \mu_{\text{top-down}}$ curve are derived from the upper inset plot and a magnification of the curve between $\alpha = 1/4$ and $\alpha = 1/3$ is shown in the bottom inset.

This analytical result agrees very well with numerical results for the one-dimensional dipolar system: the intervals for fractions $\frac{1}{2}$, $\frac{2}{5}$, $\frac{1}{3}$, $\frac{2}{7}$, and $\frac{1}{4}$ are 6.58, 0.092, 0.948, 0.022, and 0.236 numerically and 6.580, 0.0914, 0.950, 0.022, 0.236 according to Eqn. 4.1.

Eqn. 4.1 can be proved in the following way. Each adsorbed atom creates a charge-transfer dipole with the membrane underneath. In our system with $K$ on both sides of the membrane, $K$ on top generates a upward dipole while underneath $K$ generates a downward dipole. Thus we refer below to these atoms as “dipoles”
with the direction of the dipole indicating the side of adsorption. We define \( \alpha \) as the fraction of dipoles in the minority direction (i.e. \( \alpha \leq \frac{1}{2} \)), without loss of generality assumed to be upward. Although the two-dimensional case is intractable analytically, Hubbard [171] and Bak [172] have examined a one-dimensional Wigner lattice with an infinite-range convex electrostatic repulsion and no on-site interaction, obtaining results that can provide qualitative insight into our two-dimensional membrane system. They showed that \( \alpha \) can be any rational number, and any given \( \alpha \) can be written as

\[
\alpha = \frac{1}{C_1(\alpha) \pm \frac{1}{C_2(\alpha) \pm \frac{1}{C_3(\alpha) \pm \ldots \pm \frac{1}{C_n(\alpha)}}}}
\] (4.2)

The set of integers \( \{C_1, \ldots, C_n\} \) are uniquely determined by \( \alpha \): \( C_1 \) is the integer closest to \( 1/\alpha \), while \( C_2 \) is the integer closest to the inverse of the residual and so on. The \( \pm \) sign to the right of \( C_i \) matches the sign of \( \gamma_i \). Calling the residuals \( \gamma_1, \ldots, \gamma_{n-1} \), one obtains

\[
C_1 = \frac{1}{\alpha} - \gamma_1
\]
\[
C_2 = \frac{1}{\gamma_1} - \gamma_2
\]
\[
C_3 = \frac{1}{\gamma_2} - \gamma_3
\]
\[
\vdots
\]
\[
C_{n-1} = \frac{1}{\gamma_{n-2}} - \gamma_{n-1}
\]
\[
C_n = \frac{1}{\gamma_{n-1}}
\]

where all \( \gamma_i \in (-\frac{1}{2}, \frac{1}{2}] \).

According to Hubbard [171], the lowest energy structure for a given \( \alpha \) is unique and can be constructed recursively from knowledge of \( \{C_1, \ldots, C_n\} \). We will consider
only the case of uniform + signs in Eqn. 4.2 here, but the cases with minus signs can be handled in a similar manner. We define $X_0 \equiv \downarrow$ to be a downward-directed dipole (i.e. an adatom on the under-side of the 1D chain) and $Y_0 \equiv \uparrow$ to be an upward-directed dipole. When $n = 1$, the lowest energy state has $C_1 - 1$ downward pointing dipoles followed by one upward-pointing dipole, a configuration that we call $X_1$:

$$X_1 = \underbrace{\downarrow \cdots \downarrow}_{(C_1 - 1) \text{ total}} \uparrow = [\downarrow]^{C_1-1} \uparrow.$$ 

For example, when $\alpha = \frac{1}{3}$, we have $n = 1$ and $C_1 = 3$. The lowest energy configuration is:

$$X_1 = \downarrow \downarrow \uparrow.$$

To construct a ground state for $n = 2$, we define

$$Y_1 = \underbrace{\downarrow \cdots \downarrow}_{C_1 \text{ total}} \uparrow = [\downarrow]^{C_1} \uparrow.$$ 

The lowest energy configuration is $C_2 - 1$ instances of configuration $X_1$, followed by a single $Y_1$:

$$X_2 = X_1 \cdots X_1 Y_1 = [X_1]^{C_2-1} Y_1.$$ 

For example, when $\alpha = \frac{4}{13}$ we have $n = 2$ with $C_1 = 3$ and $C_2 = 4$. The ground state is

$$X_2 = X_1 X_1 X_1 Y_1 = [X_1]^3 Y_1 = \downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow.$$

In general, the lowest energy configuration for arbitrary $n$ can be constructed iteratively:

$$X_0 = \downarrow$$
$$Y_0 = \uparrow$$
$$X_1 = [X_0]^{C_1-1} Y_0$$
$$Y_1 = [X_0]^{C_1} Y_0$$
$$\vdots$$
$$X_n = [X_{n-1}]^{C_n-1} Y_{n-1}$$
$$Y_n = [X_{n-1}]^{C_n} Y_{n-1}$$
To determine the phase behavior, we need the left and right derivatives of the energy per adsorbate versus \( \alpha \). To calculate these quantities, we need to know the ground state configurations for values of \( \alpha \) slightly above and below the value of interest. Call them \( \alpha_+ \) and \( \alpha_- \); they can be obtained by simply extending the continued fraction by one additional term, \( C_{n+1} \):

\[
\alpha_{\pm} = \frac{1}{C_1(\alpha) + \frac{1}{C_2(\alpha) + \frac{1}{C_3(\alpha) + \cdots + \frac{1}{C_n(\alpha) \mp 1/C_{n+1}}}}
\]

We also define \( X_i^+ \) and \( X_i^- \) to describe dipolar configurations for \( \alpha_+ \) and \( \alpha_- \):

\[
X_{n+1}^+ = [X_n]^{C_{n+1}-1}Y_n
\]

\[
= [X_n]^{C_{n+1}-1}[X_{n-1}]^{C_n}Y_{n-1}
\]

\[
X_{n+1}^- = [X_n]^{C_{n+1}-1}[X_{n-1}]^{C_n-2}Y_{n-1}.
\]

Comparing these to a corresponding quantity for \( \alpha \),

\[
[X_n]^{C_{n+1}} = [X_n]^{C_{n+1}-1}[X_{n-1}]^{C_n-1}Y_{n-1}
\]

\( X_{n+1}^+ \) has one more \( X_{n-1} \) than does \( [X_n]^{C_{n+1}} \) and \( X_{n+1}^- \) has one less. Write the length of the unit cell for some configuration \( X_i \) as \( L(X_i) \), and write the number of upward pointing spins (dipoles) inside the unit cell as \( S(X_i) \). The following recursive formulas determine the values of \( L(X_i) \) and \( S(X_i) \):

\[
L(X_k) = C_k \cdot L(X_{k-1}) + L(X_{k-2})
\]

\[
L(X_0) = L(Y_0) = 1
\]

\[
S(X_k) = C_k \cdot S(X_{k-1}) + S(X_{k-2})
\]

\[
S(X_0) = 0
\]

\[
S(X_1) = S(Y_0) = S(Y_1) = 1
\]
Next, we take the limit where $C_{n+1} \to \infty$, i.e. the $\alpha_\pm$ are very close to $\alpha$. In this limit, $\alpha$ is symmetrically bracketed by its two partners: $\Delta \alpha \equiv \alpha_+ - \alpha = \alpha - \alpha_-$. The fractional occupations $\alpha$ (or $\alpha_\pm$) can be written as a ratio of $S$ to $L$, and some algebraic manipulation yields

$$
\Delta \alpha = \frac{L(X_n)S(X_{n-1}) - L(X_{n-1})S(X_n)}{C_{n+1}L^2(X_n)}
= \frac{(C_nL(X_{n-1}) + L(X_{n-2}))S(X_{n-1}) - L(X_{n-1}) (C_nS(X_{n-1}) + S(X_{n-2}))}{C_{n+1}L^2(X_n)}
= \frac{L(X_{n-2})S(X_{n-1}) - L(X_{n-1})S(X_{n-2})}{C_{n+1}L^2(X_n)}
= \frac{L(X_{n-2})S(X_{n-3}) - L(X_{n-3})S(X_{n-2})}{C_{n+1}L^2(X_n)}
= \vdots
= \frac{L(X_2)S(X_1) - L(X_1)S(X_2)}{C_{n+1}L^2(X_n)}
= \frac{1}{C_{n+1}L^2(X_n)}
$$

As expected, the increment in $\alpha$ goes to zero as $C_{n+1}$ becomes large. Remember that $L(X_n)$ is the size of the unit cell for $\alpha$. Define the range of chemical potential across which $\alpha = \alpha(X_n)$ is the preferred phase as $\Delta \mu(\alpha)$, which we can write in terms of the right and left derivatives of the lattice energy with respect to $\alpha$:

$$
\Delta \mu(\alpha) = \frac{E(X_{n+1}^+) - E([X_n]_{C_n+1})}{\Delta \alpha L(X_n)} - \frac{E([X_n]_{C_n+1}) - E(X_{n+1}^-)}{\Delta \alpha L(X_n)}
$$

Thus we need the energy differences between $[X_n]^{C_n+1}$, $X_{n+1}^+$ and $X_{n+1}^-$. Starting from the simplest cases, we underline in the formulas below the terms that differ between successive lines:

- $X_0Y_0 = [\downarrow][\uparrow]
- Y_0X_0 = [\uparrow][\downarrow]
- X_1Y_1 = [\downarrow]^{C_1-1}[\uparrow][\downarrow]^{C_1}[\uparrow] = [\downarrow]^{C_1-1}[\uparrow][\downarrow][\downarrow]^{C_1-1}[\uparrow]
- Y_1X_1 = [\uparrow]^{C_1}[\uparrow][\downarrow]^{C_1-1}[\uparrow] = [\uparrow]^{C_1-1}[\uparrow][\uparrow][\downarrow]^{C_1-1}[\uparrow]
- X_2Y_2 = [X_1]^{C_2-1}[Y_1][X_1]^{C_2}[Y_1] = [X_1]^{C_2-1}[Y_1][X_1][X_1]^{C_2-1}[Y_1]$
Thus the only difference between right cell because they contribute 0 to inter-cell interaction due to the long buffer energy in Eqn. 4.4. We dropped

\[
\begin{align*}
[\mathcal{X}_1]^{C_2 - 1} &[\mathcal{X}_1]^{C_1 - 1} [\mathcal{Y}]^{C_1 - 1} [\mathcal{Y}]^{C_1 - 1} [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1] \\
Y_2X_2 &= [\mathcal{X}_1]^{C_2} [\mathcal{Y}_1] [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1] = [\mathcal{X}_1]^{C_2 - 1} [\mathcal{X}_1] [\mathcal{Y}_1] [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1] \\
&= [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}]^{C_1 - 1} [\mathcal{Y}]^{C_1 - 1} [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1] \\
&\vdots \\
X_nY_n &= [\mathcal{X}_n]^{C_2 - 1} [\mathcal{X}_{n-2}]^{C_2 - 1} [\mathcal{X}_{n-3}]^{C_2 - 1} \cdots [\mathcal{X}_2]^{C_2 - 1} [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1]^1 \\
&\vdots \\
Y_nX_n &= [\mathcal{Y}_n]^{C_2 - 1} [\mathcal{X}_{n-2}][\mathcal{X}_{n-3}]^{C_2 - 1} \cdots [\mathcal{X}_2]^{C_2 - 1} [\mathcal{X}_1]^{C_2 - 1} [\mathcal{Y}_1]^1 \\
&\vdots \\
\end{align*}
\]

Thus the only difference between \(X_kY_k\) and \(Y_kX_k\) is the same as between \([\mathcal{T}][\mathcal{U}]\) and \([\mathcal{U}][\mathcal{T}]\).

To find the energy difference between \([\mathcal{X}_n]^{C_n + 1}\) and \(X_{n+1}^-\), keep in mind that these are unit cells of infinitely long periodic structures and we can choose how we cut the unit cell. We can write the periodic structures schematically as:

\[
[[[\mathcal{X}_n]^{C_n}]] \approx [[[[[\mathcal{X}_n]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{\infty} \\
= [[[\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [[[\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{\infty} \\
[\mathcal{X}_{n+1}]^{\infty} = [[[\mathcal{X}_n]^{C_n - 2} [\mathcal{Y}_{n-1}] [\mathcal{X}_{n-1}]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [\mathcal{X}_{n-1}]]^{\infty} \\
= [[[\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [[[\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{\infty}
\]

Consider two adjacent unit cells (which we separate by a “\(\mid\)” for \([[\mathcal{X}_n]^{C_n + 1}]\)):

\[
[\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [[[\mathcal{X}_n]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} \\
\mid [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [[[\mathcal{X}_n]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} (4.3)
\]

The inter-cell interaction energy in Eqn. 4.3 is the same as the inter-cell interaction energy in Eqn. 4.4. We dropped \([\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]\) from left cell and \([\mathcal{X}_{n-1}]^{C_n - 2}\) from right cell because they contribute 0 to inter-cell interaction due to the long buffer created by the large number of interior repeats when \(C_{n+1} \rightarrow \infty\).

\[
[[[\mathcal{X}_n]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} \\
\mid [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}] [[[\mathcal{X}_n]^{C_n - 2} [\mathcal{X}_{n-1}] [\mathcal{Y}_{n-1}]]^{C_n + 1 - 1} [\mathcal{X}_{n-1}]^{C_n - 2} (4.4)
\]
and similarly for \([X_{n+1}]^\infty\) the inter-cell interaction energy of

\[
[X_{n-1}] [Y_{n-1}] [X_{n-1}] ([X_{n-1}]^{C_n-2} [Y_{n-1}] [X_{n-1}] )^{C_{n+1}-1} [X_{n-1}]^{C_n-2}
\]

is equal to the inter-cell interaction energy of:

\[
[[X_{n-1}]^{C_n-2} [Y_{n-1}] [X_{n-1}] ]^{C_{n+1}-1} [X_{n-1}]^{C_n-2}
\]

Comparing Eqn 4.4 and Eqn 4.6, the underlining points out the only terms ((\([X_{n-1}] [Y_{n-1}]\) and \([Y_{n-1}] [X_{n-1}]\)) which contribute to the difference in the inter-cell interactions between these two cases in the limit where \(C_{n+1} \to \infty\). When calculating \(E(X_{n+1}^-) - E([X_n]^{C_{n+1}})\), the relevant intercell interaction is between:

\[
[[X_{n-1}]^{C_n-2} [X_{n-1}] - [Y_{n-1}] [X_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2}
\]

The \([X_{n-1}]^{C_n-2}\) inside \([X_{n-1}]^{C_n-2}\) is canceled out in inter-cell interaction. We keep it in Eqn 4.7 for the sake of showing the structures between left and right side of “ | ”. We can perform a similar analysis for the energy difference between \([X_n]^{C_{n+1}}\) and \(X_{n+1}^-\). The periodic structures can be written:

\[
[X_{n+1}^-]^{\infty} = [[[X_{n-1}]^{C_n-2} [X_{n-1}] [Y_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2} [Y_{n-1}] ]^{\infty}
\]

\[
= [[Y_{n-1}] [X_{n-1}]^{C_n-2} [X_{n-1}] [Y_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2} [Y_{n-1}]^{\infty}
\]

\[
[[X_{n}]^{C_{n+1}}]^{\infty} = [[[X_{n-1}]^{C_n-2} [X_{n-1}] [Y_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2} [Y_{n-1}] [X_{n-1}] ]^{\infty}
\]

\[
= [[Y_{n-1}] [X_{n-1}] [X_{n-1}]^{C_n-2} [Y_{n-1}] [X_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2} ]^{\infty}
\]

When calculating \(E([X_n]^{C_{n+1}}) - E(X_{n+1}^-)\), the relevant intercell interaction is between:

\[
[[X_{n-1}]^{C_n-2} [X_{n-1}] - [Y_{n-1}] [X_{n-1}] ]^{(C_{n+1}-1)} [X_{n-1}]^{C_n-2}
\]

\[
| [Y_{n-1}] [X_{n-1}]^{C_n-2} [X_{n-1}] [Y_{n-1}] ]^{(C_{n+1}-1)} ]^{(C_{n+1}-1)}
\]

(4.8)
In the expression \( (E(X_{n+1}^+) - E([X_n]^{C_{n+1}})) - (E([X_n]^{C_{n+1}}) - E(X_{n-1}^-)) \), the various interactions between dipoles within a given unit cell cancel out overall within the specific unit cells chosen above. Due to the large cell size in the limit \( C_{n+1} \to \infty \), interactions between second-neighbor and further cells are negligible. The only terms surviving in \( (E(X_{n+1}^+) - E([X_n]^{C_{n+1}})) - (E([X_n]^{C_{n+1}}) - E(X_{n-1}^-)) \) are those that arise from interactions between adjacent unit cells. The difference between Eqn. 4.7 and Eqn. 4.8 on the right side of the \(|\) is again between \([X_{n-1}] [Y_{n-1}]\) and \([Y_{n-1}] [X_{n-1}]\). We have already shown that the difference between \([X_{n-1}] [Y_{n-1}]\) and \([Y_{n-1}] [X_{n-1}]\) is the same as between \([\uparrow][\downarrow]\) and \([\downarrow][\uparrow]\). Thus \( (E(X_{n+1}^+) - E([X_n]^{C_{n+1}})) - (E([X_n]^{C_{n+1}}) - E(X_{n-1}^-)) \) is equal to 4 times the interaction energy across the “\(|\)” for the following case:

\[
\cdots \uparrow [\downarrow] \cdots \uparrow [\downarrow] \cdots \uparrow [\downarrow] \cdots | \uparrow [\downarrow] \cdots \uparrow [\downarrow] \cdots \uparrow [\downarrow] \cdots
\]

The distance between each \([\uparrow][\downarrow]\) pair is \(L(X_n)\). In one dimension, the dipole-dipole interaction energy is proportional to the inverse of distance cubed.

\[
\Delta \mu(\alpha) = \frac{E(X_{n+1}^+) - E([X_n]^{C_{n+1}})}{\Delta \alpha L(X_n)} - \frac{E([X_n]^{C_{n+1}}) - E(X_{n-1}^-)}{\Delta \alpha L(X_n)}
\]

\[
= 4L(\alpha) \sum_{m=1}^{\infty} m \left( \frac{1}{(mL(\alpha) - 1)^3} + \frac{1}{(mL(\alpha) + 1)^3} - \frac{2}{(mL(\alpha))^3} \right)
\]

\[
= -2L \frac{d}{dL} \sum_{m=1}^{\infty} \left( \frac{1}{(mL - 1)^2} + \frac{1}{(mL + 1)^2} \right) - 4L \sum_{m=1}^{\infty} \left( \frac{2}{m^2 L^3} \right)
\]

By considering the Fourier transform of \( x + \pi \cot \left( \frac{\pi}{L} \right) \) \( \exp \left( \frac{\pi}{L} \right) \), we derive the series: \( \sum_{m=-\infty}^{\infty} \frac{1}{(mL-1)^2} = \left( \frac{L \sin(\frac{\pi}{L})}{L \sin(\frac{\pi}{L})} \right)^2 \). We finally obtain

\[
\Delta \mu(\alpha) = -2L \frac{d}{dL} \left( \frac{\pi^2}{L^2 \sin^2(\frac{\pi}{L})} \right) - 4L \left( \frac{\pi^2}{3L^3} \right) = 4\pi^2 \left( \frac{1}{L^2} - \frac{\pi \cos(\frac{\pi}{L})}{L \sin^2(\frac{\pi}{L})} - \frac{1}{3} \right)
\]

Thus the interval length of chemical potential corresponding to a given fraction is a function only of the unit cell length \( L \), which is varies with the fraction’s denominator. In other words, the complexity of the fraction in question, as embodied by the size of its denominator, controls the width of the window in chemical potential over
which that phase is seen.

In fact for every point in one dimension or two dimension $E$ versus $\alpha$ curve,

\[
\left(\frac{dE}{d\alpha}\right)_{\text{Right}} \neq \left(\frac{dE}{d\alpha}\right)_{\text{Left}}.
\]

The derivative difference gives the chemical potential interval occupied by that fraction. Eqn. 4.1 shows that the interval for a fraction is monotonically decreasing on the denominator of the fraction in one dimension. This general trend that simple fractions have the widest stability windows continues in the two-dimensional case: $\frac{1}{2}, \frac{1}{4}, \frac{1}{5}$ and especially $\frac{1}{3}$ dominate the sequence. For $\frac{1}{3}, \frac{1}{4},$ and $\frac{1}{5}$, one side hosts a square $\sqrt{3} \times \sqrt{3}, 2 \times 2$ or $3 \times 3$ sublattice (respectively) within the overall $6 \times 6$ adsorption pattern. This infinite sequence of fractional steps EVOKES (TH) the Devil’s Staircase [171–179]. This novel phenomenon has been observed in dipolar gases [173,174], Ising model [172,175,176], smectic liquid crystals [177–179] and magnetic structures [180–182]. Hubbard [171] and Per Bak [172] examined one-dimensional Wigner lattice with an infinite-range convex electrostatic repulsion (i.e. a positively curved with respect to interparticle separation) and no on-site interaction, proved that the filling factor versus chemical potential act as a complete Devil’s Staircase for $\alpha \in (0,1)$. There is no general analytic solution for 2D Devil’s Staircase [174,183]. We also expect that the difference between any two consecutive fractions are infinitely small in two dimension case.

There are 3 Devil’s Staircase side by side in phase diagram Fig. 4.5. Each Staircase has infinite number of small steps. Thus it is easy to find 4 phases close to one point in the phase diagram. For example in the circled areas in Fig. 4.5, 4 phases almost co-exist at one point in the phase diagram, close in violating the Gibbs’ phase rule. If we are able to plot complete phase diagram with larger $n$ included, we are able to find 4 phase coexist in a region as small as you wish. The Gibbs’ phase rule state:

\[
F = C - P + 2
\]

where $C$ is the number of components and $P$ is the number of phases in thermodynamic equilibrium with each other. $F$ is the number of degrees of freedom, which means the number of intensive properties such as temperature or pressure. The Dual side adsorption phase has one component (K) and two degrees of freedom ($\mu_{\text{top}}$ and $\mu_{\text{bottom}}$). When 4 phases coexists at one point, $F = 0$, $C = 1$ and $P = 4$, the equation is violated. The ostensible explanation is that 3 Devil’s Staircase are side by side, one for each $n$ of $n \times n$ : $\alpha$. The fundamental reason is in fact that we
have 2 components in equation 4.9 instead of 1. Top side K and bottom side K are independent.

In conclusion, we have explored the theory of a dual-sided adsorption bilayer. We considered in detail the case of potassium on both sides of a suspended graphene membrane, but the general physics should apply more broadly. Each of the $5 \times 5$, $6 \times 6$ and $8 \times 8$ potassium superlattices can be considered a distinct Ising system with a “which side?” degree of freedom for the adsorbate atoms. As the chemical potential difference between the two sides varies – acting as an effective magnetic field – the system evolves discontinuously through an infinite series of fractions, with the simpler fractions occupying a wider window of relative chemical potential and the more complex fractions forming a Devil’s staircase of intermediate phases. The chemical potential windows across which this step-wise phase behavior occurs are reasonably wide, especially for the higher density $5 \times 5$ case. The need for a suspended membrane suggests that intrinsic quenched disorder will be weak, and thus there are prospects to observe fine-grained phase behavior. It should be accessible experimentally, if the system can equilibrate on experimental timescales. These phenomena are geometric in origin, but do depend on a sufficiently strong cross-membrane interaction. Charge transfer systems provide a natural landscape in which to search for these phenomena, wherein adsorbates interact via either direct Coulombic interactions or indirect interactions mediated by electronic or structural modulations of the membrane.
5.1 Half metal and half semiconductor

A half metal [184–188] is metallic for one spin channel and insulating for the other. Its electron states close to fermi level are thus fully spin polarized. Half metallicity has attracted much attention due to their utility in spintronics [185–188], such as magnetoresistance [189–191] sensors and spin-polarized transport [185, 192–194] devices. Half metallicity has been observed in a few systems, notably, Heusler alloys [184], zinc-blende structure compounds [195] and sulfides [196, 197]. LDA calculations show the potential of half metallicity of zigzag graphene nanoribbons [198,199] with an in-plane transverse electric field as the edge state associated with one spin orientation close their gap, while those associated with the other widen theirs. By extending from the concept of half metal, we define a half semiconductor [198] as a semiconductor in which the top of the valence bands/the bottom of the conduction bands are fully spin polarized. They differ from half metals by having a bandgap for both spin channels.
5.2 Mn intercalation

According to the definition of half-Semiconductor, it is semiconducting in both spin channels while has a net magnetization. Dilute magnetic semiconductors [214–217] are non-magnetic when undoped. The doped systems are usually metastable or have low solubility, and hence the low Curie temperature and the low density of polarized carriers. Organic-based ferrimagnetic semiconductors [218,219] are fascinating. But they don’t have long range structural order and are subject to low thermal tolerance and air sensitivity. Half semiconducting compounds has a moderate band gap (a few tenth eV), a quantity describes the energy difference between the non-magnetic solution and magnetic solution implies they half semiconductivity should survive in room (or higher) temperature. They don’t need doping or electric field to become half semiconducting and could support fully spin polarized current. They are having great potential in making high efficient, even room temperature spin diodes, spin filters, spin injection [194,220,221] and spin tunneling devices. The fully polarized current will also resulted in low energy cost. Hence half semiconductor is immune to all the up mentioned difficults and shortcomings. Further more, the electrically insulating and magnetic properties make half semiconductor a promising candidate in microwave devices [222,223] with low microwave loss. Half semiconductor could also be used in making Kerr rotation, Faraday rotation device and Optical cavity.

We began searching for half semiconductors starting from known semiconductors. Transition metal dichalcogenides (TMDs) have great potential in electronic [65–69] and optoelectronic [70–72] applications because their bandgaps are sizable. TMDs also show lots of fascinating phenomena such as superconductivity [77–79], charge density wave [77,80,81] and Mott transition [82]. Metallic TMDs like TaS$_2$/NbS$_2$ are able to intercalate Mn with varies ratios. These Mn intercalated transition metal dichalcogenides (e.g. Mn$_{1/4}$TaS$_2$) are spin polarized where most of the magnetization comes from Mn ion. The magnetization and fermi level could be adjusted by Mn concentration. The intercalated Mn atoms transfer some of their 3$d$ electrons (2~3$e$/Mn) to metallic transition metal dichalcogenide’s conduction bands in which the energy is lower. Hence the intercalated structure is stable. Semiconducting transition metal dichalcogenides like WS$_2$/MoS$_2$ have a moderate band gap ($\sim$ 1 eV). They are not able to intercalate Mn because they are not able to accommodate any Mn 3$d$ electrons and hence energetically unfavorable. If we
are able to dope Mn intercalated Metallic transition metal dichalcogenides to make the fermi level reach a gap while still keep the magnetization. We may find a half semiconductors.

We studied the intercalated structure within density functional calculations using projector augmented waves, as implemented within the VASP [147–151]. Ionic relaxations were converged to less than 0.01 $\text{eV/Å}$, and all lattice constants were relaxed. Spin polarized PBE [11] and LDA [146] calculation were applied to Mn$_{1/4}$TaS$_2$ with lattice structure described in Tomishima etc’s work [224]. LDA result does not agree well with experimental values of magnetization and lattice constant. PBE result is 3.88µ$_B$/Mn and 12.4Å which is in good agreement with experimental values 3.9-4.2µ$_B$/Mn and 12.5Å [225,226]. Hence, We chose PBE for our intercalated structure calculation hereafter.

MoS$_2$ and TaS$_2$ layered materials have been well studied. Mo/Ta ions form triangular lattices and each sheet of Mo/Ta is sandwiched between 2 layers of S atoms. Each Mo/Ta ion is trigonal prismatic coordinated by 6 S atoms and each sulfur is connected to 3 Mo atoms. MoS$_2$/TaS$_2$ share the same space group P63/mmc (194). However, the stacking sequences of MoS$_2$ and TaS$_2$ are different. MoS$_2$ has a ...ABAB... stacking and TaS$_2$ has a ...ABCABC... stacking. Even though Mn$_{1/9}$MoS$_2$ is not a stable compound, its band structure may give us some hints on questing for half semiconductors. We calculated Mn$_{1/9}$MoS$_2$ band structure

**Figure 5.1.** Crystal structure of Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$ with two viewing directions.
**Figure 5.2.** Band structures of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/9}\text{MoS}_2$. Spin up bands are in Blue and spin down bands are in red.

**Figure 5.3.** Band structures of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/9}\text{Mo}_{8/9}\text{Ta}_{1/9}\text{S}_2$. Spin up bands are in Blue and spin down bands are in red. Green color is added to the blue color bands (up spin bands) and the red color bands (down spin bands) based on each K point’s Mn 3$d$ states weight.
Figure 5.4. Band structures of Mn intercalated transition metal dichalcogenides Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$. Spin up bands are in Blue and spin down bands are in red. Green color is added to the blue color bands (up spin bands) and the red color bands (down spin bands) based on each K point’s Mn 3$d$ states weight. The fermi-level is lowered to the gap as more Mo replaced by Ta.

Figure 5.5. Band structure of Mn intercalated transition metal dichalcogenide Mn$_{1/9}$Mo$_{13/18}$Ta$_{5/18}$S$_2$. Compared with Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$, the fermi level is below the $d$-gap because of increased Ta doping amount.
Figure 5.6. Band structure of Mn intercalated transition metal dichalcogenide \( \text{Mn}_{1/9}\text{Mo}_{6/9}\text{Ta}_{3/9}\text{S}_2 \). Compared with \( \text{Mn}_{1/9}\text{Mo}_{7/9}\text{Ta}_{2/9}\text{S}_2 \), the fermi level is lower due to more Ta doping.

as it is shown in in Fig. 5.2. However, the MoS\(_2\) stacking we choose here is the same as TaS\(_2\)’s stacking (...ABCABC... stacking). You will see why later. We call this MoS\(_2\) with TaS\(_2\) structure as parent structure. The "parent structure" refers to stacking sequence. Below the fermi level, We see a \( \sim 0.5 \) eV band gap below the fermi level. We may able to find a half semiconductor if we are able to lower the fermi level to this gap while keep the band structure sequence. To lower the fermi level to the \( \sim 0.5 \) eV gap, the total number of electron per cell need to decrease by 4 which can be realized by replacing \( \frac{2}{9} \) of the Mo by Ta. Hence the resulted compound is \( \text{Mn}_{1/9}\text{Mo}_{7/9}\text{Ta}_{2/9}\text{S}_2 \).

The parent structure of \( \text{Mn}_{1/9}\text{Mo}_{7/9}\text{Ta}_{2/9}\text{S}_2 \) is TaS\(_2\) structure. Mo atoms replace \( \frac{7}{9} \) of the Ta atoms. Mn atoms are intercalated between Mo-Mo, Ta-Ta or Mo-Ta atoms. Several different Ta, Mn position combinations were tested for lowest energy configuration. We found that there are a few configurations having similar lowest energy. As long as Mn atoms are sandwiched between Ta and Ta atoms, these configurations have similar lowest energies and similar band structures. When choosing MoS\(_2\) as the mother structure with \( \frac{2}{5} \) Mo replaced by Ta (...ABAB... stacking), Mn can not be intercalated between Ta atoms (intercalated between
Ta and S instead) due to the MoS$_2$ stacking geometry. The inter-layer distance between transition metal dichalcogenide layers is bigger and the energy is a few tenth eV higher when compared with TaS$_2$ as mother structure case although they are having similar energies when not intercalated.

Will the rigid band model work and fermi level be lowered to the gap when go from MoS$_2$ to Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$. The answer is YES. The calculated band of Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$ is shown in Fig. 5.4. Blue lines are up spin bands and red lines are down spin bands. We have decomposed the wavefunction of each K point into atom orbital states. Green color is added to the blue color bands (up spin bands) and the red color bands (down spin bands) based on each K point’s Mn 3$d$ states weight. In another word, if there is more Mn 3$d$ states in a K point’s wavefunction, more green is added to blue (red) for that K point on band structure plot. The yellow color in the band structure is a result of green added to red. It is clear that most Mn 3$d$ states are mixing into the spin up bands below fermi level and spin down bands above fermi level. The Mn 3$d$ bands are splitting and spin down bands energy are higher than spin up bands energy. Each Mn transfers 2 electrons to transition metal dichalcogenides. The remaining 5 outer shell electrons are all on the Mn 3$d$ spin up bands with each band single occupied. The Mn 3$d$ bands are quite flat since Mn concentration is not high. The bands of transition metal dichalcogenides do not change significantly after intercalation. Mo$_{7/9}$Ta$_{2/9}$S$_2$ receives 2 electrons from each Mn, compensates the effect of $\frac{2}{9}$ Mo replaced by Ta, makes the bands filled up to the gap. Hence most of the magnetization located on Mn site. The total magnetization is $10\mu_B$ per unit cell or $5\mu_B$/Mn. The polarization of the intercalated Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$ should survive large range of temperature. The energy of spin unpolarized solution is $1.2$ eV/Mn higher in energy than polarized solution. Our calculation also show an indirect band gap of about $0.58$ eV with the valence band maximum at $\Gamma$ and the conduction band minimum between $\Gamma$ and M. The band gap size is suitable for a lot of applications, such as high-speed analog transistors and quantum confined structures. Keep increasing the Ta doping ratio results in the fermi level below the gap and the compound become metallic as two excessive Ta doping case are shown in Fig. 5.5 and Fig. 5.6

Extending from Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$ that each Mn transfers 2 electrons to Mo$_{7/9}$Ta$_{2/9}$S$_2$ and the remaining 5 Mn 3$d$ outer shell electrons are all on the Mn 3$d$ spin up bands with each single occupied, We derived a formular for a series
**Figure 5.7.** Band structure of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$. Blue lines are up spin bands and red lines are down spin bands.

**Figure 5.8.** Band structure of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Nb}_{2/7}\text{S}_2$ with spin-orbit interaction included in calculation. The band structure shows almost no change compared with the no spin-orbit interaction included band structure.
Figure 5.9. Band structure of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$ with MoS$_2$ as parent structure case. Blue lines are up spin bands and red lines are down spin bands. It shows similar magnetization and band gap but less Mn 3$d$ band dispersion compared with $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$ with TaS$_2$ as parent structure case.

Figure 5.10. Band structure of Mn intercalated transition metal dichalcogenides $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Nb}_{2/7}\text{S}_2$ has similar band structure with $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$. 
Figure 5.11. Band structure of Mn intercalated transition metal dichalcogenide Mn$\frac{1}{4}$Mo$\frac{1}{2}$Ta$\frac{1}{2}$S$_2$. Compared with Mn$\frac{1}{9}$Mo$_{\frac{7}{9}}$Ta$_{\frac{2}{9}}$S$_2$, larger $x$ leads to smaller band gap.

Figure 5.12. Band structure of Mn intercalated transition metal dichalcogenide Mn$\frac{1}{4}$Mo$\frac{1}{2}$Ta$\frac{1}{2}$S$_2$ with spin-orbit interaction included in calculation. The band structure shows almost no change compared with the no spin-orbit interaction included band structure.
of half semiconductor: Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$. A example of $x = \frac{1}{7}$ is shown in Fig. 5.7. Similar with $x = \frac{1}{9}$, the $x = \frac{1}{7}$ case has a 0.50 eV band gap, smaller than $x = \frac{1}{9}$ case. Larger $x$ means more Mn 3$d$ bands dispersion and smaller band gap. When Mn ions distance are close enough, the dispersion of the Mn 3$d$ bands will cross the band gap and destroy the band gap. Hence $x$ can not be too large. We did a test for $x = \frac{1}{4}$ as the band structure is shown in 5.11. The band gap is significantly smaller than of $x = \frac{1}{9}$. Spin-orbit interaction is important for transition metal electronic structure. One may wonder how much the spin-orbit interaction will affect the band structure and magnetization of Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$. Here we re-calculated the band structure of Mn$_{1/7}$Mo$_{5/7}$Ta$_{2/7}$S$_2$ and Mn$_{1/4}$Mo$_{1/2}$Ta$_{1/2}$S$_2$ with spin-orbit interaction included. We find that spin-orbit interaction affects the band structure and magnetization very little. The band structures show minimum changes.

Interestingly, MoS$_2$ parent structure case of Mn$_{1/7}$Mo$_{5/7}$Ta$_{2/7}$S$_2$ has 5$\mu_B$/Mn magnetization and similar band structure compared to that of TaS$_2$ mother structure case as shown in Fig. 5.9. But MoS$_2$ mother structure case has flater Mn 3$d$ bands, smaller splittings in Mn 3$d$ bands and smaller band gap. The choose of transition metal dichalcogenides stacking sequence is not important in establishing half-semiconducting character.

Known compounds are the biggest challenges when considering the the stability of this Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ compound. In the Compositional Phase Diagram of Mn, Mo, Ta and S, MnS MnS$_2$, TaS$_2$ and Mn$_{1/3}$TaS$_2$ are the most notable compounds that could challenge the stability of Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ compound. Hence we test $x = \frac{1}{9}$, $\frac{1}{7}$ and $\frac{1}{4}$ case against decomposition into a few scenarios:

1. Mo$_{1-2x}$Ta$_{2x}$S$_2$ + Mn
2. MoS$_2$ + TaS$_2$ + Mn
3. Mn$_{1/3}$TaS$_2$ + MoS$_2$ + Mn
4. Mn$_{1/4}$TaS$_2$ + MoS$_2$ + Mn
5. MnS$_2$ + TaS$_2$ + MoS$_2$ + Mo
6. MnS$_2$ + TaS$_2$ + MoS$_2$ + Ta
7. MnS + TaS$_2$ + MoS$_2$ + Mo
8. MnS + TaS$_2$ + MoS$_2$ + Ta

None of these scenario has a lower total energy than Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ crystal. Scenario 3 is closest in energy but still about 0.1 eV/Mn higher. Therefore we believe that the Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ crystal is quite stable and very possible of being manufactured. We also considered the case of Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ under a
Figure 5.13. Band structure of Mn intercalated transition metal dichalcogenide Mn$_{1/7}$Mo$_{6/7}$Ti$_{1/7}$S$_2$.

giving chemical potential of sulfur. Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ is stable with low sulfur chemical potential. Increasing the sulfur chemical potential will resulted the Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ converted to MnS$_2$, TaS$_2$, MoS$_2$. Therefore, the amount of sulfur need be controlled when making Mn$_2$Mo$_{1-2x}$Ta$_{2x}$S$_2$ compound. Typically for Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$, the threshold of sulfur chemical potential is higher than the sulfur atom energy in sulfur crystal. Hence sulfur crystal can not coexists with Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$. There are reports claiming that they have successfully obtain complete miscibility in the systems TaS$_2$-MoS$_2$, NbS$_2$-MoS$_2$ and TaSe$_2$-MoSe$_2$ [227, 228]. Semiconductor-metal transition has been observed in low-level Nb doping of MoS$_2$ particles [228]. Hoshyargar [229] _etc_ have synthesised Graphene-type sheets of Nb$_{1-x}$W$_x$S$_2$ and Zhu [230, 231] _etc_ have synthesized Tungsten-Niobium-sulfur composite nanotubes. Previous Theoretic calculation also shown that Mo$_{1-2x}$Ta$_{2x}$S$_2$ is a stable compound [232]. Hence, synthesising of Mn$_x$Mo$_{1-2x}$Ta$_{2x}$S$_2$ should be within reach.

Replacing Ta with Nb or Mo with W/Cr will result in similar band structure and same magnetization of 5$\mu_B$/Mn. Here we showed the band structure of Mn$_{1/7}$Mo$_{6/7}$Nb$_{2/7}$S$_2$ in Fig. 5.10. We has also test its stability against the 8 mentioned scenarios. Again scenario 3 is the biggest threat with almost equal
Figure 5.14. Band structure of Mn intercalated transition metal dichalcogenide $\text{Mn}_{1/9}\text{W}_{7/9}\text{Ta}_{2/9}\text{S}_2$. Compared with $\text{Mn}_{1/9}\text{Mo}_{7/9}\text{Ta}_{2/9}\text{S}_2$, replacing Mo with W can generate similar half semiconductor.

Figure 5.15. Band structure of Mn intercalated transition metal dichalcogenide $\text{Mn}_{1/9}\text{Mo}_{8/9}\text{Ti}_{1/9}\text{S}_2$. Compared with $\text{Mn}_{1/9}\text{Mo}_{7/9}\text{Ta}_{2/9}\text{S}_2$, replacing Ta with Ti can generate similar half semiconductor. But the formula has to be modified to $\text{Mn}_x\text{Mo}_{1-x}\text{Ti}_x\text{S}_2$. 
Figure 5.16. Band structure of Mn intercalated transition metal dichalcogenide Mn$_{1/9}$Cr$_{8/9}$Ti$_{1/9}$S$_2$. Compared with Mn$_{1/9}$Mo$_{7/9}$Ta$_{2/9}$S$_2$, replacing Mo with Cr and Ta with Ti can generate similar half semiconductor.

Figure 5.17. Band structure of Mn intercalated transition metal dichalcogenide Mn$_{1/4}$Mo$_{3/4}$Ti$_{1/4}$S$_2$. 

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energy as $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Nb}_{2/7}\text{S}_2$. The $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Nb}_{2/7}\text{S}_2$ case has a band gap of 0.54 eV which is larger than that of $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$. This is because $\text{Mo}_{5/7}\text{Nb}_{2/7}\text{S}_2$’s bands are lower than those of $\text{Mn}_{1/7}\text{Mo}_{5/7}\text{Ta}_{2/7}\text{S}_2$’s. There are many more choice that can derive half semiconductors. We have shown the band structures of some Ta/Nb and Cr/Mo/W combinations. Replacing Nb with Ti is another way to generate half semiconductor, but the formula has to be modified to $\text{Mn}_x\text{Mo}_{1-x}\text{Ti}_x\text{S}_2$.

In conclusion. We have developed a strategy on designing half semiconductors (half metal) compound and this strategy has been applied to Mn intercalated transition metal dichalcogenide. A formular of half semiconducting Mn intercalated transition metal dichalcogenide was proposed. The resulted transition metal dichalcogenide conduction band has been filled up by electrons transferred from Mn. The Mn 3$d$ band has been tuned flat so that there is band gap available. The strategy is not limited to transition metal dichalcogenide system it could be employed to other systems such as intercalating Mn in B rich BN.

### 5.3 Mn doping

TMDs such as MoS$_2$ and WS$_2$ have great potential in electronic [65–69] and optoelectronic [70–72] applications because of their reasonable bandgaps size (0.5 to 2 eV). (The bandgaps are in the visible portion of the spectrum.) The TMDs also show many fascinating phenomena such as superconductivity [77–79], charge density wave [77,80,81] and Mott transition [82]. Can we design a TMD based half metal which may combine the unique properties of both TMD and half metal? Theoreticcal works [200–203] have shown that Mn substitution onto the metal site could introduce magnetism in TMDs. However, most of these Mn substituted TMDs are conductors for both spin channels. For most trigonal-prismatic coordinated TMDs (for example: MoS$_2$, WS$_2$ or TaS$_2$), the transition metals’ outer shell $d$ orbitals with different symmetry are gapped of 1-2 eV due to ligand field. These 1-2 eV gaps may not be the band gap. For MoS$_2$ monolayer system, Mo’s 4$dz^2$ orbitals are about 1.9 eV below Mo’s other 4$d$ orbitals. The 1.9eV gap between them does correspond to the semiconducting gap. But TaS$_2$ is metallic and the fermi level is below the gap between Ta’s 5$dz^2$ and Ta’s other 5$d$ orbitals due to the smaller number counting of the electrons. To distinguish from the semiconducting gap, we define these gaps as $d$-gaps. Mn substitution in MoS$_2$ is not themaldynamic
Figure 5.18. Unit cell of Mn$_{1/16}$Mo$_{14/16}$Ta$_{1/16}$S$_2$ monolayer with the lowest energy. Different Mn and Ta position combinations were tested for the lowest energy configuration. When Mn is next to Ta, the energy is the lowest as shown in the pic.

Prefered because MoS$_2$’s bands below the $d$-gap are fully filled and there is a penalty in energy to accommodate Mn’s extra electrons. On the other hand, Mn can be substituted in TaS$_2$ because its $5dz^2$ below the $d$-gap is partially filled. In all systems, the bands below $d$-gap show strong overlap with no energy gap even in case of spin splitting. If the Fermi level is inside this pervasive band overlapping area, it will cuts both spin channels. Therefore, to generated a half metal with Mn substitution, the Fermi level of Mn substituted TMD has to be tuned through compensate co-doping so that it remains near the $d$-gap edges of the undoped system. Because Mn has one more valence electron than Mo while Ta has one less, we examined Mn$_x$Mo$_{1-x}$Ta$_x$S$_2$ mono layer so that the compensation doping make the Fermi energy near the gap edge. The introduction of co-doped Ta in the compound can also stabilize the doping of Mn since it opens up valence vacancy.

We studied the doped MoS$_2$ mono layer structure within spin polarized density functional theory using PBE [11] exchange correction function, as implemented within the VASP [147–151]. The calculations used projector augmented waves. Ionic relaxations were converged to less than 0.01 $eV/\AA$, and all lattice constants were relaxed. Single layered structures used a fixed 20Å out-of-plane periodicity.
Figure 5.19. Band structure of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$. Bands close to Fermi level (shaded area) are zoomed in and showed on upper side of each panel. Spin up bands are in Blue and spin down bands are in red. The band structure of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ shows no spin polarization or magnetization.

Figure 5.20. Band structures of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ with 0.2 electron per Mn doping.
Figure 5.21. Band structures of Mn\(_{\frac{1}{16}}\)Mo\(_{\frac{14}{16}}\)Ta\(_{\frac{1}{16}}\)S\(_2\) with 1 electron per Mn doping.

Figure 5.22. Band structures of Mn\(_{\frac{1}{16}}\)Mo\(_{\frac{14}{16}}\)Ta\(_{\frac{1}{16}}\)S\(_2\) with -0.2 electron per Mn doping.
Figure 5.23. Band structures of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ with -1 electron per Mn doping. Green color is added to the blue color bands (up spin bands) and the red color bands (down spin bands) based on each K point’s Mn 3$d$ states weight. More green color is added if there is more Mn 3$d$ orbitals mixed into a band. Note the orange color band is result from superposition of red and green color.

In a MoS$_2$ or TaS$_2$ mono layer, Mo or Ta ions form triangular lattices and each sheet of Mo/Ta is sandwiched between 2 layers of S atoms. Each Mo or Ta ion is trigonal prismatic coordinated by 6 S atoms and each sulfur is coordinated to 3 Mo atoms. We focused on $x = 1/16$ for more explicit analyzing of $\text{Mn}_x\text{Mo}_{1-2x}\text{Ta}_x\text{S}_2$ alloy. $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ monolayer has same number of valence electrons as of MoS$_2$ monolayer. $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ may have a higher Mn concentration than actually experimental values. However, the Manganese’s 3$d$ bands are already flat in this doping level which indicate this simulation cell size can be expand to lower doping experimental achievable. Several Ta and Mn position combinations were tested for lowest energy configuration of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$. The lowest energy configuration has Mn next to Ta as shown in Fig 5.18. The compensation doping strategy works well and $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ is semiconducting (Fig 5.19). Subsequent orbital analysis show that the a few bands below the fermi energy are from Ta and Mo d orbitals while the a few flat bands above the fermi energy are from Mn d orbitals. Since the band just below and above the Fermi level is very flat, small deviation from perfect compensation doping may cause these
flat bands spin splitting and create a half metal. This could be achieved either through electric-static gating or a slightly more Mn than Ta or Vice Versa. The Fermi level could cut just one spin band and make the compound a half metal. Jellium background calculation were performed for dopings of $1e$/Mn, $0.2e$/Mn, $-0.2e$/Mn and $-1e$/Mn and resulting band structures are shown in Fig 5.20, Fig 5.21, Fig 5.22 and Fig 5.23. At a doping of $+0.2e$/Mn, the spin up conduction band is partial filled with 0.2e on it. Hence the magnetization is $0.2\mu_B$/Mn and all electron carriers are polarized. As electron doping increases to $1e$/Mn (5.21), the spin up conduction band is completely filled and magnetization reaches $1\mu_B$/Mn. The Fermi level splits one pair of spin up and spin down band which means the spin splitting is bigger than bandwidth. The just over 0.5 eV spin splitting indicates the magnetization should be stables under room temperature. We suggests that the splitting would work better for smaller $x$ since smaller $x$ means flater bands. Hole dopings also show magnetization and 100 percent carrier polarization. For the band structure of $-1e$/Mn doping, green color is added to the blue color bands (up spin) and the color bands (down spin) based on each K point’s Mn 3$d$ states weight. In another word, more green color is added if there is more Mn 3$d$ orbitals mixed into a band. The a few spin up and spin down bands just below the $d$-gap don’t have much green color which indicate that the magnetization is mainly on Ta and Mo. We believe that the magnetization on Ta and Mo is related to their proximity of Mn. The a few flat bands just above the $d$-gap are mostly green and orange (orange color is a result of red and green color superposition) which means that these bands are mainly from 3$d$ orbitals. Hence the magnetization is mainly on Mn for electron doping. So the spin splitting in electron doping is much bigger than that of hole doping since Mn is magnetization prone. $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ is not the only choice for half metal. Nb is an alterante for Ta. For all doped and undoped cases, the band structures and the magnetizations of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Nb}_{1/16}\text{S}_2$ are very similar with that of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$. Same doping strategy can also be applied to bulk materials. Examples of both Mn and Ta compensated doped in MoS$_2$ bulk material are $\text{Mn}_{1/32}\text{Mo}_{29/32}\text{Ta}_{2/32}\text{S}_2$ as the bands are shown in Fig 5.27 and Fig 5.28. $\text{Mn}_{1/32}\text{Mo}_{29/32}\text{Ta}_{2/32}\text{S}_2$ is one valence electron per Mn less than MoS$_2$. MoS$_2$ and TaS$_2$ mono layers has same structures and point group symmetry. But in bulk MoS$_2$ and TaS$_2$, the stacking between two neighboring layers are different. $\text{Mn}_{1/32}\text{Mo}_{29/32}\text{Ta}_{2/32}\text{S}_2$ may take either MoS$_2$ or TaS$_2$ stacking sequence. Both
Figure 5.24. Band structures of Mn$_{1/16}$Mo$_{14/16}$Nb$_{1/16}$S$_2$. Bands structure close to Fermi level (shaded area) are zoomed in and showed on upper side of each panel. Spin up bands are in blue and spin down bands are in red.

stacking geometries are calculated for lowest energy configuration. We found that MoS$_2$ stacking sequence is about 0.022 eV per sulfur lower in energy than that of TaS$_2$ stacking sequence. Both stacking geometry show very similar band structures. Both have a magnetization of 1$\mu_B$/Mn with the Fermi level separating a pair of spin up and spin down bands. Over all, we have confirmed that Mn doping in MoS$_2$-TaS$_2$ alloys can result in half metal.

Are these compensated doped compounds stable enough for applications? It is known that MnS$_2$ cannot form stable alloy with MoS$_2$ and our calculation also confirmed that Mn$_{1/16}$Mo$_{15/16}$S$_2$ is 0.61 eV/Mn higher in energy than separate MnS$_2$ and MoS$_2$ monolayers. Previous experiments [204–212] and calculations [213] show that MnS$_2$ could form alloys with TaS$_2$ or NbS$_2$. Our calculations show that Mn$_{1/16}$Mo$_{14/16}$Ta$_{1/16}$S$_2$ is 0.43 eV/Mn lower in energy than separate MnS$_2$ and MnS$_2$-TaS$_2$ alloy. Introducing TaS$_2$ into MoS$_2$ can significantly enhance the doping of MnS$_2$. To further test the stability, we have also tested Mn$_{1/16}$Mo$_{14/16}$Ta$_{1/16}$S$_2$ against decomposition into the following case:

1. MoS$_2$, TaS$_2$ and MnS$_2$
2. Mn$_{1/3}$Ta$_{2/3}$S$_2$(MnS$_2$ doped TaS$_2$), MoS$_2$ and MnS$_2$
3. Mn$_{1/2}$Ta$_{1/2}$S$_2$(MnS$_2$ doped TaS$_2$), MoS$_2$ and MnS$_2$
We found that the biggest threat for $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ is case 3 which is about $0.06 \text{ eV/Mn}$ lower in energy. $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ has a large unit cell hence large configuration entropy. The entropy effect should be a much factor than $0.06 \text{ eV}$ energy difference. We hence conclude that $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Ta}_{1/16}\text{S}_2$ tends to form a stable homogeneous alloy at room temperature.

In conclusion, with DFT calculation we have demonstrated that doping Mn in $\text{MnS}_2$-$\text{TaS}_2$ alloy can generate half metal compound with 100 percent polarized carriers, holes or electrons. This half metal compound should be room temperature stable and can be manufactured. For example, it may be manufactured from a precursor of known compound $\text{Mo}_{1-x}\text{Ta}_{x}\text{S}_2$ or direct from $\text{MnS}_2$, $\text{TaS}_2$ and $\text{MnS}_2$. The carrier density and magnetization of the compound can be modulated with Mn or Ta concentration or gate voltage which implies great potential in electronics applications.

### 5.4 TMD based best thermoelectric material

Prof. Mahan and Sofo [233] suggested that a delta function like transport distribution function near Fermi level can result in best thermoelectric. A material with a low dispersive band that aligned with bottom of conduction band or top of
Figure 5.26. Band structures of $\text{Mn}_{1/16}\text{Mo}_{14/16}\text{Nb}_{1/16}\text{S}_2$ with $-0.2e$/Mn doping.

Figure 5.27. Band structures of bulk $\text{Mn}_{1/32}\text{Mo}_{29/32}\text{Ta}_{2/32}\text{S}_2$. 

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valence band could be a good candidate for good thermoelectric material. To be a good thermoelectric material, the low dispersive band also need to have some band hybridization with conduction band or valence band. Covalent binding a molecule to TMD mono layer provide a realistic mean to make such material. There is a 1-2 $eV$ band gap in MoS$_2$ or WS$_2$ mono layer. Polycyclic aromatic hydrocarbon molecule’s orbital level can be fine tuned with molecule size and atomic replacement.

We first test the case with phenyl group covalent connect to WS$_2$. DFT calculations used PBE exchange-correlation function and projector augmented waves at 400 $eV$ plane-wave energy cutoff, as implemented within the VASP [147–151]. Ionic relaxations were converged to less than 0.01 $eV/Å$, and all lattice constants were relaxed. The resulted band structure shows that the both the highest occupied and lowest unoccupied molecule orbitals energy levels are far from the WS$_2$ conduction band bottom or valence band top. We would like to lower the lowest unoccupied molecule orbital to align it with the WS$_2$ conduction band bottom. We used the same method in chapter 3 and replaced 3 of the C in phenyl group with N. The resulted group is -C$_3$N$_3$H$_2$ (Fig. 5.29) and the resulted band structure is shown in Fig. 5.30. The LUMO of -C$_3$N$_3$H$_2$ group is aligned with the

Figure 5.28. Band structures of bulk Mn$_{1/32}$Mo$_{29/32}$Ta$_{2/32}$S$_2$ with a stacking geometry same as TaS$_2$. 
Figure 5.29. $\text{-C}_3\text{N}_3\text{H}_2$ group covalent bonded to WS$_2$, the S atom in WS$_2$ that connected to $\text{-C}_3\text{N}_3\text{H}_2$ need to be replaced by P.

Figure 5.30. Band structure of $\text{-C}_3\text{N}_3\text{H}_2$ group covalently bonded to WS$_2$, the S atom in WS$_2$ that connected to $\text{-C}_3\text{N}_3\text{H}_2$ is replaced by P.

We have found that the S atom in WS$_2$ that connected to $\text{-C}_3\text{N}_3\text{H}_2$ need to be replace by P. If the S is not being replaced, the bonded $\text{-C}_3\text{N}_3\text{H}_2$ would bend and the molecule level would not align with the bottom of WS$_2$’s conduction bands.
The structure of -C₃N₃H₂ connect to WS₂ without P atom are shown in Fig. 5.31 and the band structure is shown in Fig. 5.32. Even in the case of -C₆H₅, the LUMO is not high enough to aligned with the bottom of WS₂’s conduction bands.

We have successfully align the bonded molecule energy level with WS₂ conduction band bottom and this suggest that TMD can be used to design high thermoelectric material. There are many different molecules can be covalently bonded to TMD and lots of choices for designing high thermoelectric material.
Figure 5.32. Band structure of -C$_3$N$_3$H$_2$ group covalently bonded to WS$_2$. The S atom in WS$_2$ that connected to -C$_3$N$_3$H$_2$ is NOT replaced by P.

Figure 5.33. Band structure of -C$_6$H$_5$ group covalently bonded to WS$_2$. The S atom in WS$_2$ that connected to -C$_6$H$_5$ is NOT replaced by P. Even in the case of no C being replaced by N. The -C$_6$H$_5$ LUMO would not align with the bottom of WS$_2$’s conduction bands.
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