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ELECTRONIC, OPTICAL, AND MAGNETIC PROPERTIES OF GRAPHENE AND SINGLE-LAYER TRANSITION METAL DICHALCOGENIDES IN THE PRESENCE OF DEFECTS

by

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Major Professor: Michael N Leuenberger
ABSTRACT

Two-dimensional (2D) materials, such as graphene and single-layer (SL) transition metal dichalcogenides (TMDCs), have attracted a lot of attention due to their fascinating electronic and optical properties. Graphene was the first 2D material that has successfully been exfoliated from bulk graphite in 2004. In graphene, charge carriers interacting with the honeycomb lattice of carbon atoms of graphene to appear as massless Dirac fermions. Massless quasiparticles with linear dispersion are also observed in surface states of 3D topological insulators and quantum Hall edge states. My first project deals with the two-dimensional Hong-Ou-Mandel (HOM) type interference experiment for massless Dirac fermions in graphene and 3D topological insulators. Since massless Dirac fermions exhibit linear dispersion, similar to photons in vacuum, they can be used to observe the HOM interference intensity pattern as a function of the delay time between two massless Dirac fermions. My further projects and the major part of this dissertation deal with single-layer (SL) transition metal dichalcogenides (TMDCs), such as MoS$_2$, WS$_2$, MoSe$_2$ and WSe$_2$, which have recently emerged as a new family of two-dimensional (2D) materials with great interest, not only from the fundamental point of view, but also because of their potential application to ultrathin electronic and optoelectronic devices. In contrast to graphene, SL TMDCs are direct band semiconductors and exhibit large intrinsic spin-orbit coupling (SOC), originating from the d orbitals of transition metal atoms. Wafer-scale production of SL TMDCs is required for industrial applications. It has been shown that artificially grown samples of SL TMDCs through various experimental techniques, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and molecular beam epitaxy (MBE), are not perfect, instead certain type of imperfections such as point defects are always found to be present in the grown samples. Defects compromise the crystallinity of the sample, which results in reduced carrier mobility and deteriorated optical efficiency. However, defects are not always unwanted; in fact, defects can play an important role in
tailoring electronic, optical, and magnetic properties of materials. Using Density functional theory we investigate the impact of point defects on the electronic, optical, and magnetic properties of SL TMDCs. First, we show that certain vacancy defects lead to localized defect states, which in turn give rise to sharp transitions in in-plane and out-of-plane optical susceptibilities of SL TMDCs. Secondly, we show that a naturally occurring antisite defect MoS in PVD grown MoS$_2$ is magnetic in nature with a magnetic moment of 2$\mu_B$, and remarkably exhibit an exceptionally large atomic scale magnetic anisotropy energy (MAE) of $\sim$ 500 eV. Both magnetic moment and MAE can be tuned by shifting the position of the Fermi level which can be achieved either by gate voltage or by chemical doping. Thirdly, we argue that the antisite defect Se$_W$ in WSe$_2$ leads to long lived localized excited states, which can explain the observed single quantum emitters in CVD grown WSe$_2$ samples, with potential application to quantum cryptography.
Dedicated to my parents, Afra Sayab Khan and Imroza Begum, and to my late grandfather,
Muhammad Afzal Khan, for all their love, patience, kindness and support.
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After an intensive period that spans over six years, writing this note of thanks is the finishing touch on my dissertation. It has been a period of rigorous learning for me, not only in the scientific arena, but also on a personal level. I would like to reflect on the people who have supported and helped me so much throughout this period.

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CHAPTER 1: INTRODUCTION

2D Materials

For decades, scientists and researchers believed that two-dimensional (2D) crystals are thermodynamically unstable and could not exist. It has been argued that thermal fluctuations in 2D crystals lead to displacements of atoms comparable to their inter-atomic distances at finite temperatures [1, 2]. This argument was later strongly supported by experimental observations which show that the melting point of thin films decreases with decreasing thickness and they become unstable at a thickness of typically dozens of atomic layers [3, 4]. For this reason scientists were skeptical about the existence of single-layer materials until the year 2004 [5, 6], when graphene, an atomically thick carbon material was obtained through mechanical exfoliation, the so-called scotch-tape method. The discovery of graphene opened up the novel research field of two-dimensional (2D) materials, with potential high-tech applications. From a fundamental perspective, in graphene the interaction between electrons and honeycomb lattice of carbon atoms causes the electrons/holes to behave as massless Dirac fermions. Therefore graphene allows one to see relativistic effects that have never been observed before in condensed matter physics, such as Klein tunneling [7], half integer [8] and anomalous-quantum Hall effect [9]. From a technological point of view, graphene exhibits superior mechanical and electronic properties, i.e. graphene is so far the strongest 2D material on earth and also it shows exceptionally high mobility with measured values from around 1,000 cm²V⁻¹sec⁻¹ for CVD grown graphene up to 10⁶ cm²V⁻¹sec⁻¹ for suspended mechanically exfoliated graphene [10]. All these observations have attracted extensive attention throughout the Academia, and great efforts have been made to push graphene into real applications in the fields of radio-frequency integrated circuits, optical detection and communication, terahertz plasmonics, energy conversion and storage, nano-electro-mechanical systems, advanced chemical and/or bio-
After the discovery of graphene, the scotch-tape method was later applied to other van der Waals structures, and now we have number of atomically thin materials including insulators such as Boron nitrite, metals such as NbSe$_2$, semiconductors such as transition metal dichalcogenides MX$_2$ (M = Mo, W; X = S, Se) and phosphorene (a single layer of phosphorous atoms).

Figure 1.1: Electromagnetic spectrum. Applications that utilize the different spectral ranges are presented in the top portion of the panel. NIR, MIR and FIR indicate near-, mid- and far-infrared, respectively. The atomic structures of hBN, MoS$_2$, BP and graphene are shown in the bottom of the panel, left to right. The crystalline directions (x and y) of anisotropic BP are indicated. The possible spectral ranges covered by different materials are indicated using coloured polygons. b–e, Bandstructures of single-layer hBN (b), MoS$_2$ (c), BP (d) and graphene (e). (taken from Ref. 11)
The basic structures and energy band structures of the various 2D materials are shown in Fig. 1.1 [11]. An important property of 2D materials is their large surface-to-volume ratio that makes them extremely vulnerable to external perturbations. It has been shown that the band gap in 2D materials can be tuned as a function of external pressure, a property which is highly desirable in modern day electronics industry. Secondly, the Fermi level or the charge density in 2D materials can be tuned by applying a gate voltage, which enables the large modulations of the electrical and optical properties in SL 2D materials. It has been show that doped 2D semiconductors are superior to 3D semiconductors because the charge density in 2D semiconductors is more stable against thermal fluctuations [12].

Since graphene is a zero-bandgap semiconductor and exhibits semi-metallic behavior, without band gap opening, it cannot be applied directly to semiconductor devices such as field-effect transistors (FETs), which cannot operate as expected in the absence of a band gap in the material. In order to overcome this obstacle, both theoretical and experimental studies were performed on bilayer graphene and graphene nanoribbons, from which a small band gap can be opened to accomplish an acceptably high on-off current ratio of graphene transistors. Nevertheless, neither method is sufficient to provide high on-off current ratio while retaining the advantage of the ultrahigh mobility. This is where alternative 2D materials such as transition metal dichalcogenides (TMDCS), which have a sizable band gap, can help.

**Single-Layer Transition Metal Dichalcogenides**

Single-layer (SL) TMDCs ($MX_2$; $M =$ transition metal such as Mo, W, and $X =$ S, Se) have been attracted a great deal of attention because of their intriguing electronic and optical properties with a wide range of promising applications, ranging from nanoelectronics and nanophotonics to sensing at the nanoscale. Interest in SL TMDCs has been sparked by the implementation of the first SL
MoS$_2$ based transistor and by the discovery of strong photoluminiscence in SL MoS$_2$. Group-VI TMCDs consist of a trilayers, each trilayer consists of transition metal atoms sandwiched between two layers of chalcogen atoms in the trigonal prismatic structure Fig. 1.2 (a). Stacking monolayers in the ABAB... sequence forms the bulk structure in the most commonly available 2H polytype. Fig. 1.2.2 (b) shows the top view of the 2H-MoS$_2$ direct lattice and Brillouin zone along the high symmetry points. Bulk TMCDs are indirect-band gap semiconductors with conduction-band minimum and valence-band maximum located, respectively, at the $Q$ and the $\Gamma$ points. In the SL limit, they have been shown to cross over to become direct-band gap semiconductors with gaps located at the K and the K' points. This effect can be understood as a result of an increased indirect-gap size due to the significant quantum confinement effect in the out-of-plane direction, whereas the direct gap at the K and the K' points remains mostly unaffected. The electronic structure of SL TMDCs near Fermi energy, which essentially determines most of the material’s electronic and optical properties can be explained by considering d-orbitals of the M atoms only \[13, 14\]. The group of wave vectors at the band edges (K) is $C_{3h}$ and the symmetry adapted basis functions are

$$|\phi_c\rangle = |d_{z^2}\rangle, \quad |\phi_v\rangle = \frac{1}{\sqrt{2}}\left(|d_{x^2-y^2}\rangle + i\tau |d_{xy}\rangle\right).$$ \hspace{1cm} (1.1)

Figure 1.2: (a) The unit cell of bulk MoS$_2$ red (blue) spheres are Mo (S) atoms. The unit cell has an inversion center located in the middle plane. SL MoS$_2$ lacks an inversion center. b) Top view of the SL MoS$_2$, $R_i$'s are vectors connecting nearest M atoms. Brillouin zone of MoS$_2$ of honey comb lattice is also shown. c) Band structure of SL MoS$_2$ band gap and SOC values are also shown. d) Band structure of bulk MoS$_2$ with an indirect band gap of $1.3eV$. 

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Table 1.1: Fitting parameters of SL TMDCs obtained through first-principle calculations. (Ref. 13)

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To the first order in k, the $k \cdot p$ Hamiltonian has the form [13]

$$\hat{H} = at(\tau k_x \hat{\sigma}_x + k_y \hat{\sigma}_y) + \frac{\Delta}{2} \hat{\sigma}_z,$$

(1.2)

where $\sigma_i$’s denote the Pauli matrices, a is the lattice constant, $\tau = \pm 1$ is the valley index, $\Delta$ is the energy gap, and $t$ the effective hopping matrix element. These parameters obtained through first principle calculations are shown in Table. 1.1 [13]. This Hamiltonian resembles the Hamiltonian of graphene with staggered sub-lattice potential. This is not surprising as both systems have similar symmetry properties.

The optical absorption of SL TMDCs in the near-infrared and visible spectral region is dominated by the direct transitions between valence and conduction band states around K and K$'$ points. In the absence of excitonic effects, direct band-to-band transitions in 2D are generally characterized by a step function like spectrum originating from the energy-independent joint-density-of-states and transition matrix elements near the parabolic band edges. The experimental absorption spectrum with sharp resonance features provides the first evidence of strong excitonic effects in these materials. Indeed, theoretical calculations have predicted very large exciton binding energies $E_B$ (0.5–1 eV, corresponding to an exciton Bohr radius $a_B \approx 1$ nm) for monolayer TMDCs [15, 16, 17, 18]. Recent experiments based on optical spectroscopy [15, 19, 20, 21] and scanning tunnelling spectroscopy [22, 23] have verified the large binding energies, although discrepancies exist in terms of detailed values of $E_B$ from different experiments and interpretations.

An important property, which distinguishes 2D TMDCs from graphene, is the presence of strong
spin-orbit coupling (SOC), originating mainly from the d-orbitals of the M atoms. SOC has its
green in relativistic quantum mechanics, where the spin is the fundamental and inseparable com-
ponent of electrons, as described by the Dirac equation. SOC is most familiar in atomic physics,
where it gives rise to the atomic fine structure splitting, representing the coupling between an elec-
tron spin and its orbital momentum. In crystalline solids, however, such a splitting is forbidden
due to crystal symmetries unless the inversion symmetry is broken. As a fundamental principle
of quantum mechanics, an electronic state $\psi(r, s)$ and its complex conjugate $\psi^*(r, s)$ are always
connected through time reversal operations. At any k-point one can write for the energy

$$E(k, \uparrow) = E(-k, \downarrow)$$  \hspace{1cm} (1.3)

The Kramer’s degeneracy is unaffected when including spin orbit coupling term in the Hamilto-
nian. If the crystalline lattice also has an inversion symmetry, one will obtain

$$E(k, \uparrow) = E(-k, \uparrow), E(k, \downarrow) = E(-k, \downarrow)$$  \hspace{1cm} (1.4)

From combination of eq. 1.5 and eq. 1.5 it becomes clear that if both time reversal symmetry and
inversion symmetry are present, the band structure should satisfy the condition

$$E(k, \uparrow) = E(k, \downarrow)$$  \hspace{1cm} (1.5)

Consequently, for crystals which have inversion symmetry, the spin splitting is not allowed in bulk,
and these solids keep their spin degeneracy [24].

However, if the crystalline structure lacks inversion symmetry, such as in GaAs, electrons moving
through the lattice experience an asymmetrical crystal potential, which results in the intrinsic SOC.
This type of interaction was first described by Dresselhaus and its strength depends only on the
atomic elements forming the crystal. SOC in solid state systems have been known to exist since
the early days of quantum mechanics and band theory [25]. However, these phenomena have moved to the forefront of condensed matter physics only recently. This renewal of interest has been sparked by a number of exciting proposals [26] for spintronic devices. Apart from these potential useful applications, SOC in solids turn out to exhibit an amazing variety of fundamentally new and fascinating phenomena: spin-Hall effect [27], topological insulators [28], Majorana fermions [29], and Weyl fermions [30], just to name a few. The broken inversion symmetry in SL TMDCs together with the presence of heavy transition metal atoms gives rise to large spin splittings at the valence band edges (Table. 1.1). Approximating the SOC as the onsite or intra-atomic contribution, the SOC Hamiltonian can be written as

\[ \hat{H}^{SOC} = -\frac{\xi}{2} \mathbf{L} \cdot \mathbf{S} = \frac{\xi}{2} \begin{pmatrix} L_z & 0 \\ 0 & -L_z \end{pmatrix}, \]  

(1.6)

where \( \xi \) is the spin splitting at the valence band edge caused by SOC and \( \hat{S}_z \) is the Pauli matrix for the spin. The spin-up and spin-down components are completely decoupled and \( \hat{S}_z \) remains a good quantum number. Time-reversal symmetry requires that the spin splitting at different valleys must be opposite.

To date research in SL TMDCs is continuously growing both on a fundamental level and from a technological perspective. They are considered to be ideal candidates for future electronic, optoelectronics, and spintronic devices. Also, TMDCs provide new opportunities for exploring the internal degrees of freedom of electrons and their potential for new electronic and opto-electronic phenomena. These degrees of freedom are the real electron spin, the layer pseudospin, and the valley pseudospin. New methods for the quantum control of the spin and these pseudospins arise from the existence of Berry phase-related physical properties and strong SOC.
Hong–Ou–Mandel interference is a two-photon quantum interference effect whereby two indistinguishable photons, one in each of the two input ports of a balanced beam splitter, will always be detected to coalesce at one or the other output port of the beam splitter, but never with one photon at each output port [31]. This interference effect diminishes as the distinguishability of the photons is increased. It was first demonstrated in 1987 using photons produced via parametric down-conversion [32]. The importance of this effect in optical implementations of quantum information processing schemes was realized later [33]. It is the basis of nondeterministic gates in linear optical quantum computation [34], it may be used for preparing maximally entangled Bell states [35], and it may be used to assess the quality of single-photon sources [36]. This has motivated
further experiments, both with single sources [37, 38] and with two independent sources [39, 40] of photons. In addition to these pulsed interference experiments, two-photon quantum interference using continuously driven sources of resonant fluorescent light has been demonstrated [41]. HOM type of interference can be explained with in a simplified mathematical model (Fig. 1.3.3), keeping in mind that photons are bosons and they follow Bose-Einstein statistics i.e.

$$[a_i^+, a_j^+] = 0$$  \hspace{1cm} (1.7)$$

where \(a_i^+\)'s are photon creation operators. The in puts and out puts of the beam splitter are related by the following transformation

$$
\begin{pmatrix}
    a_{01}^+ \\
    a_{02}^+
\end{pmatrix} =
\begin{pmatrix}
    \sqrt{T} & i\sqrt{R} \\
    i\sqrt{R} & \sqrt{T}
\end{pmatrix}
\begin{pmatrix}
    a_1^+ \\
    a_2^+
\end{pmatrix}
$$  \hspace{1cm} (1.8)$$

$$
|1_{01}, 1_{02}\rangle = a_{01}^+ a_{02}^+ |0, 0\rangle
= (\sqrt{T}a_1^+ + i\sqrt{R}a_2^+)(\sqrt{T}a_2^+ + i\sqrt{R}a_1^+) |0, 0\rangle
= (T - R) |1_{11}, 1_{12}\rangle + i\sqrt{2RT} |2_{11}, 0_{22}\rangle + i\sqrt{2RT} |0_{11}, 2_{22}\rangle
$$  \hspace{1cm} (1.9)$$

\(T - R = 0\) for a 50/50 beam splitter.

Interestingly, it is possible to replace the bosons in the HOM interference experiment by fermions, which leads to the exact opposite behavior. Due to the Fermi-Dirac quantum statistics, fermions appear in different outputs, as identical fermions have the tendency of antibunching over small distances, leading to a peak in the coincidence measurement at zero delay. While photons in vacuum exhibit a linear dispersion relation, electrons in gapped semiconductor materials typically have a quadratic dispersion relation, which is a major obstacle for observing the fermionic analog.
of the HOM interference due to the spreading of electronic wave function. In order to overcome this obstacle, it is essential to identify physical systems where the electrons have a linear dispersion relation [42].

Defects In Semiconductors

The broader family of 2D materials offers new opportunities to be explored and tailored for various applications ranging from electronic, optoelectronics to catalysis and energy storage. Large-scale synthesis of 2D materials is one of the significant issues for fabricating layered materials into practical devices. Different fabrication techniques such as chemical vapor deposition, physical vapor deposition and molecular beam epitaxy, has been employed to obtain the micro scale samples. It has been observed that samples obtained through these techniques are highly poly crystalline and include interfaces such as edges, heterostructures, grain boundaries and most importantly point defects. These imperfections do not always degrade the materials properties but they often bring new physics and even useful functionality. Defects usually play an important role in tailoring electronic, optical and magnetic properties. Point defects in semiconductors can trap charge carriers and localize excitons. Excitons bound to defects, if recombine radiatively, lead to light emission at lower energies than the band to band optical transition. This interaction between these defects and charge carriers becomes stronger at reduced dimensionalities due to tighter localization of electron wave function, and is expected to greatly influence physical properties of the hosting material. This can be understood in a simplified Hydrogenic model of excitons, e.g., in 3-dimensions shallow defects bind electrons at ground state binding energy equal to $13.6 \text{eV} \times \frac{m^*}{\varepsilon_r^2}$, where $m^*$ and $\varepsilon_r$ are effective mass and relative dielectric constant. this is increased to $54.4 \text{eV} \times \frac{m^*}{\varepsilon_r^2}$ in 2D [43] simply due to the dimensionality effect. Although point defects in semiconductors are known to exist for decades but their physics and
behavior in 2D semiconductors such as SL TMDCs is still illusive. Here, we briefly review two of the physical phenomena which are experimentally observed and are believed to exist due to the presence of defects in 2D materials.

*Defect induced magnetism*

In the original publication of Heisenberg about the basic concepts on the origin of magnetic order in solids [44], it is written at the end of the paper that the principal quantum number of the electrons responsible for the magnetism must be $n \geq 3$. There is, however, a recent awareness that the possibility of magnetic order can also occur in materials without open $d$ or $f$ shells. Experimental evidence of these type of magnetism was found in thin films of certain materials [45, 46, 47, 48]. The field on magnetism in thin films is still in infancy and more experimental evidences are required, however, theory provides a mechanism for the appearance of magnetism without $d$ or $f$ open shells. It has been argued that in some lattices, intrinsic point defects lead to the formation of local magnetic moments, a preliminary condition for the existence magnetic order. This is the case in graphite [49], graphene [50, 51] and II-VI semiconductors [52].

There has been an intense research over the past few decades for materials that exhibit both ferromagnetism and semiconductor properties, the so called dilute magnetic semiconductors (DMS). The comprehensive research on these systems has been stimulated by a succession of demonstrations of outstanding low-temperature functionalities in (Ga,Mn)As, $p$-(Cd,Mn)Te and related structures, some examples being spin injection [53], the control of magnetism by means of electric fields [54] and electric currents [55].

In 2D systems the long range order is strongly suppressed by thermal fluctuations, according to the Mermin-Wagner theorem [56]: however these fluctuations can be counteracted by magnetic anisotropy. Long range order has also been predicted in graphene [51], phosphorene [57] due to the presence of point defects. Also, large magnetic anisotropy is predicted in transition metal atoms.
adsorbed on the surface of MoS$_2$. For spintronics, which aims to utilize the spin degree freedom of electrons for novel information storage and logic devices [26, 58, 59], 2D materials are very attractive. The ultra-low spin orbit coupling in graphene already made it one of the most promising candidates for spin channel [60, 61, 62]. The unique spin-valley coupling in 2D TMDCs provides a platform to use valley for manipulating the spins [13].

*Single-Photon emission*

The surge of search for single photon sources have been sparked by the intense research in the field of Quantum information science over the last few decades [63]. Quantum information involves the encoding, communication, manipulation, and measurement of information using quantum mechanical objects. Research has shown that using quantum objects for this purpose allows certain computational tasks to be performed more efficiently than thought possible using classical objects [64], and potentially allows unconditionally secure communication [65]. Photonic qubits, where information is encoded in the quantum state of the photon using degrees of freedom such as polarization, momentum, energy, etc., are an ideal choice for many of these applications, since (a) photons travel at the speed of light and interact weakly with their environment over long distances, which results in lower noise and loss and (b) photons can be manipulated with linear optics. While quantum communication applications often make use of single photons, many quantum cryptography protocols, in the form of quantum key distribution (QKD) in particular, demand single photons traveling over a channel [66, 67], as more than one photon can compromise the security of the communication by allowing an eavesdropper to gain information [68].

There are a variety of systems that have been investigated for use as on-demand sources of single photons. Most of these are “single-emitter” quantum systems, such as semiconductor quantum dots [69, 70, 71], mesoscopic quantum wells [72], single molecules [73, 74], and color centers [75, 76]. While each of these single-emitter approaches uses a different material system, most rely
on similar principles of operation. When single-photon emission is desired, some external control is used to put the system into an excited state that will emit a single photon upon relaxation to some lower energy state. Often coupling techniques using optical cavities are used to engineer the emission characteristics.

Recent photoluminescence (PL) experiments [77, 78, 79] reveal that localized excitonic states related to VDs can serve as single-photon emitters in WSe$_2$. The 2D nature of the host material offers potential advantages over traditional solid state quantum emitters. For example, effects in 2D materials can be introduced using standard lithography tools. Moreover, photons from localized emitters in three dimensional materials have to travel through the host media with a high-refractive index, whereas here photons can be immediately utilized with a greatly enhanced photon extraction efficiency.

Significance of This Work

The aim of this dissertation is to systematically study the electronic, optical and magnetic properties of SL TMDCs in the presence of point defects. The significance of this dissertation is three fold. First we will systematically study the electronic and optical properties of various vacancy defect in SL TMDCs. In particular we show that vacancy defects induce out-of-plane transitions in SL TMDCs which can not be explained with in the two band model [13]. Secondly, we show that antisite defect (Mo$_S$) is magnetic in nature. Also the magnetic moment associated with each Mo$_S$ defect can be tuned by shifting the position of the Fermi level, which can be achieved either by chemical doping or by gate voltage. Finally, we argue that single quantum emitters in WSe$_2$ is due to the presence of Se$_W$ defect. We also show that background dielectric material can increase the radiative decay time by a factor of $10^2$. We justify our findings investigations by calculating the radiative decay time, our findings are in good agreement with experimental results.
This dissertation is organized as follows. Chapter 2 describes the HOM interference with Dirac Fermions observed in graphene or surface states of topological insulators. Chapter 3 and 4 describe the electronic and optical properties of TMDCs in the presence of vacancy defects. Chapter 5 deals with magnetic properties of SL MoS$_2$ in the presence of a naturally occurring antisite defect (Mo$_S$) in PVD grown MoS$_2$. In chapter 6 we try to explain the origin of recently observed single photon emission in SL WSe$_2$. 
CHAPTER 2: TWO-DIMENSIONAL FERMIONIC HONG-OU-MANDEL INTERFERENCE WITH MASSLESS DIRAC FERMIONS

1 We propose a two-dimensional Hong-Ou-Mandel (HOM) type interference experiment for massless Dirac fermions in graphene and 3D topological insulators. Since massless Dirac fermions exhibit linear dispersion, similar to photons in vacuum, they can be used to obtain the HOM interference intensity pattern as a function of the delay time between two massless Dirac fermions. We show that while the Coulomb interaction leads to a significant change in the angle dependence of the tunneling of two identical massless Dirac fermions incident from opposite sides of a potential barrier, it does not affect the HOM interference pattern. We apply our formalism to develop a massless Dirac fermion beam-splitter (BS) for controlling the transmission and reflection coefficients. We calculate the resulting time-resolved correlation function for two identical massless Dirac fermions scattering off the BS.

Introduction

When two indistinguishable bosons are incident on opposite sides of a 50/50 BS, Bose-Einstein quantum statistics demands bunching, i.e. the outgoing bosons must leave together in one of the two outputs, which was first observed with photons in the HOM experiment [80]. Observation of zero coincidence for simultaneous photons is identified by a dip in the correlation function and rises with time delay [80]. HOM type interference has been utilized in quantum tests of non-locality [81] and can be used to investigate the degree of indistinguishability of the incident particles. Also, the HOM experiment is one of the key elements of linear-optics based quantum computation [82].

Several experiments have already demonstrated the HOM interference with photons [80, 83], plasmons [84], levitons [85], and electrons [86, 87, 88, 89]. Interestingly, it is possible to replace the bosons in the HOM interference experiment by fermions, which leads to the exactly opposite behavior. Due to the Fermi-Dirac quantum statistics fermions appear in different outputs as identical fermions have the tendency of antibunching over small distances, leading to a peak in the coincidence measurement at zero delay. While photons in vacuum exhibit linear dispersion relation, electrons in gapped semiconductor materials typically have a quadratic dispersion relation, which is a major obstacle for observing the fermionic analogue of the HOM interference due to the spreading of electronic wavefunction. In order to overcome this obstacle, it is essential to identify physical systems where the electrons have linear dispersion relation.

One such example is the one-dimensional edge states of quantum Hall systems exhibiting ballistic conductance and linear dispersion, where the one-dimensional fermionic HOM experiment [89] has been successfully implemented. Similar results are expected theoretically for quantum spin Hall states [90, 91, 92, 93]. In order to create a two-dimensional fermionic HOM interference pattern, we need fermionic particles with a linear dispersion relation in two dimensions. Ideal candidates are massless Dirac fermions in graphene [6, 94] and on the surface of 3D topological insulators [95]. Here we show that it is possible to create two-dimensional fermionic HOM interference pattern by considering the scattering of two massless Dirac fermions in the case of a rectangular potential barrier. We show that at specific incident angles a 50/50 BS for massless Dirac fermions can be realized, even when considering the Coulomb interaction between the massless Dirac fermions. Interestingly, the Coulomb interaction leads to a substantial change in angle distribution of the transmission and reflection coefficients. The idea of using a potential barrier as a beam splitter has already been proposed in the context of a two-dimensional electron gas in a wide bandgap semiconductor [96]. In Ref. [88] electronic HOM interference is demonstrated by using quantum Hall edge states. This experiment shows that the cross correlation function at zero time delay is reduced, which has been attributed to the reduction in the indistinguishability due to
the interaction between the copropagating edge states [97]. Here, in the case of massless Dirac fermions in graphene and 3D topological insulators, we show that within the eikonal approximation the Coulomb interaction between the two incident massless Dirac fermions at the beam splitter does not affect the correlation function, which thus is solely determined by the quantum statistics of the particles.

In the case of one-dimensional edge states in topological insulators the antibunching of two counterpropagating electrons with opposite spins is known to be due to time reversal symmetry, commonly referred to as $\mathbb{Z}_2$ dip [90, 91, 92, 93]. The $\mathbb{Z}_2$ dip in the noise comes from the fact that there is no backscattering from any Hermitian potential $V$ in a topological insulator, including a Hermitian beam splitter. Our results are in agreement with the $\mathbb{Z}_2$ dip for normal incidence. However, no such phenomenon is found for the massless Dirac fermions in graphene because the real spin is not locked to the momentum due to the negligibly small spin-orbit coupling in graphene.

The realization of fermionic HOM interference experiment is provided by a three-step process: (i) Generation of single electron source. (ii) Construction of BS, which is the primary focus of this work. (iii) Detector for counting the coincidences. In Ref. [98] a single electron pump (SEP) in graphene has been demonstrated experimentally. The pump is made of two lithographically defined graphene islands that are coupled to each other and to source and drain contacts by narrow constrictions. By rapid modulation of the gate voltages, a single electron can be pumped to the drain contact. The frequency $f$ of the oscillating voltage applied to the gates determines the rate at which a single charge is transferred and thus the size of the pump current $I = e f$. The frequency $f$ is of the order of GHz. As stated by the authors in Ref. [98], this single electron pump can be used as a single massless Dirac fermion source in graphene in the field of electron quantum optics.

This setup is not constrained to edge states, but can also be used for a two-dimensional graphene sheet. The basic idea of this setup can be transferred to the case of massless electrons in topological insulators. A scanning probe microscope (SPM) tip can be used to image quantum interference and ray like propagation of electrons [99, 100]. Alternatively, the interference can be probed by
measuring the fluctuations of electrical current in the outputs channels related to the fluctuations of number of particles transmitted \[88, 89\].

The manuscript is organized as follows. In Sec. 2 we define the model Hamiltonians for graphene and 3D topological insulators. In Sec. 2 we calculate the phase change due to the Coulomb interaction within the eikonal approximation. Sec. 2 describes the tunneling through a potential barrier including the Coulomb interaction due to scattering of two massless Dirac fermions. The evaluation of the two-dimensional fermionic HOM interference is performed in Sec. 2.

Model

It has been shown \[101\] that the transmission probability \(T\) of massless Dirac fermions (in graphene) with energy \(E\) through a rectangular potential barrier of height \(V_0\) and width \(D\) varies as a function of incident angle \(\phi\). 100\% transmission probability is observed at normal incidence \(\phi = 0\), a feature known as Klein tunneling. Exactly the same result can be obtained for surface electronic states of 3D topological insulators. The reason for this coincidence is that in both systems the dynamics of electrons is defined by similar Hamiltonians. The only difference between the two systems is that in graphene the pseudo-spin is locked parallel to the linear momentum and in 3D topological insulators the real spin is locked perpendicular to linear momentum, respectively, i.e

\[
\hat{H}_{0,g} = v_F \sigma \cdot p, \quad \hat{H}_{0,\text{TI}} = v_{\text{eff}} (\sigma \times p)_z, \tag{2.1}
\]

where \(\sigma_i\)'s are Pauli matrices, corresponding to the pseudo-spin in the case of graphene and to the real spin in the case of 3D topological insulators, respectively, and \(p\) is the momentum operator. The angle dependent transmission probability through a potential barrier can be used to make a BS for massless Dirac fermions. For observing the HOM type interference we need to inject two massless Dirac fermions from the opposite sides of the barrier as shown in Fig. 2.1 and their
transmissions and reflections will produce the desired interference.

Coulomb Interaction in the Eikonal Approximation

We take advantage of the eikonal approximation [102], to calculate the phase change acquired by a massless Dirac electron when scattering from a second massless Dirac electron due to the Coulomb interaction. First it is important to verify the validity of the eikonal approximation. Inside the barrier kinetic energy of the massless Dirac fermions is described by $|V_0 - E|$, where $V_0$ is the height of the barrier and $E$ is the energy of the incident particles. Here we consider the screened Coulomb potential, represented by the Yukawa potential $V(r) = U_0 e^{-\mu r}/\mu r$, where $\mu^{-1}$ is the screening length. For graphene $\mu = g_v g_s e^2 k_F/4\pi \kappa \epsilon_0 \hbar v_F$, $\kappa$ is the background lattice dielectric constant, $U_0 = e^2 \mu/4\pi \kappa \epsilon_0$, and $k_F$ is the Fermi wave vector. $g_v$ and $g_s$ are valley and
spin degeneracies respectively. Averaging the Yukawa potential over 5 screening lengths we obtain

\[ \langle V(r) \rangle = \frac{1}{\int_0^{5/\mu} d^2r} \int_0^{5/\mu} V(r) d^2r \approx 10 \text{ meV} \]  

(2.2)

After 5 screening lengths the strength of the Yukawa potential can be approximated to be zero. We take the values of \( E = 80 \text{ meV} \) and \( V_0 = 200 \text{ meV} \) so that \( \langle V(r) \rangle \ll |V_0 - E| \).

Although we solve the Coulomb scattering for massless Dirac fermions in graphene, our results are general and applicable to surface states of 3D topological insulators as well because the Coulomb interaction does not depend on the spin. Working in the eikonal approximation the exact wave function \( \Psi \) of the Hamiltonian \( H = H_0 + V(r) \) can be approximated by

\[ \Psi \sim \begin{pmatrix} \alpha \\ \beta \end{pmatrix} e^{i S(r)/\hbar}. \]  

(2.3)

Starting from the Dirac equation shown in eq. (2.1) and expanding in powers of \( \hbar \), we obtain in zeroth order the relativistic Hamilton-Jacobi equation

\[ |\partial_x S(r)|^2 + |\partial_y S(r)|^2 \approx E^2/v_F^2 - 2V(r)E/v_F^2. \]  

(2.4)

We compute \( S(r) \) from Eq. 2.4 by assuming that the trajectory is a straight line, which is valid for large energies and small deflection angles [102]. Eq. 2.4 then yields in linear approximation in \( V \).

\[ \frac{S(x)}{\hbar} \approx kx - \frac{1}{\hbar v_F} \int_{-\infty}^{x} 2V(b',x') dx'. \]  

(2.5)
here $b'$ is the impact parameter [102]. Similar to the non-relativistic derivation, [102] we obtain the relativistic scattering amplitude

$$f (k, k') = - i \sqrt{\frac{k}{2\pi}} \int_{-\infty}^{\infty} db e^{-ikb} \left[ e^{2i\Delta(b')} - 1 \right], \quad (2.6)$$

where $\xi(b') = -\frac{1}{2\hbar v_F} \int_{-\infty}^{\infty} dx'V(b', x')$ and $\theta$ is the angle between $k$ and $k'$. Eq. 2.6 is in agreement with the optical theorem in scattering theory [102]. Eq. (2.6) can be solved for the screened Coulomb potential, i.e. the Yukawa potential with $V(b', x') = U_0 \exp \left( -\mu \sqrt{b'^2 + x'^2} / \mu \sqrt{b^2 + x^2} \right)$. In the lab frame $\theta \to \theta/2$. The phase change $\Delta$ in the forward direction acquired by the particle while passing through the scattering region can be evaluated by setting $|k| = |k'| = k_F$ for elastic scattering, i.e.

$$\Delta = \lim_{\theta \to 0} Re \left( \sqrt{k_F} f (k, k') \right) = -\frac{\sqrt{\frac{2\pi}{\hbar v_F}} k_F}{\mu} U_0 \frac{k_F}{\mu}. \quad (2.7)$$

Tunneling Through Rectangular Barrier

It is now straightforward to solve the tunneling problem shown in Fig. 2.1. The electron is incident on the barrier from right at an angle $\phi$ with respect to the $x$ axis. It propagates at an angle $\theta$ in region 2 and is transmitted in region 3 at the same angle $\phi$. Following Ref. [96], the components
of the massless Dirac spinor $\Psi_1$ and $\Psi_2$ can be written as $\Psi_i(x, y) = \psi_i(x)e^{ik_y y}$, $i = 1, 2$, with

$$
\Psi_1(x) = \begin{cases} 
  e^{ik_x x} + re^{-ik_x x} & x < 0 \\
  ae^{iq_x x} + be^{-iq_x x} & 0 < x < \frac{D}{2} \\
  ae^{iq_x x + i\Delta} + be^{-iq_x x - i\Delta} & \frac{D}{2} < x < D \\
  t'e^{ik_x x + i\Delta} & x > D
\end{cases} , 
$$

(2.8)

$$
\Psi_2(x) = \begin{cases} 
  s \left[ e^{ik_x x + i\phi} - r e^{-ik_x x - i\phi} \right] & x < 0 \\
  s' \left[ ae^{iq_x x + i\theta} - be^{-iq_x x - i\theta} \right] & 0 < x < \frac{D}{2} \\
  s' \left[ ae^{iq_x x + i\theta + i\Delta} - be^{-iq_x x - i\theta - i\Delta} \right] & \frac{D}{2} < x < D \\
  st'e^{ik_x x + i\phi + i\Delta} & x > D
\end{cases} , 
$$

(2.9)

where $k_x = k_F \cos \phi$, $k_y = k_F \sin \phi$ are the components of the wavevector outside the barrier and $q_x = \sqrt{(E - V_0)^2 / (\hbar v_F)^2 - k_y^2}$ and $\tan \theta = k_y / q_x$ is the refraction angle, $s = \text{sgn}(E)$ and $s' = \text{sgn}(E - V_0)$. The transmission coefficient $t'$ can be evaluated by using the continuity conditions at $x = 0$ and $x = D$ and is

$$
t' = 2 \exp(-ik_x D) \cos \theta \cos \phi / \left\{ ss' \left[ e^{-i(q_x D + \Delta)} \cos (\theta + \phi) + e^{i(q_x D + \Delta)} \cos (\theta - \phi) \right] - 2i \sin (q_x D + \Delta) \right\} . 
$$

(2.10)

In Fig. 2.2 the transmission coefficient $T = t'^* t'$ is plotted as a function of incident angle $\phi$ for the cases when $D = 0$(red curve) and $\Delta = -\sqrt{2\pi U_0 k_F} / \hbar v_F \mu^2$ (blue curve). Interestingly, the Coulomb interaction results in a substantial shift of the transmission peaks while preserving Klein tunneling. This result is in agreement with previous findings [103]. It has been experimentally demonstrated that Coulomb interaction results in the renormalization of the Fermi velocity in...
graphene like systems and fails to create any energy gap. The energy gap is the only possibility for the removal of Klein tunneling [103]. In the limit $V_0 \ll E$,

$$T = \frac{\cos^2 \phi}{1 - \cos^2(q_xD+\Delta)\sin^2 \phi}.$$  \hspace{1cm} (2.11)

For normal incidence $T = 1$, regardless of the height and width of the barrier. Away from normal incidence, the other transmission peaks correspond to the condition of constructive interference, which occurs when $q_xD + \Delta = n\pi$, where $n = 0, \pm1 \pm 2, \ldots$.

Figure 2.2: Transmission probability $T$ as a function of incident angle $\phi$. The electron concentration $n$ outside the barrier is chosen as $0.5 \times 10^{12}$ cm$^{-2}$. This corresponds to a Fermi energy and wavelength of incident electrons of $E_F \approx 80$ meV and $\lambda \approx 50$ nm, respectively. The barrier height $V_0 = 200$ meV. The red curve is the solution for $D = 0$ and the blue curve is the solution for $D = -0.63$. Black (dashed) semicircle is drawn at 50% transmission probability.
Comparing Eq. (2.11) with the result in Ref. [101], there is an additional phase $\Delta$ in the denominator, which comes from the Coulomb interaction. It can be seen from Fig. 2.2 that at certain angles $T = 50\%$. For these angles of incidence this modified barrier can be used as a 50/50 BS. At the same $\phi$, the Coulomb interaction leads to an asymmetry in $T$ and $R$. In addition, we can change $T$ and $R$ to any desired value ranging between 0 and 1 by tuning $\phi$.

Fermionic HOM Interference

The schematic diagram of the HOM experiment is shown in Fig. 2.1. It consists of two wave packets triggered by two SEP’s, a BS (orange line) and two SPM tips (blue pentagons) to measure the electron flux [100]. The BS is considered to be lossless, i.e. $T + R = 1$. Let us now consider two massless Dirac fermions that are incident on the BS from opposite sides. Let $\tau_1$ be the time it takes for the electrons to get from the source to the detector. We define $\delta\tau$ as the time delay between the two incident electrons. $\delta\tau$ can be introduced either by displacing the position of the BS towards one of the sources or by introducing the time delay between the switching pulses of the two SEP’s. Our goal is to calculate the correlation function corresponding to the coincidence counts at the two detectors as a function of the time delay $\delta\tau$. The inputs of the BS are described by the indices $01,02$ i.e. $c_{01}^\dagger |0_{01},0_{02}\rangle = |1_{01},0_{02}\rangle$ and $c_{02}^\dagger |0_{01},0_{02}\rangle = |0_{01},1_{02}\rangle$, where $c_{01}^\dagger (c_{01})$ are electron creation (annihilation) operators. We omit the spin index because we assume that the two electrons have parallel spins. The $Z_2$ dip is associated with the massless Dirac fermions of opposite spin for normal incidence in topological insulators, as mentioned earlier. As our main focus here is to investigate the HOM type interference, a consequence of the indistinguishability of quantum particles, electrons of the same spin are considered. Similarly, the outputs are described by the indices $1,2$. The output operators are related to the input operators through the following
linear scattering relations

\[
\hat{c}_1(t) = \sqrt{T} \hat{c}_{01}(t - \tau_1) + i \sqrt{R} \hat{c}_{02}(t - \tau_1 + \delta \tau), \quad (2.12)
\]

\[
\hat{c}_2(t) = \sqrt{T} \hat{c}_{02}(t - \tau_1) + i \sqrt{R} \hat{c}_{01}(t - \tau_1 - \delta \tau), \quad (2.13)
\]

where \(i\) corresponds to a \(\pi/2\) phase shift and \(\hat{c}_{0j}(t) = \xi_j(t) \hat{c}_0\). \(\xi_j(t)\) is the distribution function in time, considering a general temporal form of the wave packet \(\xi_j(t) = \Theta(t) \exp(-\Gamma_j t/2) \exp(i \omega t)\) [88]. \(\Theta(t)\) is the Heavyside step function and \(\Gamma_j\) is the SEP emission rate of the electron. The correlation function describing the joint probability of detection of electrons at the two detectors at times \(t\) and \(t + \tau\) is

\[
P_{12}(t) = C \left\langle 0 \left| \hat{c}_{02} \hat{c}_1^\dagger(t + \tau) \hat{c}_2(t + \tau) \hat{c}_1(t) \hat{c}_0 \right| 0 \right\rangle. \quad (2.14)
\]

\(C\) is the normalization constant. This can readily be evaluated by means of Eqs. (2.12) and (2.13). The number of coincidence counts \(N_c(1, 2)\) can be obtained by integrating \(P_{12}(t)\) over time \(t\). This yields

\[
\frac{N_c(\delta \tau)}{C} = \tilde{N}_c(\delta \tau) = T^2 + R^2 + RT \frac{8 \Gamma_1 \Gamma_2}{(\Gamma_1 + \Gamma_2)^2} \times \{ \exp(\Gamma_1 \delta \tau) \Theta(-\delta \tau) + \exp(-\Gamma_2 \delta \tau) \Theta(\delta \tau) \}, \quad (2.15)
\]

where \(\tilde{N}_c(\delta \tau)\) is the normalized number of coincidences. Eq. (2.15) is our main result. The coincidence counts depend both on the time delay \(\delta \tau\) and the transmission and reflection coefficients. The coincidence counts can be tuned by introducing an asymmetry in the reflection and transmission coefficients. For perfect transmissions and reflections \(\tilde{N}_c(\delta \tau)\) remains at unity regardless of the value of \(\delta \tau\). For large \(\delta \tau\) the third term on the right hand side of Eq. (2.15) goes to zero, and the expression for the coincidence counts reduces to \(T^2 + R^2\).
In case of identical electron sources, i.e. $\Gamma_1 = \Gamma_2$, Eq. (2.15) simplifies to

$$\tilde{N}_c(\delta \tau) = T^2 + R^2 + 2RT \left\{ \exp(\Gamma_1 \delta \tau) \Theta(-\delta \tau) + \exp(-\Gamma_2 \delta \tau) \Theta(\delta \tau) \right\} .$$

(2.16)

Note that for $\delta \tau = 0$ $\tilde{N}_c(\delta \tau) = (T + R)^2 = 1$, no matter what the values of $T$ and $R$ are, which reflects the antibunching of fermions. In Fig. 2.3 we plot the coincidence counts for different values of $R$, $T$, and $\Gamma$’s (blue) as a function of the time delay $\delta \tau$. For the asymmetric case, i.e. for incident electrons with different decay rates, the HOM peak is substantially reduced, as can be seen in Fig. 2.3. This decrease in the coincidence counts is accounted for by the reduction in degree of indistinguishability of incident wave packets and is in agreement with existing literature [104].

If we consider the effect of the bandwidth of the wavepacket in the case of the Coulomb interaction, it is possible for the Coulomb interaction to induce decoherence. However, in our case the
Fermi energy is much larger than the bandwidth, i.e. $E_F \approx 80\text{ meV} \gg \Gamma \approx 1\text{ meV}$, giving rise to about 1% spread in the phase $\Delta$ in Eq. (2.7). Therefore the interaction-induced decoherence is negligibly small.

Conclusion

We developed the theoretical model of the two-dimensional HOM type interference with massless Dirac fermions in graphene and in 3D topological insulators. The two-dimensional setup allows for the tuning of the transmission and reflection coefficients by varying the angle of incidence of the two massless Dirac fermions. We provide the description of a realistic BS for massless Dirac fermions, including the effects of Coulomb interaction. Our results show that the Coulomb interaction does not affect the fermionic HOM peak (Pauli peak) for massless Dirac fermions within the eikonal approximation. However, asymmetry in the emission rates of the two massless Dirac fermions lifts the indistinguishability and this leads to the reduction of the HOM peak. The larger the asymmetry, the smaller is the peak.
We show that pristine MoS\(_2\) single layer (SL) exhibits two bandgaps \(E_{g\parallel} = 1.9\) eV and \(E_{g\perp} = 3.2\) eV for the optical in-plane and out-of-plane susceptibilities \(\chi_{\parallel}\) and \(\chi_{\perp}\), respectively. In particular, we show that odd states bound to vacancy defects (VDs) lead to resonances in \(\chi_{\perp}\) inside \(E_{g\perp}\) in MoS\(_2\) SL with VDs. We use density functional theory, the tight-binding model, and the Dirac equation to study MoS\(_2\) SL with three types of VDs: (i) Mo-vacancy, (ii) S\(_2\)-vacancy, and (iii) 3\(\times\)MoS\(_2\) quantum antidot. The resulting optical spectra identify and characterize the VDs.

Introduction

Monolayer transition metal dichalcogenides (TMDCs) (MX\(_2\); M= transition metal such as Mo, W and X=S, Se, Te) have attracted a lot of attention due to their intriguing electronic properties. Monolayer TMDCs are semiconductors with direct bandgap \(E_{g\parallel}\) in the visible range, which makes them suitable for optoelectronic, spintronic, valleytronic, and photodetector devices [13, 14, 105, 106, 107, 108, 109]. In order to increase the performance of such devices based on TMDC single layer (SL), it is crucial to characterize the defects present in TMDC SLs. Here we show that the bandgap \(E_{g\perp} = 3.2\) eV for the optical out-of-plane susceptibility \(\chi_{\perp}\) in pristine MoS\(_2\) SL provides a large energy window to characterize vacancy defects (VDs). Pristine MoS\(_2\) SL is invariant with respect to \(\sigma_h\) reflection about the \(z = 0\) (Mo) plane, where the \(z\) axis is oriented perpendicular to the Mo plane. Therefore, electron states break down into two classes: even and odd, or symmetric and anti-symmetric with respect to \(\sigma_h\). We show below that this leads

to the nontrivial consequence that $\chi_z = \chi_\perp$ has a bandgap of $E_{g\perp} = 3.2$ eV, which is substantially larger than the bandgap $E_{g\parallel} = 1.9$ eV for the in-plane component of the optical susceptibility $\chi_x = \chi_y = \chi_\parallel$. As we show, due to the optical selection rules for the even and odd states, there are no $\pi$ transitions, driven by $z$-polarized photons, below 3.2 eV. Hence, $\chi_\perp$ for pristine MoS$_2$ SL must vanish for energies below 3.2 eV.

Several studies on VDs in 2D materials have emerged. The minibands resulting from quantum antidot (QAD) superlattices can be used to tune the bandgaps of graphene [110] and MoS$_2$ SL [111, 112]. In another study, we have shown that substitutional defects in the form of MoO$_3$ not only lead to strong suppression of the conductivity [113] but also to photoluminescence quenching [114]. Recently, VDs in MoS$_2$ SL have been characterized theoretically in terms of magnetic properties [115]. A recent experimental study used scanning transmission electron spectroscopy to characterize several types of defects in MoS$_2$ SL, including Mo, S, and S$_2$ VDs [116]. MoS$_2$ SL with S-vacancies might catalyze alcohol synthesis from syngas [117].

Here we show that VDs yield strong resonances in $\chi_\perp$, which provides the opportunity to optically characterize VDs in MoS$_2$ SL with VDs (denoted by MoS$_2$ SLVD). We consider the optical signatures of states bound to three types of VDs in MoS$_2$ SLVD: (i) Mo-vacancy, (ii) S$_2$-vacancy, and (iii) a hexagonal $3 \times$ MoS$_2$ QAD (see Fig. 3.1).

Figure 3.1: (a) Bandstructure of MoS$_2$ SL, showing the out-of-plane bandgap $E_{g\perp} = 3.2$ eV determined by the transition $T_0$. The Fermi level is set at $\epsilon_F = 0$ eV. (b) Mo-vacancy in 7x7 supercell. (c) S$_2$-vacancy consisting of a pair of S atoms removed in 7x7 supercell. (d) hexagonal $3 \times$ MoS$_2$ QAD in 8x8 supercell.
First we start with the numerical bandstructure calculation of MoS\textsubscript{2} SLVD using standard Density Functional Theory (DFT) with meta-GGA functionals [118], providing accurate estimates of bandgaps without the need to perform computationally intensive DFT calculations using the GW approximation [119, 120]. The calculations are implemented within Atomistix Toolkit [121]. The resulting bandstructures are shown in Fig. 3.2. The periodic structure of the superlattice allows one to characterize the electron states by the bandstructure $\epsilon_n(k)$, where $k$ is the vector in the first Brillouin zone of the superlattice and $n$ enumerates different bands. We consider supercells with dimensions $7 \times 7 \times 1$ (Fig. 3.2 b, c) and $8 \times 8 \times 1$ (Fig. 3.2 d) having 147 and 192 number of atoms, respectively. For Brillouin zone integration we consider $k$ sampling of $7 \times 7 \times 1$. The cut off energy is set to 300 eV and the structure is optimized by using a force convergence of 0.01 eV/Å.

**Tight-Binding Model (TBM) and Symmetries**

Within the TBM approximation the electron wavefunction can be presented as

$$|\psi\rangle = \sum_{j,\mu \in O_j} \psi^{(j)}_{\mu} \varphi^{(j)}_{\mu}(r - R^{(j)})$$

where \(j\) enumerates atoms in the layer and the summation over \(\mu\) runs over respective atomic orbitals, whose set for the \(j\)-th atom is denoted \(O_j\). Choosing \(e_x, y, z\) in the plane of the layer and \(e_z\) perpendicularly, for Mo the real orbitals of main importance are the \(d\)-orbitals \(d_{x^2-y^2}, d_{xy}\) and so on, while for S atoms these are \(p\)-orbitals \(p_{i}^{(t,b)}\) with \(i = x, y, z\) and \(t\) and \(b\) denoting the top and bottom layers, respectively. The classification of the electron states simplifies when the symmetry with respect to \(\sigma_h: z \mapsto -z\) is taken into account. The electron states transform according to \(A\) and \(A'\), the irreducible representations of \(Z_2 = \{e, \sigma_h\}\). The respective even and odd orbitals are locally spanned by the bases [122]:

$$\{d_{x^2-y^2}, d_{xy}, d_{z^2}, (p_{x,y}^{(t)}, p_{x,y}^{(b)})\}$$
\[ p^{(b)}_{x,y} / \sqrt{2}, (p_x^{(t)} - p_z^{(b)}) / \sqrt{2} \] and \( \{ dx_z, dz_x, (p_{x,y}^{(t)} - p_{x,y}^{(b)}) / \sqrt{2}, (p_z^{(t)} + p_z^{(b)}) / \sqrt{2} \}. \)

The full group of the point symmetries of MoS\(_2\) SLVD with our considered VDs is \( D_{3h} = C_{3v} \otimes Z_2 \).

Thus the states bound to the VDs, even and odd with respect to \( \sigma_h \), must transform according to \( A_{1,2} \) and \( E \), the irreducible representations of \( C_{3v} \). Respectively, the bound states must appear as singlets and doublets. It should be noted that such classification holds if the overlap between states bound to different VDs is absent, as is illustrated by Figs. 3.2a and 3.2b.

![Figure 3.2: Bandstructure of different kinds of VDs. The Fermi level is set at \( \epsilon_F = 0 \) eV. Red (blue) lines show odd (even) states. Arrows indicate transitions corresponding to resonances in \( \chi_\perp (\omega) \) (see Eq. (3.4) and below) shown in Fig. 3.4. (a) Mo-vacancy. (b) S\(_2\)-vacancy. Here singlets and doublets are in different half-planes with respect to the Fermi level. Therefore there are no \( \pi \) transitions. (c) S\(_2\)-vacancy with charge added to MoS\(_2\) SLVD, raising the Fermi level such that \( \pi \) transitions become allowed. (d) 3\( \times \)MoS\(_2\) QAD.](#)
The simplest model describing the arrangement of the bound states is the TBM considering only the atoms on the edge of the VD, which is inferred by the small localization radius of the bound states. For the case of the hexagonal $3\times\text{MoS}_2$ QAD one finds

$$\epsilon = \bar{\epsilon} \pm \sqrt{\delta \epsilon^2 + 4|t|^2 \cos^2(\xi)}, \quad (3.1)$$

where $\bar{\epsilon} = (\epsilon_{\text{Mo}} + \epsilon_{\text{S}})/2$, $\delta \epsilon = (\epsilon_{\text{Mo}} - \epsilon_{\text{S}})/2$ and $\xi = 0$ for singlet states (invariant with respect to $C_3$ rotations) and $\xi = 2\pi/3$ for doublets (states aquiring the phase factor $\exp(\pm i 2\pi/3)$). Here $\epsilon_{\text{Mo}}, \epsilon_{\text{S}}$ are the phenomenological parameters describing the energy of the electron on Mo and S atoms, respectively, and $t$ is the hopping parameter. Equation (3.1) correctly reproduces the sequence $\{A'_1, E', E', A'_1\}$ for even and $\{A''_1, E'', E'', A''_1\}$ for odd states, i.e. \{singlet, doublet, doublet, singlet\}, while traversing the gap $E_{g\parallel}$ from the bottom of the conduction band down over the bound states (see Fig. 3.2d).

It may appear that this model contradicts the numerical results for the Mo-vacancy, where the numerical calculations show only 5 bound states (see Fig. 3.2a). However, the TBM model suggests that in addition to the bound states appearing inside the gap $E_{g\parallel}$ of MoS$_2$ SL there must be states, in this particular case a singlet state, hidden inside the bands. Indeed, there is such a state inside the valence band at energy $\epsilon \approx -0.5 \text{ eV}$ below the top of the valence band (see Fig. 3.3b).

Moreover, the parameters $\epsilon_{\text{Mo}}$ and $\epsilon_{\text{S}}$ are determined by the microscopic Hamiltonian, e.g. $\epsilon_{\text{S}} = \langle \phi^{(S)}_\mu | \mathcal{H} | \phi^{(S)}_\mu \rangle$. Thus, we can expect that there is a variety of states bound to VDs besides the ones inside the gaps $E_{g\parallel}, E_{g\perp}$. An example of such states is provided by the case when the bound state is made of Sulfur’s s-orbitals (see Fig. 3.3c) at energy $\approx -12 \text{ eV}$ below the Fermi level.
Figure 3.3: Examples of the electron probability distributions in states bound to Mo-vacancy. Single supercell is shown, black and gray dots indicate positions of Mo and S atoms, respectively. The distances are measured in Å. (a) Odd doublet at energy $\approx 0.5$ eV above the top of the valence band, (b) odd singlet inside the valence band at energy $\approx 0.5$ eV below the top of the valence band, (c) deep defect state at energy $\approx -12$ eV below the Fermi level formed by Sulfur’s $s$ orbitals.

Dirac Model

The TBM considered above relates the structure of the spectrum of the bound states to the symmetry of the VD. Due to the fact that its parameters should be fitted to the energies of electron states obtained by other means, however, it cannot explain neither the smallness of the localization radius of the bound states nor their energies. In particular, it cannot explain why the odd states may form bound states inside the gap $E_{g\parallel}$. These features, however, can be understood with the help of an analysis of circularly symmetric QADs based on the Dirac equation which emerges as the two-band model within the $k \cdot p$-approximation near the $K$-point of the Brillouin zone of MoS$_2$ SL.
Considering two bands with the energy separation $2\Delta$ between them, the equation describing the spatial distribution of the pseudo-spin has the form $H_{\tau}\Phi_{\tau} = \epsilon\Phi_{\tau}$, where $\tau = \pm 1$ enumerates the valleys, the energy reference level is chosen to be positioned at the center between the bands, and $H_{\tau} = \tau\sigma_z\Delta + v\sigma \cdot p$. Assuming that the QAD has circular shape, we rewrite this equation in the polar coordinates and with respect to $\tilde{\Phi}_{\tau} = \exp(i\sigma_z\phi/2)\Phi_{\tau}\sqrt{r}$ we obtain $\tilde{H}_{\tau}\tilde{\Phi}_{\tau} = \epsilon\tilde{\Phi}_{\tau}$, where

$$\tilde{H}_{\tau} = \tau\sigma_z\Delta - iv\left[\sigma_x \frac{\partial}{\partial r} + \sigma_y \frac{1}{r} \frac{\partial}{\partial \phi}\right].$$

(3.2)

The solution is subject to the condition of vanishing radial component of the probability current at the boundary [123, 124] $\langle \Phi(r_0) | n_B \cdot \sigma | \Phi(r_0) \rangle = 0$, where $r_0$ is the radius of the QAD and $n_B$ is the unit vector perpendicular to the boundary. The straightforward implementation of such boundary condition is provided by the infinite mass model [125], where the QAD is represented by a region with renormalized width of the gap $\Delta \to \Delta(1 + d(r))$, with $d(r) = 0$ for $r > r_0$ and $d(r) \to \infty$ when $r < r_0$. In our case we identify $\Delta = E_{g\parallel}$. Within this model the boundary condition is satisfied if $|\Phi(r_0)\rangle \propto |\tau y\rangle$, i.e. the pseudo-spin $|\Phi(r_0)\rangle$ is tangent to the boundary of the QAD. Next, observing that $\sigma_z |\tau y\rangle = |\tau y\rangle$ and $\sigma_x |\tau y\rangle = i\tau |\tau y\rangle$, one can see that $\tilde{H}_{\tau}$ has an angularly independent solution $|\Phi(r_0)\rangle \propto \exp(-r/r_c) |\tau y\rangle$ corresponding to $\epsilon = 0$, which exponentially decays for $r > r_0$ with the localization radius $r_c = \Delta/v$.

Thus, independently of its radius the QAD may support a bound state with very short localization length and with the energy in the middle between the energies of the coupled bands. Comparing this finding to the distribution of energies of even and odd bands [122] the conclusion can be drawn that, indeed, both even and odd bands may support bound states with the energy near the energy of the Fermi level, i.e. inside the gap $E_{g\parallel}$ of MoS$_2$ SL.
In view of nontriviality of the appearance of odd bond states inside the gap \( E_{g\parallel} \) it is important to note that the presence of the bound states of different parities manifests itself in the optical spectrum of MoS\(_2\) SLVD. Therefore, they are available for a direct experimental observation. When VDs form a superlattice the problem of the optical response can be approached along the same line as for single layered systems [126]. Let \( \mathbf{k} \) be a point in the first Brillouin zone of the superlattice. At this point the electron wave function satisfies

\[
\epsilon_n(\mathbf{k}) |\psi_n(\mathbf{k})\rangle = \mathcal{H}(\mathbf{k}) |\psi_n(\mathbf{k})\rangle ,
\]

where \( n \) enumerates the superlattice bands. Implementing the \( k \cdot p \)-approximation of Eq. (3.3) in the usual way and using the Peierls substitution we obtain the Hamiltonian of interaction with the electromagnetic field \( \mathcal{H}_{EM} = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} \). Treating \( \mathcal{H}_{EM} \) as a perturbation within the linear response theory we find the Kubo-Greenwood optical susceptibility (see e.g. Ref. [127])

\[
\hat{\chi}(\omega) = \frac{\pi e^2 \hbar^4}{m^2 \epsilon_0 \omega^2} \sum_{n,n'} \int d\mathbf{k} \mathbf{P}_{n,n'}(\mathbf{k}) \otimes \mathbf{P}_{n',n}(\mathbf{k}) \times \frac{f[\epsilon_n(\mathbf{k})] - f[\epsilon_{n'}(\mathbf{k})]}{\epsilon_n(\mathbf{k}) - \epsilon_{n'}(\mathbf{k}) - \omega - i\gamma},
\]

where \( f(\epsilon) \) is the Fermi distribution, \( \otimes \) denotes the tensor product and \( \mathbf{P}_{n,n'}(\mathbf{k}) = \langle \psi_n(\mathbf{k}) | \mathbf{p} | \psi_{n'}(\mathbf{k}) \rangle \). The appearance of the states inside the gap \( E_{g\parallel} \) of MoS\(_2\) SL leads to resonances at frequencies of corresponding transitions. Several transitions, however, are prohibited due to symmetry, i.e. when \( \mathbf{P}_{n,n'}(\mathbf{k}) \) does not transform according to the symmetric representation of the symmetry group of the superlattice. \( \mathbf{P}_{n,n'}(\mathbf{k}) \) transforms according to \( I(C_{3v})^2 \otimes I(Z_2)^2 \otimes I(P) \), where \( I(G) \) and \( I(P) \) denote irreducible representations of group \( G \) and the momentum operator \( \mathbf{P} \), respectively, and powers are shorthand notations for direct products. One needs to consider separately the in-plane
and out-of-plane components of $P_{n,n'}$ because they transform according to different irreducible representations of $D_{3h}$, namely, $E' = E \otimes A'$ and $A''_2 = A_1 \otimes A''$, respectively. Taking into account the multiplication rules for $C_{3v}$: $A^2_{1,2} = A_1$, $A_{1,2} \otimes E = E$ and $E^2 = A_1 \oplus A_2 \oplus E$, we find that the out-of-plane component of $P_{n,n'}(k)$, which gives rise to $\pi$ transitions, is nonzero only between odd and even states of the same multiplicity (either between singlets or between doublets), while the in-plane components, which lead to $\sigma$ transitions, are nonzero for all states of the same parity. Thus $\hat{\chi}$ is diagonal in the basis spanned by $e_{x,y,z}$ and is isotropic in the plane of the layer and, thus, is characterized fully by two eigenvalues $\chi_\parallel$ and $\chi_\perp$.

The numerical results for the optical spectrum are shown in Fig. 3.4. The difference between $\chi_\perp(\omega)$ for pristine MoS$_2$ SL and for MoS$_2$ SLVD is drastic. For pristine MoS$_2$ SL the lowest energy transition $T_0$ yielding nonzero $\chi_\perp$ (see Fig. 3.4a) corresponds to the transition between the top of the valence band to the CB+1 band with energy 3.2 eV (see Fig. 3.1a). In turn, for MoS$_2$ SLVD the lowest energy resonance is due to the transition between bound states of the same degeneracy with the energy difference smaller than 1 eV (see Fig. 3.4b, c, and d). This result is in stark contrast to true 2D systems where $\pi$ transitions are absent, and the effect of non-zero small thickness may be expected to be observed at energies at least significantly higher than those characteristic to $\sigma$ transitions. In addition, the selection rules governing $\pi$ transitions present a great opportunity for experimental characterization of states bound to VDs.

The qualitative picture based on the symmetry properties establishes the connection between the main features of spectrum of the bound states and the optical response. For example, for the Mo-vacancy the $T_3$ resonance in $\chi_\perp(\omega)$ involves a bound state hidden in the valence band. In the case of S$_2$-vacancy the symmetry analysis predicts that $\chi_\perp(\omega)$ is featureless at low energies due to the smallness of $f_f - f_i$, which is confirmed by the numerical calculations (see Fig. 3.4b). The Fermi level $\epsilon_F$, however, can be shifted by means of a gate voltage to lie between equally degenerate states with different parities, which support transitions contributing to $\chi_\perp(\omega)$. Then $\chi_\perp(\omega)$ should demonstrate a low-energy resonance. In the numerical simulations we modified the posi-
tion of the Fermi level by adding charge to the whole layer by means of a charge concentration of $1.4 \times 10^{21}\text{cm}^{-3}$, leading to a resonance in $\chi_{\perp}(\omega)$ (see Fig. 3.4c). Fig. 3.4d shows the resonances due to transitions between states bound to $3\times\text{MoS}_2$.

Considering the case when there is no overlap between bound states of neighboring VDs, we can use $\text{Im}\chi_{\perp,T_i} = \rho(d_{T_i}/\epsilon_0h)\gamma/\left[\gamma^2 + (\epsilon_n - \epsilon_{n'} - \omega)^2\right]$ for the transition $T_i$ of a dilute gas of VDs [128], where $\rho = N/V$ and $N$ are the concentration and number of VDs, respectively.

Figure 3.4: (a) Resonances of $\text{Im}\chi_{||}(\omega)$ (blue) and $\text{Im}\chi_{\perp}(\omega)$ (red) in pristine MoS$_2$ SL. (b) MoS$_2$ SLVD with Mo-vacancy: $T_3$ resonance in $\chi_{\perp}(\omega)$ is due to the odd singlet state inside the valence band. (c) MoS$_2$ SLVD with S$_2$-vacancy: If uncharged (green line), $\pi$ transitions are suppressed; if charged (red line), $\pi$ transitions are allowed. (d) MoS$_2$ SLVD with $3\times\text{MoS}_2$. 

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\[ d_{T_i} = \left\langle \psi_{nF_1}(r) \left| r \right| \psi'_{nF_1}(r) \right\rangle \] denotes the dipole moment of the transition \( T_i \). This formula is in excellent agreement with the numerical calculations shown in Fig. 3.5 for supercell sizes from 7x7 up to 13x13. The peak for the 5x5 supercell does not follow this formula because the overlap between neighboring VDs is substantial, which leads to a peak shift and homogeneous peak broadening due to the formation of minibands. Additional inhomogeneous peak broadening is expected due to random distribution of VDs in the MoS\(_2\) SL.

![Graphs showing magnitude of \( \chi (\omega) \) as a function of VD concentration \( \rho \) for Mo-vacancy around the peak \( T_2 \) and linear dependence of \( \chi (\omega) \) at maximum of peak \( T_2 \).](image)

**Figure 3.5:** (a) Magnitude of \( \chi (\omega) \) as a function of VD concentration \( \rho \) for Mo-vacancy around the peak \( T_2 \) (see Fig. 3.4b) for the five supercells 5x5, 7x7, 9x9, 11x11, and 13x13. (b) Linear dependence of \( \chi (\omega) \) at maximum of peak \( T_2 \).

**Conclusion**

We show that in order to describe the electron states bound to VDs in MoS\(_2\) SLVD, it is necessary to consider odd states, which lead to the appearance of resonances in the out-of-plane optical response \( \chi (\omega) \). Our results pave the way to the optical characterization of VDs in TMDC SLVD, which is of utmost importance for the future realization of high-performance electronic and optoelectronic devices based on TMDC SLs.
A detailed first-principle study has been performed to evaluate the electronic and optical properties of single-layer (SL) transition metal dichalcogenides (TMDCs) (MX$_2$; M= transition metal such as Mo, W and X= S, Se, Te), in the presence of vacancy defects (VDs). Defects usually play an important role in tailoring electronic, optical, and magnetic properties of semiconductors. We consider three types of VDs in SL TMDCs i) X-vacancy, X$_2$-vacancy, and iii) M-vacancy. We show that VDs lead to localized defect states (LDS) in the band structure, which in turn give rise to sharp transitions in in-plane and out-of-plane optical susceptibilities, $\chi_{\parallel}$ and $\chi_{\perp}$. The effects of spin orbit coupling (SOC) are also considered. We find that SOC splitting in LDS is directly related to the atomic number of the transition metal atoms. Apart from electronic and optical properties we also find magnetic signatures (local magnetic moment of $\sim \mu_B$) in MoSe$_2$ in the presence of Mo vacancy, which breaks the time reversal symmetry and therefore lifts the Kramers degeneracy. We show that a simple qualitative tight binding model (TBM), involving only the hopping between atoms surrounding the vacancy with an on-site SOC term, is sufficient to capture the essential features of LDS. In addition, the existence of the LDS can be understood from the solution of the 2D Dirac Hamiltonian by employing infinite mass boundary conditions. In order to provide a clear description of the optical absorption spectra, we use group theory to derive the optical selection rules between LDS for both $\chi_{\parallel}$ and $\chi_{\perp}$.

Introduction

Single-layer (SL) transition metal dichalcogenides (TMDCs) have attracted a lot of attention due to their intriguing electronic and optical properties, with a wide range of promising applications[15, 129]. SL TMDCs are direct band gap semiconductors [105, 106], which can be used to produce smaller and more energy efficient devices, such as transistors and integrated circuits. Moreover, the band gap lies in the visible region which makes them highly responsive when exposed to visible light, a property with potential applications in optical detection. In contrast to graphene, SL TMDCs exhibit large intrinsic spin-orbit coupling (SOC), originating from the d orbitals of transition metal atoms. The presence of considerably high SOC (up to few hundred meV) [13, 14, 130] makes them a candidate material for exploring spin physics and spintronics applications.

Wafer-scale production of SL TMDCs is required to fully appreciate their technological potential. The most common experimental techniques used to produce large chunks of SL MoS$_2$ are i) mechanical exfoliation, ii) chemical vapor deposition, and iii) physical vapor deposition. It has been observed that samples produced by all of these techniques have considerably lower carrier mobility than the theoretically predicted values [131, 132]. It has recently been suggested that this discrepancy between the predicted and observed values of carrier mobility is due to the presence of impurities created during the growth process [131, 132]. The most common and energetically favorable types of impurities are vacancy defects (VDs) [116].

Defects usually play an important role in tailoring various electronic and optical properties of two dimensional materials and have been the subject of intense research over the last few decades. VDs in semiconductors act as trapping centers for charge carriers and their interaction with charge carriers becomes stronger at reduced dimensionalities. Point defects in SL TMDCs have been explored both theoretically and experimentally [133, 134, 135, 136, 137, 138]. Recent photoluminescence (PL) experiments [136, 137, 138] reveal that localized excitonic states related to VDs can serve as
Figure 4.1: Different types of vacancy defects. Yellow sphere is X while black sphere is M (a) X-vacancy in $7 \times 7 \times 1$ supercell, (b) X$_2$-vacancy consisting of a pair of X atoms (surrounded by M atoms) removed in $7 \times 7 \times 1$ supercell, (c) M vacancy (surrounded by X atoms) in $7 \times 7 \times 1$ supercell.

single-photon emitters in WSe$_2$. Magnetism in low dimensional systems is another area of interest [139, 140]. It has been shown that[141] certain LDS related to VDs can induce ferromagnetism in SL TMDCs, suggesting that they could be good candidates for spin channels in spintronic devices. LDS can also be used to open and tune a band gap in graphene [142] and SL MoS$_2$ [111, 143].

Various atomic defects can be realized artificially by using different experimental techniques. It has been shown that hexagonal pits ($3\times$MoS$_2$) can be removed through etching of MoS$_2$ crystals by using XeF$_2$ as a gaseous reactant [111]. Point defects can be induced by irradiating the SL TMDCs with $\alpha$-particles or by thermal annealing [144]. Several experimental studies have been reported regarding the effects of point defects or of grain boundaries on SL TMDCs [145, 146, 147]. Strong PL enhancement has been observed as a result of oxygen adsorption at sulfur vacancy sites [146]. Also, sulfur vacancies are observed in MoS$_2$ through transmission electron microscopy experiments [147].

Pristine TMDCs are invariant with respect to the reflection $\sigma_h$ about the Mo or W plane of atoms $(z = 0$ plane). Therefore, electron states can be classified into two catagories: even and odd or symmetric and antisymmetric with respect to the $z = 0$ plane. We found that the even and odd bands in TMDCs have two different band gaps $E_{g\parallel}$ and $E_{g\perp}$, respectively [148]. $E_{g\perp}$ has been usu-
ally neglected for pristine TMDCs because of its substantially larger value (Table 4.1) and weak optical response (Fig: 4.2 b) as compared with $E_{g//}$. Earlier studies [143, 148] show that the presence of VDs gives rise to LDS in addition to the normal extended states present in conduction or valence bands in SL MoS$_2$. These LDS appear within the band gap region and they can also be present deep inside the valence band depending on the type of VD. Optical transitions between LDS across Fermi level appear as resonance peaks, both in $\chi_{//}$ and $\chi_{\perp}$, which shows that odd states are necessary for understanding the properties of VDs in SL MoS$_2$ [148].

In this paper, our aim is fourfold. First, we provide a comprehensive study of VDs in 4 types of SL TMDC materials, MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. Second, we provide detailed analytical models about the description of LDS within the Dirac equation formulation and by using the tight binding model. Third, we include the effects of SOC on VDs, which has not been considered so far. As mentioned earlier, SOC in these materials is large and therefore needs to be taken into account in order to obtain a better understanding of the electronic and optical properties of TMDCs. Fourth, we briefly discuss defect induced magnetism in some cases. Throughout this work, we consider 3 types of VDs: i) Single $X$-vacancy ii) $X_2$-vacancy, and iii) $M$-vacancy.

This chapter is organized as follows. Section 4 describes the numerical results obtained for band structures. Sections 4 and 4 describes qualitative models for the existence of defected states. Section 4 deals with the optical response of defected SL TMDCs.

**Band Structure**

The model system consists of a periodic 2D superlattice of TMDCs (Fig: 4.1 a, b, c). All numerical calculations are carried out using density functional theory (DFT). The local density approximation (LDA) is used with the Perdew-Zunger (PZ) parametrization [149] of the correlation energy of a homogeneous electron gas calculated by Ceperley-Alder [150]. The calculations are implemented
Table 4.1: Calculated in-plane and out-of-plane band gaps $E_g^\parallel$ and $E_g^\perp$ and spin-orbit splitting $\Delta_{SO}$ of the highest occupied valence band at K point.

<table>
<thead>
<tr>
<th>System</th>
<th>MoS$_2$</th>
<th>WS$_2$</th>
<th>MoSe$_2$</th>
<th>WSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g^\parallel$ [eV]</td>
<td>1.716</td>
<td>1.684</td>
<td>1.438</td>
<td>1.45</td>
</tr>
<tr>
<td>$E_g^\perp$ [eV]</td>
<td>3.109</td>
<td>3.263</td>
<td>2.516</td>
<td>2.66</td>
</tr>
<tr>
<td>$\Delta_{SO}$ [meV]</td>
<td>150</td>
<td>438</td>
<td>195</td>
<td>480</td>
</tr>
</tbody>
</table>

within Atomistix Toolkit [121] in order to be able to perform DFT calculations on large supercells in a reasonable amount of time. The periodic structure of the superlattice allows one to characterize the electron states by the bandstructure $\epsilon_n(k)$, where $k$ is the vector in the first Brillouin zone of the superlattice and $n$ enumerates different bands.

We consider a $7 \times 7 \times 1$ (Fig. 4.1) supercell having 147 number of atoms with an edge length of 21.354 Å. The Brillouin zone of the supercell is sampled by a $3 \times 3 \times 1$ $k$-mesh. All the structures are geometrically optimized with a force tolerance of 0.05 eV/Å. SOC is taken into account via the norm conserving pseudo potentials [151, 152]. Band structures are calculated along the $\Gamma - M - K - \Gamma$ path. Band structures of SL TMDCs for the pristine cases are plotted in Fig. 4.2 and calculated values are given in Table 4.1. The results are in good agreement with previously reported values both for band gap and SOC energy [13, 14, 153, 154]. We consider LDA because it is computationally less expensive and therefore allows us to perform DFT calculations on large supercells. A drawback of the generalized gradient approximation (GGA) is that the Atomistix Toolkit 2015.1 gives rise to an indirect band gap for SL TMDCs, which is in contradiction to the already established results for TMDCs. Nonetheless, we obtain approximately the same values for both band gap and SOC using either LDA or GGA. Figures 4.4 and 4.5 show the band structure of various SL TMDCs in the presence of vacancies. Black lines denote regular electronic states within the valence or conduction bands while colored lines denote the LDS. Vertical arrows show some of the allowed optical transitions observed in the optical spectra (see Fig. 4.10).
Figure 4.2: (a) Band structures and (b) electrical susceptibility of pristine $MX_2$ monolayers. Band gaps $E_g^\parallel$ (blue), $E_g^\perp$ (red) and spin-orbit splitting $\Delta_{SO}$ in the valance band are given in Table 4.1. Spin splitting can also be seen in the diagonal electric susceptibility in the in-plane component $\text{Im}(\chi_\parallel)$.

Tight Binding Model (TBM) and Symmetries

*General considerations*

The simplest qualitative model that can explain the existence of LDS in the band structure due to VDs is the TBM. Within the TBM approximation the electron wavefunction can be presented as $|\psi\rangle = \sum_{j,\mu \in O_j} \psi_{\mu}^{(j)} \varphi_{\mu}^{(j)} (r - R^{(j)})$, where $j$ enumerates atomic positions surrounding the vacancy and $\mu$ runs over the atomic orbitals $O_j$. In our tight binding analysis only the atoms surrounding the VD are considered in order to make the calculations simple enough for capturing the essential physical properties of the problem. The three VDs can be classified into two groups on the basis of symmetries. The $X$-vacancy lacks spatial inversion symmetry with respect to the $M$-plane of atoms, i.e. the $\sigma_h$ symmetry is broken, and is therefore described by the group $C_{3v}$. In contrast,
the $X_2$ and $M$-vacancy preserve the $\sigma_h$ symmetry of the crystal and thus can be described by the group $D_{3h}$ [130, 155]. For the latter the electronic states break down into even and odd parity with respect to the $\sigma_h: z \mapsto -z$ symmetry. $d$-orbitals of the transition metal and $p^{(t,b)}$-orbitals ($t$ and $b$ denoting the top and bottom layers) of the chalcogen atoms give the largest contribution to the conduction and valence band structure of TMDCs [153, 156]. Based on the $\sigma_h$ symmetry, the even and odd atomic orbitals are spanned by the bases \{\(d_{x^2-y^2}, d_{xy}, d_{z^2}\), \(p_{x,y}^{(t)} = (p_{x,y}^{(t)} + p_{x,y}^{(b)})/\sqrt{2}\), \(p_{z}^{(t)} = (p_{z}^{(t)} - p_{z}^{(b)})/\sqrt{2}\)\} and \{\(d_{xz}, d_{yz}, p_{x,y}^{(t)} = (p_{x,y}^{(t)} - p_{x,y}^{(b)})/\sqrt{2}\), \(p_{z}^{(t)} = (p_{z}^{(t)} + p_{z}^{(b)})/\sqrt{2}\)\}, respectively. We also include the effects of intrinsic SOC of the form $\sim \mathbf{L} \cdot \mathbf{S}$. The resulting spin-orbit states transform according to irreducible representations (IRs) of the double groups $C_{3v}^D$ and $D_{3h}^D$. Group representation theory is an efficient tool for determining the allowed optical transitions across the Fermi level in solids. This will be discussed in detail in the last section. The aim of this section is to present a qualitative description of LDS appearing in the band structure (Fig: 4.2 b, c, d). Here following Refs. [14, 148, 156] we first develop the TBM Hamiltonian by allowing the hopping between atomic orbitals of the atoms surrounding the VD only. Also we consider a large supercell in order to suppress the intervacancy couplings. Consequently, the effects of SOC are considered as VD onsite couplings.

**X- and $X_2$-vacancy**

Both X- and $X_2$-vacancies are surrounded by 3 M atoms, as shown in Fig. 4.3. As mentioned earlier for M atoms, $d$-orbitals provide the main contribution. Considering 3 atomic sites $A, B, C$ with 5 $d$-orbitals on each site, we have 15 species of $d$-electrons. We will suppress the spin indices and denote electron operators collectively as a vector by $\psi = (\psi_1, \psi_2, \psi_3, \psi_4, \psi_5)$, with $\psi_\tau = (d_{\tau}^A, d_{\tau}^B, d_{\tau}^C)$, where $d_{\tau}^P$ denotes the annihilation operator of electrons for orbital $\tau$ at site $P$ with $\tau = 1, 2, 3, 4, 5$ standing for $d_{z^2}, d_{xy}, d_{x^2-y^2}, d_{xz}, d_{yz}$, respectively.
Figure 4.3: $X_2$-vacancy surrounded by $M$ atoms at atomic sites $A, B$ and $C$. The defect has a rotational
symmetry at angles $2\pi/3$ (or $4\pi/3$), along $z$-axis passing through $O$.

The spinless representation of the Hamiltonian can be expressed in block form as

$$
\hat{H}_{X_2}^{TB} = \begin{pmatrix}
\hat{H}_{X_2}^{e} & \hat{0}_{9\times6} \\
\hat{0}_{6\times9} & \hat{H}_{X_2}^{o}
\end{pmatrix},
$$

(4.1)

where $\hat{H}_{X_2}^{e}$ and $\hat{H}_{X_2}^{o}$ are $9 \times 9$ and $6 \times 6$ blocks with even ($e$) and odd ($o$) parity, respectively, with
respect to $\sigma_h$, and $\hat{0}_{m\times n}$ denotes a zero matrix of dimension $m \times n$. Here we take advantage of
the inversion symmetry $\sigma_h$ by decoupling the orbitals with opposite parities. Also orthogonality
between different orbitals on the same atomic site is enforced. The submatrices in Eq. (4.1) are
given by

$$
\hat{H}_{X_2}^{e} = \begin{pmatrix}
\hat{H}_1^{1,1} & \hat{H}_1^{1,2} & \hat{H}_1^{1,3} \\
\hat{H}_2^{1,1} & \hat{H}_2^{1,2} & \hat{H}_2^{1,3} \\
\hat{H}_3^{1,1} & \hat{H}_3^{1,2} & \hat{H}_3^{1,3}
\end{pmatrix}, \quad
\hat{H}_{X_2}^{o} = \begin{pmatrix}
\hat{H}_4^{4,4} & \hat{H}_4^{4,5} \\
\hat{H}_5^{5,4} & \hat{H}_5^{5,5}
\end{pmatrix},
$$

(4.2)
where each of $\hat{H}^{i,j}_{e^{(o)}}$ is a $3 \times 3$ matrix $i, j = 1, 2, 3, 4, 5$. The blocks in the above Hamiltonians read

$$
\hat{H}_{e^{(o)}}^{\alpha,\beta} = \begin{pmatrix}
\epsilon_{e^{(o)}}^{\alpha,\beta} & t_{e^{(o)}}^{\alpha,\beta} e^{i\theta} & t_{e^{(o)}}^{\alpha,\beta} e^{-i\theta} \\
t_{e^{(o)}}^{\alpha,\beta} e^{-i\theta} & \epsilon_{e^{(o)}}^{\alpha,\beta} & t_{e^{(o)}}^{\alpha,\beta} e^{i\theta} \\
t_{e^{(o)}}^{\alpha,\beta} e^{i\theta} & t_{e^{(o)}}^{\alpha,\beta} e^{-i\theta} & \epsilon_{e^{(o)}}^{\alpha,\beta}
\end{pmatrix}.
$$

(4.3)

The diagonal elements $\epsilon_{e^{(o)}}^{\alpha,\beta}$ (0 for $\alpha \neq \beta$) and the off-diagonal elements $t_{e^{(o)}}^{\alpha,\beta}$ are phenomenological parameters describing the onsite energy and hopping between $d$-orbitals at different atomic sites, respectively. It can be easily shown that Hamiltonian (4.3) is invariant under $\sigma_h$ and $C_3$ symmetry operations, for $\theta = 0, \pm 2\pi/3$. But, in addition to $\sigma_h$ and $C_3$ symmetry operations, $D_{3h}$ group also contains $\sigma_v$ symmetry operations, i.e. reflection by the planes perpendicular to the xy-plane and passing through the lines OA, OB and OC (Fig. 4.3). $\sigma_v$ demands all the complex factors appearing in Equation (4.3) to be 1 or equivalently $\theta = 0$.

Figure 4.4: Band structures of $7 \times 7 \times 1$ MX$_2$ SL TMDCs with X-vacancy (a) and X$_2$-vacancy (b). The Fermi level is set at $\epsilon_F = 0$ eV. Red (blue) horizontal lines show odd (even) states w. r. to $\sigma_h$, while green horizontal lines in (a) represents the states with no definite symmetry. Different LDS transform according to IRs $D_{1/2}$, $2S_2$ and $2S_1$ ($E_{1/2}$ and $E_{3/2}$) of the double group $D_{3h}^D$ ($C_{3v}^D$).
Equations (4.2, 4.3) provides an initial insight into the nature of LDS. One can easily show that e.g. $\hat{H}_{o}^{X_2}$ has a pair of 3 eigenvalues, i.e. $\bar{\epsilon} + t - \sqrt{(\delta \epsilon + h)^2 + 4t_h^2}$, $\bar{\epsilon} - t/2 - \sqrt{(\delta \epsilon - h/2)^2 + t_h^2}$, $\bar{\epsilon} - t/2 - \sqrt{(\delta \epsilon - h/2)^2 + t_h^2}$ and $\bar{\epsilon} + t + \sqrt{(\delta \epsilon + h)^2 + 4t_h^2}$, $\bar{\epsilon} - t/2 + \sqrt{(\delta \epsilon - h/2)^2 + t_h^2}$, $\bar{\epsilon} + t/2 - \sqrt{(\delta \epsilon - h/2)^2 + t_h^2}$, where $\bar{\epsilon}$, $\delta \epsilon$ are related to addition and subtraction of onsite energies for orbitals $d_{xz}$, $d_{yz}$; $t$, $h$ are related to addition and subtraction of hopping parameters of the same orbitals at different sites, and $t_h$ is the hopping parameter of different orbitals at different atomic sites. Each pair contains a two-fold doublet, which explains the existence of triplets within the band structure [148]. However, the apparent two-fold degeneracy, which arises from the overlap of neighboring atomic orbitals, is lifted in the presence of SOC. Here we emphasize that each $d$-orbital appears in the form of triplets in the band structure. Thus, there is a total of 15 LDS (in the absence of SOC) for the case of the $X_2$-vacancy. It may appear that the simplest TBM may contradict the numerical results in Fig. 4.4, where calculations show a lower number of LDS. A closer inspection of the numerical results, however, resolves this contradiction in favor of the TBM. In fact, in addition to the LDS appearing within the band gap region, there are also LDS deep inside the valence bands, with possibility to mix with the extended states in the bulk.

SOC in the Hamiltonian is included by a pure atomic term [14] and for simplicity we consider only the onsite contribution arising from the M atoms surrounding the vacancy. Using the basis $|d_{z^2}, \uparrow\rangle$, $|d_{xy}, \uparrow\rangle$, $|d_{x^2-y^2}, \uparrow\rangle$, $|d_{xz}, \uparrow\rangle$, $|d_{yz}, \uparrow\rangle$ and $|d_{z^2}, \downarrow\rangle$, $|d_{xy}, \downarrow\rangle$, $|d_{x^2-y^2}, \downarrow\rangle$, $|d_{xz}, \downarrow\rangle$, $|d_{yz}, \downarrow\rangle$, we can write the SOC Hamiltonian as

$$\hat{H}_{X_2}^{SOC} = \frac{\Delta}{2} \mathbf{L} \cdot \mathbf{S} = \frac{\Delta}{2} \begin{pmatrix} \hat{L}_z & \hat{L}_- \\ \hat{L}_+ & -\hat{L}_z \end{pmatrix},$$

(4.4)
where

\[
\hat{L}_z = \begin{pmatrix}
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\
\hat{0}_3 & \hat{0}_3 & 2i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\
\hat{0}_3 & -2i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -i \times \hat{I}_3 \\
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & i \times \hat{I}_3 & \hat{0}_3 \\
\end{pmatrix},
\] (4.5)

\[
\hat{L}_+ = \begin{pmatrix}
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \sqrt{3} \times \hat{I}_3 & i \sqrt{3} \hat{I}_3 \\
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -i \times \hat{I}_3 & -1 \times \hat{I}_3 \\
\hat{0}_3 & \hat{0}_3 & \hat{0}_3 & -1 \times \hat{I}_3 & i \times \hat{I}_3 \\
-\sqrt{3} \times \hat{I}_3 & i \times \hat{I}_3 & \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\
-i \sqrt{3} \times \hat{I}_3 & \hat{I}_3 & -i \times \hat{I}_3 & \hat{0}_3 & \hat{0}_3 \\
\end{pmatrix},
\] (4.6)

and \(\hat{L}_- = \hat{L}_+^\dagger\). The off-diagonal elements \(\hat{L}_\pm\) in Eq. (4.4) couple the even to the odd blocks of the Hamiltonian matrix shown in Eq. (4.1) and are related to the spin flip processes due to the SOC, which give rise to virtual transitions [157]. Because of the large spatial anisotropy of an atomically thin layer of TMDC, for the pristine case these off-diagonal terms can be neglected, which is substantiated by our DFT calculations (see below). A generalized SOC states has the form

\[
|\Psi\rangle = \alpha |\zeta\rangle |\uparrow\rangle + \beta |\xi\rangle |\downarrow\rangle.\] (4.7)

Here, \(|\zeta\rangle\) and \(|\xi\rangle\) are orbital states of the spin-up and spin-down states \(|\uparrow\rangle\) and \(|\downarrow\rangle\), respectively, and \(\alpha, \beta\) are probability amplitudes for the up and down spinors. DFT calculations reveal that for SOC Bloch states corresponding to LDS, either \(\alpha \ll \beta\) or \(\alpha \gg \beta\) in the majority of cases (Fig: 4.6), corresponding to strong polarizations of the LDS in \(z\) direction (b), which is due to the large spatial anisotropy. It can be calculated that LDS are spin polarized for \(X_2\)-vacancy or the Bloch states for \(X_2\)-vacancy preserve the \(\sigma_h\) symmetry. Therefore we anticipate that the effects of \(\hat{L}_\pm\) can safely be
neglected for the $X_2$-vacancy. The full tight binding Hamiltonian can be written as

$$\hat{H}_{X_2} = I_2 \otimes \hat{H}^{TB}_X + \hat{H}^{SOC}_{X_2}$$

$$= \begin{pmatrix} \hat{H}^{TB}_{X_2} + \frac{\Delta}{2} \hat{L}_z & 0_{9\times 9} \\ 0_{9\times 9} & \hat{H}^{TB}_{X_2} - \frac{\Delta}{2} \hat{L}_z \end{pmatrix}.$$  \quad (4.8)

The Hamiltonian appears to be block diagonal, which indicates that spin states in $z$ direction are not mixed by spin flip processes and therefore the spin in $z$ direction is still a good quantum number due to $\sigma_h$ symmetry. As mentioned above, the absence of spin flip processes can be attributed to the 2D character of TMDCs or due to the large anisotropy between $xy$-plane and $z$-axis. In case of the $X$-vacancy, due to lack of $\sigma_h$ symmetry, defect states appear with no definite parity (Fig: 4.6) (a). Therefore, here we argue that for the $X$-vacancy the off-diagonal terms $\hat{L}_\pm$ in Eq. (4.4) need to be taken into account.

In the absence of SOC each energy band is doubly degenerate (spin-up and spin-down states at each $k$ point). SOC lowers the symmetry and can break the spin degeneracy at $k$ points away from high symmetry points. However, time reversal symmetry leads to the condition that $\varepsilon(k, \uparrow) = \varepsilon(-k, \downarrow)$, commonly known as Kramers degeneracy. This degeneracy is reflected in the band structure (Fig. 4.4), where each energy level is doubly degenerate for both types of vacancies. In solids or 2D surfaces spin splitting depends both on the size of atomic SOC and of the gradient of electric potential [158]. This difference in the gradient of electric potential leads to the different spin splittings for same types of defects in different TMDCs as shown in Fig. 4.4 and in Table 4.2.
Figure 4.5: (a) Band structures of $7 \times 7 \times 1$ MX$_2$ SL TMDCs with M-vacancy. The Fermi level is set at $\epsilon_F = 0$ eV. Red (blue) lines show odd (even) states w. r. to $\sigma_h$. Different LDS transform according to IRs $D_{1/2}$, $2S_2$ and $2S_1$ of double group $D_{3h}^D$. (b) Spin polarized density of states of $7 \times 7 \times 1$ MX$_2$ SL TMDCs with M-vacancy for spin up(down) are shown in red(blue).

**M-vacancy**

There are 6 chalcogen X atoms in the top and bottom layers, surrounding the transition metal M-vacancy. Thus, there are 18 species of electrons corresponding to six possible combinations of $p$-orbitals (3 of them even and 3 odd with respect to $\sigma_h$) at 3 in-plane atomic positions. Proceeding as before the TBM for the M-vacancy can be written as
where each of $\hat{H}_{e(o)}^j$ is a $3 \times 3$ matrix corresponding to even (odd) combinations of $p$ orbitals, with $j = 6, 7, 8, 9, 10, 11$ being indices reserved for the $p_x, p_y, p_z, p'_x, p'_y, p'_z$ orbitals, respectively. Each $\hat{H}_{e(o)}^\beta$ in Eq. (4.10) has the same form as in Eq. (4.3). SOC is included by considering the Hamiltonian described in Eq. (4.4). The M-vacancy also preserves the $\sigma_h$ symmetry. Again, the $\hat{L}_zS_z$ term gives the largest contribution due to the large anisotropy.

![Figure 4.6: Bloch states corresponding to a LDS a) X and b) X₂-vacancy c) M-vacancy in MoS₂. $E_{1/2}$ and $2S_2$ and $D_{1/2}$ are corresponding IRs. Both the top ($xy$-plane) and side ($yz$-plane) views are presented. Bloch states are spin polarized in each case $\beta \gg \alpha$.](image-url)
The Bloch states are shown in Fig. 4.6, from which it can be concluded that LDS are spin polarized also in the case of M-vacancy. The matrices for operators $\hat{L}_z$ and $\hat{L}_\pm$ in the case of the M-vacancy can be written as

$$\hat{L}_z = \begin{pmatrix} 0_3 & -i \times 3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ i \times 3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 & \hat{0}_3 \\ \hat{3} & \hat{3} & \hat{3} & \hat{3} & \hat{3} \end{pmatrix}, \quad (4.12)$$

and

$$\hat{L}_+ = \hat{L}_- = \begin{pmatrix} 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & -1 \times \hat{3} \\ 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & i \times \hat{3} \\ 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & 0_3 & -i \times \hat{3} \\ 0_3 & 0_3 & -1 \times \hat{3} & 0_3 & 0_3 & 0_3 \\ 0_3 & 0_3 & i \times \hat{3} & 0_3 & 0_3 & 0_3 \\ \hat{3} & -i \times \hat{3} & 0_3 & 0_3 & 0_3 & 0_3 \end{pmatrix}, \quad (4.13)$$

and $\hat{L}_- = \hat{L}_+$. The DFT calculations show that the Kramers degeneracy is preserved for MoS$_2$ and WS$_2$ while it is broken for MoSe$_2$ and WSe$_2$. In Ref. [141], it has been shown that presence of Mo vacancies in MoSe$_2$ can induce spin polarization and results in long range antiferromagnetic coupling between local magnetic moments, even at a distance above 13 Å due to the large spatial extensions of spin density. The local magnetic moment on each M-vacancy breaks the time reversal symmetry and therefore lifts Kramers degeneracy in MoSe$_2$ in the presence of Mo vacancies. In Fig. 4.5 (b) we show plots for the density of states (DOS) obtained by the local density spin approximation (LSDA) method for the M-vacancy in different TMDCs, in order to confirm that indeed the Mo-vacancy in MoSe$_2$ exhibits magnetic signatures. Our spin-polarized DFT calculations
show that the exchange correlation potential leads to a spin splitting only for the MoSe$_2$ system. In Fig. 4.7(a) the isosurface plot for the spin density is shown along with the magnetic moment $\mu$ calculated by means of the Mulliken population analysis at all the nearest-neighboring atomic sites (Se atoms) and the next-nearest neighboring sites (Mo atoms) surrounding the vacancy. Our results show that the main contribution to the magnetism is due to the $p$-orbitals localized at the Se atoms and the $d$-orbitals localized at the next-nearest Mo atoms surrounding the Mo vacancy. The electronic band structure calculated by using LSDA is shown in Fig. 4.7(b). The spin states of the LDS are split whereas the bulk states do not show any magnetic moment. The magnetic moment of the LDS is governed by the unpaired electron spins according to Hund’s rules, which is $1 \mu_B$ (inset of Fig. 4.7(b)). The calculations yield a slightly smaller magnetic moment of $0.6 \mu_B$, which is acceptable within standard DFT limits. Finally, we plot the magnetic moment $\mu$ vs defect density $\rho$ in Fig. 4.7(c), where the localization of the magnetic moment is demonstrated for densities $\rho < 25 \times 10^{12}$ cm$^{-2}$. We also notice splittings in the case of WSe$_2$, but no magnetic signatures are found. We attribute this splitting as a result of interaction between adjacent vacancies due to large spatial extensions of W and Se orbitals.

Table 4.2: SOC splitting $\Delta,X,X_2,M$ in LDS appearing above the Fermi level for X, X$_2$ and M vacancies respectively, in different TMDCs.

<table>
<thead>
<tr>
<th>System</th>
<th>MoS$_2$</th>
<th>WS$_2$</th>
<th>MoSe$_2$</th>
<th>WSe$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_X$ [meV]</td>
<td>51</td>
<td>192</td>
<td>34</td>
<td>173</td>
</tr>
<tr>
<td>$\Delta_{X_2}$ [meV]</td>
<td>78</td>
<td>278</td>
<td>60</td>
<td>251</td>
</tr>
<tr>
<td>$\Delta_M$ [meV]</td>
<td>32.5</td>
<td>130</td>
<td>54</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 4.7: (a) Isosurface plot of the spin density of MoSe$_2$ monolayer with one Mo vacancy. The black and yellow balls represent Mo and Se atoms, respectively. The red isosurface shows the spin density. Magnetic moment $\mu$ at neighbouring and next neighbouring sites surrounding the vacancy is also calculated which gives a total $\mu$ of 0.6 in units of $\mu_B$. (b) Spin polarized band structure of $7 \times 7$ MoSe$_2$ with one Mo vacancy, red and blue lines show states for spin up and down, respectively. (c) Magnetic moment $\mu$ vs defect density $\rho$.

Defect States Within the Dirac Equation Formulism

The main analytical tool for describing properties of electron states in transition metals monolayers is the Dirac equation, which emerges within the $k \cdot p$-approximation as the two-band model [13, 159, 160]. Such description is valid when the main role is played by low lying excitations near the band edges. This assumption, however, is ill-justified for the case of vacancies and, indeed, as will be demonstrated below the Dirac equation fails to reproduce many important features of the defect states. At the same time, the Dirac equation allows one to establish several important features and, first of all, the sole existence of the states bound to vacancies. For example, within the framework provided by the Schrodinger equation the vacancy is naturally represented by a repulsive potential, which cannot support bound states. The Dirac equation, in turn, provides more options for describing defects and, as will be shown below, when the special boundary conditions are enforced at the boundary of the defect, the states localized near the boundary appear.
The formalism of Dirac equation can be introduced as follows. Within the $k \cdot p$-approximation the electron states are described by $\Psi(r)e^{iK \cdot r}$, where $\Psi(r)$ is a smooth function of coordinates. Adopting the two-band approximation, $\Psi(r)$ is presented as a two-component spinor, which satisfies a 2D Dirac-like equation. For example, for MoS$_2$ the two-band approximation is often implemented retaining only the dominating contribution of Mo’s d orbitals, [13, 14] so that near the inequivalent $K$-points of the Brillouin zone, $K_\tau = \tau K$ with $\tau = \pm 1$, spinors $\Psi_\tau(r)$ are spanned by $|d_{x^2-y^2} - i\tau d_{xy}\rangle$ and $|d_z\rangle$, the states representing the top of the valence band and the bottom of the conduction band, respectively. Spinors $\Psi_\tau$, thereby, satisfy $[\sigma_z \Delta + \nu (\tau \sigma_x p_x + \sigma_y p_y)] \Psi_\tau(r) = \epsilon \Psi(r)$, where $2\Delta$ is the width of the gap and $\epsilon$ is the energy counted from the center of the gap $\epsilon_c$.

In order to eliminate the valley dependence of the Hamiltonian governing the spatial distribution of $\Psi_\tau$, it is convenient to introduce $\Phi_\pm = \Psi_+ \pm \sigma_y \Psi_-$, which satisfy $H_\tau \Phi_\tau = \epsilon \Phi_\tau$, where

$$H_\tau = \tau \sigma_z \Delta + \nu \sigma \cdot p.$$  \hspace{1cm} (4.14)

Thus solutions for electrons in different valleys are related by simple reverting the sign of $\Delta$. Combining $\Phi_\pm$ into a single 4-spinor

$$\Phi = \Phi_+ \oplus \Phi_-$$  \hspace{1cm} (4.15)

the equations of motion for different valleys can be presented in a unified form $H \Phi = \epsilon \Phi$ with

$$H = \tau_z \otimes \sigma_z \Delta + \nu \tau_0 \otimes \sigma \cdot p,$$  \hspace{1cm} (4.16)

where $\tau_i$ with $i = x, y, z$ and $\tau_0$ are the Pauli matrices and the identity matrix, respectively, acting on the valley space.

Hamiltonian (4.16) possesses the cylindrical symmetry, which can be employed by presenting
\[ \mathbf{\sigma} \cdot \mathbf{p} = -i\sigma_r \partial / \partial r - ir^{-1}\sigma_\phi \partial / \partial \phi, \] where

\[
\sigma_r = \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix}, \quad \sigma_\phi = \begin{pmatrix} 0 & -ie^{-i\phi} \\ ie^{i\phi} & 0 \end{pmatrix}. \tag{4.17}
\]

The explicit angular dependence is eliminated by introducing \( \tilde{\Phi}_\tau \begin{pmatrix} \phi \end{pmatrix} = e^{i\sigma_z \phi/2} \Phi_\tau \), which accounts for rotation of the spinors \( \Phi_\tau \), while encircling the origin. It should be noted that due to the relation \( \Phi_- = \sigma_y \Psi_- \) the rotation directions of \( \Psi_+ \) and \( \Psi_- \) are different: \( \tilde{\Psi}_\tau = e^{i\tau \sigma_z \phi/2} \Psi_\tau \). Thus the winding numbers of spinors corresponding to electrons belonging to different valleys have opposite signs.

Spinors \( \tilde{\Phi}_\tau \) satisfy

\[
\tilde{\mathcal{H}}_\tau \tilde{\Phi}_\tau = e \tilde{\Phi}_\tau, \tag{4.18}
\]

where \( \tilde{\mathcal{H}}_\tau = e^{i\sigma_z \phi/2} \mathcal{H}_\tau e^{-i\sigma_z \phi/2} \) has the form

\[
\tilde{\mathcal{H}} = \tau \sigma_z \Delta - iv \left[ \sigma_x \left( \frac{\partial}{\partial r} + \frac{1}{2r} \right) + \sigma_y \frac{1}{r} \frac{\partial}{\partial \phi} \right]. \tag{4.19}
\]

Equation (4.18) is solved by separating variables \( \tilde{\Phi}_\tau(r, \phi) = \sum_{m=-\infty}^{\infty} \tilde{\Phi}_{\tau;m}(r) e^{im\phi} \). For amplitudes \( \tilde{\Phi}_{\tau;m}(r) \), we find the general solution

\[
\tilde{\Phi}_{\tau;m}(r) = \sqrt{Qr} \times \left( \begin{array}{c}
\frac{1}{\sqrt{\epsilon - \tau \Delta}} \left( a_{\tau;m} h_{m-1}^{(1)}(Qr) + b_{\tau;m} h_{m-1}^{(2)}(Qr) \right) \\
\frac{i}{\sqrt{\epsilon + \tau \Delta}} \left( a_{\tau;m} h_{m}^{(1)}(Qr) + b_{\tau;m} h_{m}^{(2)}(Qr) \right)
\end{array} \right), \tag{4.20}
\]

where \( h_{m}^{(1,2)}(Qr) \) are the spherical Hankel functions, \( Q = v^{-1} \sqrt{\Delta^2 - \epsilon^2} \), \( a_{\tau;m} \) and \( b_{\tau;m} \) are arbitrary constants.

We are interested in bound states and, therefore, in solutions of Eq. (4.18) corresponding to ener-
gies inside the gap. For such energies, we have $Q = i\kappa$ with non-negative $\kappa = \sqrt{\Delta^2 - \epsilon^2}$. From the regularity condition at infinity, it follows that $b_{r}^{(m)} = 0$, while $a_{r}^{(m)}$ are determined from the normalization condition. The solution can be written as

$$\tilde{\Phi}_{+m} = N_{+m} \left( \begin{array}{c} \frac{1}{\sqrt{\Delta - \epsilon}} g_{m-1}(\kappa r) \\ \frac{i}{\sqrt{\Delta + \epsilon}} g_{m}(\kappa r) \end{array} \right),$$

(4.21)

where we have denoted the normalization constant by $N_{+,m}$. The functions $g_{m}(z)$ are related to the modified spherical Hankel functions $g_{m}(z) = \frac{2k_{m}(z)}{\pi}$ and for $m > 0$ can be presented as

$$g_{m}(z) = (-z)^{m} \frac{d}{dz} z^{m} e^{-z}.$$

(4.22)

Taking into account the relation

$$g_{-m}(z) = g_{m-1}(z),$$

(4.23)

we can use Eq. (4.22) for finding $g_{m}(z)$ with $m < 0$ as well. With the help of this relation, one can show, starting from Eq. (4.20), that

$$\tilde{\Phi}_{-m} = c \sigma_{x} \tilde{\Phi}_{+m},$$

(4.24)

where $c$ is a phase factor, $|c| = 1$. Such connection between solutions corresponding to electrons from different valleys allows us to limit our attention to $\tau = +1$.

The functions $g_{m}(z)$ can be shown to be non-negative. Thus, we can rewrite

$$\tilde{\Phi}_{+,m} = \tilde{N}_{+,m} \left( \begin{array}{c} \cos(\chi_{m}/2) \\ i \sin(\chi_{m}/2) \end{array} \right),$$

(4.25)
with \(0 \leq \chi_m \leq \pi\). This representation shows that at any chosen distance from the center of the vacancy, the defect states have the form of a spin coherent state [161, 162] lying in the plane perpendicular to \(n_B\), the vector normal to the boundary of the anti-dot and directed outward. The angle \(\chi_m = 2 \arctan(F_m)\), where

\[
F_m = \frac{g_m(\kappa r)\sqrt{\Delta - \epsilon}}{g_{m-1}(\kappa r)\sqrt{\Delta + \epsilon}},
\]

has the meaning of the polar angle of the vector characterizing the direction of the spin coherent state. Its dependence on \(m\) is illustrated by Fig. 4.8, which shows that \(\chi_m\) monotonously increases from \(\chi_{-\infty} = 0\) to \(\chi_{\infty} = \pi\). It is also a monotonous function of \(r\) (increasing for \(m < 0\) and decreasing for \(m > 0\)) and monotonously increasing function of energy. Taking into account Eq. (4.23) one can see the important symmetry

\[
F_m(\epsilon) = 1/F_{-m}(-\epsilon).
\]

Figure 4.8: The polar angle \(\chi_m\) characterizing the defect state. (a) Dependence of \(\chi_m\) on \(m\). Curves (1), (2) and (3) correspond to \((\epsilon - \epsilon_c)/\Delta = -0.99, 0, 0.99\), respectively, where \(\epsilon_c\) stands for the center of the gap. The distance from the center of the anti-dot is taken \(r\Delta/v = 1\) (it is assumed that \(r > r_0\)). (b) For the fixed energy \((\epsilon - \epsilon_c)/\Delta = 0.4\) the dependence \(\chi_m\) on \(r\) is shown for \(m\); from top to bottom \(m = 5, 1, 0, -1, -5\). (c) For \(r\Delta/v = 1\) the dependence of \(\chi_m\) on energy is shown for the same set of \(m\) as in (b).
Thus, the states with $\tau = 1$ lie in the half plane corresponding to the positive projection on the vector tangent to the boundary $e_\phi = e_z \times n_B$, while the states with $\tau = -1$ have the opposite orientation, due to $\langle \tilde{\Phi}_{-m} | \tilde{\Phi}_{+m} \rangle = 0$, which can be easily checked.

The energies of the defects states (and their sole existence) are determined by the boundary condition on the boundary of the anti-dot. The general form of the condition is found requiring that the radial component of the probability current must vanish at the boundary, [163, 164] $\langle \Phi(r_0) | n_B \cdot J | \Phi(r_0) \rangle = 0$, where $J = v r_0 \otimes \sigma$. This condition is equivalent to $M \Phi = \Phi$, where $\Phi$ is the 4-spinor defined by Eq. (4.15) and the Hermitian matrix $M$ has the eigenvalues $\pm 1$ and anticommutes with the radial component of the current operator $\{J \cdot n_B, M\} = 0$. Within the infinite mass model, [163, 164] the anti-dot is represented as a region with renormalized width of the gap $\Delta \to \Delta(1 + d(r))$ with $d(r) = 0$ for $r > r_0$ and $d(r) \to \infty$ when $r < r_0$, so that in this case $M = (\tau \cdot e_z) \otimes (\sigma \cdot e_\phi)$. In other words, within this model in order to have decaying electron distribution inside the anti-dot $\tilde{\Phi}_r(r)$ must be proportional to $| e_\phi \rangle$ as $r$ approaches $r_0$.

The condition $\tilde{\Phi}_{+m}(r_0) \propto |e_\phi\rangle$, or $\chi_m = \pi/2$, constitutes the condition imposed on the energy of the bound state

$$F_m(\epsilon, r_0) = 1.$$  (4.28)

In virtue of Eq. (4.27), if for some $m$ there exists a bound solution with the energy $\epsilon$, then there is the solution corresponding to $m' = -m$ with the energy $-\epsilon$. Thus within the infinite mass model the spectrum of the defect states is symmetric with respect to the center of the gap.

For $m = 0$, Eq. (4.28) has the simplest form $F_0 = \sqrt{\Delta - \epsilon}/\sqrt{\Delta + \epsilon} = 1$ with the solution

$$\epsilon_0 = 0.$$  (4.29)
Thus the anti-dot independently of its size supports a bound state with the energy at the center of the gap.

States with $|m| > 0$, in turn, appear only when the defect is sufficiently large. In order to find the condition of supporting the state with some $m$ we notice that $F_m(\epsilon, r_0)$ is monotonously decreasing function of energy while $\epsilon$ changes from $-\Delta$ to $\Delta$. Since $g_m(z \to 0) \sim (2m - 1)!/(z^{m+1})$, we find that the energy of the $m$-th state is inside the gap, if

$$r_0 > R_m = \frac{v}{\Delta} \left( |m| - \frac{1}{2} \right). \quad (4.30)$$

Conversely, for the given radius $r_0$ the number of bound defect states is given by $N = 4 + 8 \left[ r_0 \Delta/v + 1/2 \right]$, where 4 accounts for states from different valleys and with different spins at $m = 0$ and the second term accounts for states with $m > 1$, here $[\ldots]$ denotes taking the integer part and 8 in addition to the spin and valley degeneracies accounts for the symmetry $m \to -m$.

The dependence of energies of the defect states on the radius of the anti-dot is shown in Fig. 4.9.

The spatial electron distribution corresponding to the defect state is conveniently characterized by the probability density $\rho_{\tau,m}(r) = \langle \Phi_{\tau,m} | \Phi_{\tau,m} \rangle$ and the vector of orientation of the (pseudo)spin coherent state $S_{\tau,m} = \langle \Phi_{\tau,m} | \sigma | \Phi_{\tau,m} \rangle / \rho_{\tau,m}$. As follows from Eq. (4.25), the pseudospin state is transversal, $S_r = 0$, with the spatial variation of the projection of $S_{\tau,m}$ onto the $(e_\phi, e_z)$-plane depending on $m$.

In the simplest case $m = 0$ the pseudospin remains in the plane of the layer, $S_{\tau,z} = 0$. States with nonzero $m$ are characterized by out of the plane distribution of the pseudospin (for $r > r_0$). The angle of maximum deviation from the plane is

$$\tan \left( \frac{\beta}{2} \right) = \frac{\tau \sqrt{\Delta + \epsilon} - \sqrt{\Delta - \epsilon}}{\sqrt{\Delta + \epsilon + \sqrt{\Delta - \epsilon}}}. \quad (4.31)$$
Figure 4.9: The dependence of the spectrum of defect states on the normalized radius of the anti-dot, $r_0v/\Delta$. The dashed lines show the edges of the gap. The section at particular $r_0$ presents the spectrum of the defect states in the infinite mass model. The central line corresponds to $m = 0$ and to states with increasing $|\epsilon - \epsilon_c|$ correspond states with increasing $|m|$. Thus curves for $m = -4, \ldots, 4$ are shown. The spectral lines outside the gap correspond to scattering resonances with complex energies.

Thus for $\tau = 1$ the pseudospin “sticks out” of the plane for $\epsilon > 0$ (that is for $m > 0$) and has the negative projection on the z-axis for $\epsilon < 0$. For $\tau = -1$ the direction of the pseudospin is reversed.

Optical Response

The presence of LDS in the band structure gives rise to sharp peaks in the optical spectrum. In Ref. [165] the relative dielectric functions $\epsilon_r$ of various TMDCs have been measured experimen-
tally, which in turn are related to the electric susceptibilities by the standard formula $\epsilon_r = 1 + \chi$. In Fig. 4.10 results for both in plane $\chi_\parallel$ and out of plane $\chi_\perp$ components of the electric susceptibility are presented for different VDs in TMDCs. The electric susceptibility provides valuable insight into the optical selection rules for transitions between states across the Fermi level. We are interested in transitions involving states with energy near the gap edges or inside the gap. The electric susceptibility tensor is evaluated using the Kubo-Greenwood formula

$$\chi_{ij}(\omega) = -\frac{e^2 \hbar^4}{m^2 e_0 V \omega^2} \sum_{p,q} \frac{f(E_q) - f(E_p)}{E_{pq} - \hbar \omega - i\hbar \Gamma_{pq}} \pi^i_{pq} \pi^j_{qp}. \quad (4.32)$$

**Figure 4.10:** Resonances of $\text{Im}\chi_\parallel(\omega)$ (blue) and $\text{Im}\chi_\perp(\omega)$ (red) $a)$ for X-vacancy, $b)$ X$_2$-vacancy, $c)$ M-vacancy for different TMDCs
Where $\pi^j_{pq} = \langle \psi_p | x_j | \psi_q \rangle$ is the $j$th component of dipole matrix element between states $p$ and $q$, $V$ the volume, $f$ the Fermi function and $\Gamma$ is the broadening, which is set to be 0.01 eV. Appearance of states inside the band gap $E_g$ or close to the band edges leads to the resonances at single energy $E_{pq} = |E_p - E_q|$. The dipole matrix element $\pi^j_{pq}$ determines the strength of an optical transition and whether it is allowed or prohibited by symmetries.

When considering defects in a crystal, the LDS transform according to the IRs of the symmetry group of the crystal site in which the defect resides. While the translational symmetry of the crystal is broken, point group symmetries are partially or completely preserved. M and X$_2$ vacancies keep the $D_{3h}$ symmetry whereas the X-vacancy exhibits the lower $C_{3v}$ symmetry. The character tables for $C_{3v}$ and $D_{3h}$ with single and double group IRs are shown in Table 4.3 and Table 4.4, respectively. Table 4.5 contains the decomposition of the direct products of the single group representations with the representation according to which the spin matrices transform, i.e. $E_{1/2}$ and $D_{1/2}$ respectively. In Fig: 4.11 band structures for WS$_2$ with S and W vacancies are shown for with and without SOC. Following Ref. [166, 167], in Fig: 4.11 we show how the single group IRs in the absence of SOC can be mapped to the corresponding double group IRs in the presence of SOC. Note that due to the nature of the DFT calculation, the superlattice defined by the supercell introduces an artificial translational symmetry, which in some cases leads to artificial splittings. These can be typically recognized by systematically changing the size of the supercell.

The appearance of LDS inside the band gap leads to sharp resonances in $\chi_\parallel$ and $\chi_\perp$ at frequencies corresponding to the energy differences between LDS. However, not all transitions are allowed. Instead, several transitions are prohibited due to symmetry, i.e. when $\pi^j_{pq}$ does not transform according to the symmetric representation of the symmetry group of the superlattice. In the matrix element $\chi^j_{pq}$, the initial state $\psi_p$, the final state $\psi_q$, and the position operator $x_j$ transform according to the IRs $\Gamma(\psi_p)$, $\Gamma(\psi_q)$ and $\Gamma(x_j)$, respectively. An electric dipole transition between two states is allowed if the direct product $\Gamma(\psi_p) \otimes \Gamma(x_j) \otimes \Gamma(\psi_q)$ includes $\Gamma(I)$ in its decomposition in terms of a direct sum. $\Gamma(I)$ denotes the IR for the identity i.e., $A_1$ and $A'_1$ for $C_{3v}$ and $D_{3h}$, respectively.
Table 4.3: Character table of the group $C_{3v}$. $E$, $C_3$, $\sigma_v$ are the single group IRs and $E_{1/2}$, $E_{3/2}$ are the corresponding double group IRs.

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>2 -2</td>
<td>1 -1</td>
<td>0 0</td>
</tr>
<tr>
<td>$E_{3/2}$</td>
<td>2 -2</td>
<td>-2 2</td>
<td>0 0</td>
</tr>
</tbody>
</table>

Table 4.4: Character table of the group $D_{3h}$. $E$, $\sigma_h$, $2C_3$, $2S_3$, $3C_2$, and $\sigma_v$ are the single group IRs and $D_{1/2}$, $2S_1$, $2S_2$ are the corresponding double group IRs.

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$\sigma_2$</th>
<th>$2C_3$</th>
<th>$2S_3$</th>
<th>$3C_2$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A''_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A''_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-2</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$D_{1/2}$</td>
<td>2 -2</td>
<td>0</td>
<td>1 -1</td>
<td>$\sqrt{3}$</td>
<td>$-\sqrt{3}$</td>
<td>0 0</td>
</tr>
<tr>
<td>$2S_1$</td>
<td>2 -2</td>
<td>0</td>
<td>-2 2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$2S_2$</td>
<td>2 -2</td>
<td>0</td>
<td>1 -1</td>
<td>$-\sqrt{3}$</td>
<td>$\sqrt{3}$</td>
<td>0 0</td>
</tr>
</tbody>
</table>

This is strictly related to the polarization of the radiation. One needs to consider separately the in plane and out of plane components of $\pi^j_{pq}$ because they transform according to different IRs of $C_{3v}$ and $D_{3h}$. The selection rules for electric dipole transitions for the double group IRs are summarized in Table 4.6.

The presence of SOC couples the spin and orbital angular momenta, thereby requiring the consideration of the double group IRs. In our case, we need to consider $D_{1/2} \otimes C_{3v}$ and $D_{1/2} \otimes D_{3h}$, where $D_{1/2}$ is the 2-dimensional spin representation. The electromagnetic field couples to the orbital part of the state, i.e. either to $|\zeta\rangle$ or to $|\xi\rangle$ [see Eq. (4.7)], polarizations induced by electromagnetic waves will not be changed in the presence of SOC. The role of the SOC is to lift some degeneracies, which gives rise to extra absorption peaks compared with the case without SOC [148].
Table 4.5: Double group representations obtained from single group representation for $C_3v$ and $D_{3h}$.

<table>
<thead>
<tr>
<th>$\Gamma_i (C_3v)$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_i \times E_{1/2}$</td>
<td>$E_{1/2}$</td>
<td>$E_{1/2}$</td>
<td>$E_{3/2} + E_{1/2}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\Gamma_i (D_{3h})$</th>
<th>$A'_1$</th>
<th>$A'_2$</th>
<th>$A''_1$</th>
<th>$A''_2$</th>
<th>$E'$</th>
<th>$E''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_i \times D_{1/2}$</td>
<td>$D_{1/2}$</td>
<td>$D_{1/2}$</td>
<td>$2S_2$</td>
<td>$2S_2$</td>
<td>$2S_1 + 2S_2$</td>
<td>$2S_1 + D_{1/2}$</td>
</tr>
</tbody>
</table>

Table 4.6: Electric Dipole selection rules in $C_{3v}$ and $D_{3h}$ symmetry. $\sigma$ represents in plane transitions while $\pi$ represents out of plane transitions.

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E_{1/2}$</th>
<th>$E_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$</td>
<td>$\sigma, \pi$</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>$E_{3/2}$</td>
<td>$\sigma$</td>
<td>$\sigma, \pi$</td>
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<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$D_{1/2}$</th>
<th>$2S_1$</th>
<th>$2S_2$</th>
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<tbody>
<tr>
<td>$D_{1/2}$</td>
<td>$\sigma$</td>
<td>$\sigma, \pi$</td>
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<tr>
<td>$2S_1$</td>
<td>$\sigma$</td>
<td>$\pi$</td>
<td>$\sigma$</td>
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<tr>
<td>$2S_2$</td>
<td>$\sigma, \pi$</td>
<td>$\sigma$</td>
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</tbody>
</table>

In the susceptibility, these extra peaks lie close to the energies predicted by the susceptibility without SOC. It is important to take care when dealing with selection rules described by double groups because double groups may allow some transitions that are prohibited by the single groups. Then such selection rules must be discarded. One such example is the $\pi$-transition for $X$-vacancy. In the absence of SOC the $\pi$-transition is allowed only between states with the IRs $E$, i.e. $E \otimes A_1 \otimes E = A_1 \oplus A_2 \oplus E$; this transition is not allowed since orbitals of the IR $E$ exist above the Fermi level only. In the presence of SOC the $\pi$-transition is allowed by the double group, i.e. $E_{1/2} \otimes A_1 \otimes E_{3/2} = A_1 \oplus A_2 \oplus E$, but is not seen in the susceptibility including SOC. This can be understood as the artefact of double groups since $\pi$-transitions are prohibited in the absence of SOC.

As a final note, as mentioned earlier, all samples are geometrically optimized before performing electronic calculations. Geometrical optimization may break certain symmetries and can affect certain selection rules or can result in concealing of some of the resonances.
Figure 4.11: Band structures without a) and with SOC b) for WS$_2$. The mapping of the LDS from the band structure without SOC to the band structure with SOC follows the mapping of the single group IRs to the double group IRs including spin, as explained in Table 4.5.

Conclusion

In this paper we have provided numerical and analytical descriptions of electronic and optical properties of SL TMDCs in the presence of VDs. We have shown that the presence of LDS gives rise to sharp transitions both in $\chi_\parallel$ and $\chi_\perp$. In order to understand these transitions, odd states need to be considered in addition to even states. A central result of our paper is that group theory can be used to derive strict selection rules for the optical transitions, which are in excellent agreement with the susceptibility calculated using the Kubo-Greenwood formula using the DFT orbitals. SOC induced splitting is observed in LDS and is seen to be larger for VDs in WX$_2$ than in MoX$_2$. Interestingly, our findings suggest magnetic properties of MoSe$_2$ in the presence of Mo vacancy, which may be enhanced by increasing the density of defects. In order to provide a
qualitative explanation of the existence of LDS, we performed analytical calculations based on the TBM and 2D Dirac formulation. All these results considerably improve the understanding of VDs in SL TMDCs and should benefit their potential applications in optoelectronic and nanoelectronic devices.
CHAPTER 5: ROOM-TEMPERATURE SUPERPARAMAGNETISM DUE TO GIANT MAGNETIC ANISOTROPY IN MoS DEFECTED SINGLE-LAYER MoS₂

Room-temperature superparamagnetism due to a large magnetic anisotropy energy (MAE) of a single atom magnet has always been a prerequisite for nanoscale magnetic devices. Realization of two dimensional (2D) materials such as single-layer (SL) MoS₂, has provided new platforms for exploring magnetic effects, which is important for both fundamental research and for industrial applications. Here, we use density functional theory (DFT) to show that the antisite defect (MoS) in SL MoS₂ is magnetic in nature with a magnetic moment of $\mu \approx 2\mu_B$ and, remarkably, exhibits an exceptionally large atomic scale MAE $= \varepsilon_\parallel - \varepsilon_\perp$ of $\sim 500$ meV. Our calculations reveal that this giant anisotropy is the joint effect of strong crystal field and significant spin-orbit coupling (SOC). In addition, the magnetic moment $\mu$ can be tuned between $1\mu_B$ and $3\mu_B$ by varying the Fermi energy $\varepsilon_F$, which can be achieved either by changing the gate voltage or by chemical doping. We also show that MAE can be raised to $\sim 1$ eV with n-type doping of the MoS₂:MoS sample. Our systematic investigations deepen our understanding of spin-related phenomena in SL MoS₂ and could provide a route to nanoscale spintronic devices.

Introduction

Single atom magnets adsorbed on the surface of nonmagnetic semiconductors has attracted a great deal of attention over the past few years, as they are potential candidates for the realization of ultimate limit of bit miniaturization for information storage and processing [168, 169, 170, 171, 172].

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Superparamagnetsim, usually dominating the magnetic behavior of a single atom magnet, has its origin in the magnetic anisotropy energy (MAE), which measures the energy barrier for flipping the spin moment between two degenerate magnetic states with minimum energy. One of the key factors that limits the performance of nanomagnetic devices is thermal fluctuations of magnetization that eventually randomize the direction of the magnetic state. This loss of information can be prevented by either lowering the operating temperature or by increasing the MAE. It has been shown experimentally that Ho atoms on the surface of MgO exhibit a magnetic remanence up to a temperature of 30 K, corresponding to 2.5 meV, and a relaxation time of 1500 s at 10 K [173]. In Ref. [174] it has recently been demonstrated experimentally that it is possible to read and write a single bit of information using the magnetic state of individual Ho atoms adsorbed on MgO. Remarkably, Ho atoms retain their magnetic information over many hours at 1.2 K. It is therefore highly desirable to engineer materials with as large as possible MAEs to produce stable magnetization above room temperatures. It has also been shown that adatoms of Co, Ru and Os on the surface of MgO shows MAE $\sim 100$ meV [175, 176]. All these efforts require deposition of transition metal atoms on the surface of non-magnetic semiconductors, such as MgO. Here, by using density functional theory (DFT) we show that an exceptionally large MAE $\sim 500$ meV can be observed in SL MoS$_2$ in the presence of an antisite (Mo$_S$, Mo replacing S) defect.

The concept of MAE, which is a preferential spatial orientation of magnetization, is not relevant in an individual isolated atom [177, 178], i.e., magnetic moments freely rotate in any direction without energy cost (Fig. 5.1(a)). However, for an adsorbed or impurity atom, crystal field effects localize the electrons to the directional bonds and effectively quench the orbital motion. SOC tries to restore partially this quenching of orbital angular momentum and ultimately leads to magnetic anisotropy.

Two dimensional (2D) materials are generally categorized as 2D allotropes of various elements or compounds, in which electron motion is confined to a plane such as graphene, phosphorene and SL MoS$_2$. Apart from their fascinating electronic and optical properties, 2D materials are very
Figure 5.1: a) Schematic diagram explaining perpendicular MAE, $\varepsilon_\parallel = \varepsilon_\perp$. For an individual atom (left) magnetization vector has the same energy for in-plane and out-of-plane directions of magnetization vector i.e. MAE = 0. While for magnetically anisotropic material (right) energy is required for switching the magnetization vector from out-of-plane to in-plane direction, i.e. MAE $\neq$ 0. b) Structure of pristine MoS$_2$ with a lattice constant of 3.161 Å. c) Band structure of pristine SL MoS$_2$, showing direct band gap of 1.76 eV at K point with SOC of 147 meV. d) Spin-polarized density of states of pristine SL MoS$_2$.

attractive for spintronic applications [179, 180, 181, 182, 183, 184, 185].

From a technological perspective 2D materials have advantages that can be employed in magnetic and spintronic devices. First, 2D materials provide an excellent control over carrier concentration through gate voltage. Secondly, it has been shown that carrier density in 2D materials is relatively stable against thermal fluctuations [12].

SL MoS$_2$ is a direct band gap semiconductor with considerable SOC ($\sim$150meV) that originates from the d-orbitals of heavy Mo atoms and due to the lack of inversion symmetry. High quantum efficiency [105, 106], acceptable value for the electron mobility [186, 187] and low power dissipation [188, 189], makes MoS$_2$ a candidate material for future electronic devices. Despite its success as a fascinating SL semiconductor, magnetism in MoS$_2$ has remained almost unexplored.

Different fabrication techniques, such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and mechanical exfoliation, have been used to produce wafer scale chunks of MoS$_2$. In Ref. [190] it has been shown that the abundance of defects present in MoS$_2$ depends on the fabrication method. In particular, the large abundance of Mo$_S$ defects has been observed in PVD-grown MoS$_2$. Although Mo$_S$ defects have been explored both experimentally and theoretically in terms
of the electronic structure [190, 191], a comprehensive investigation regarding magnetic behavior is still missing.

Here, we present a comprehensive study based on DFT calculations to show that MoS defects are magnetic in nature. In particular, we show that a sizeable localized magnetic moment ($\mu \sim 2\mu_B$) is associated with an MoS defect in MoS$_2$. In addition, $\mu$ can be tuned by changing the carrier concentration (or Fermi level), which can be achieved either by gate voltage or by doping. Remarkably, we show that antisite defects in MoS$_2$ possess exceptionally large MAE. Our calculations reveal that MAE originates from the combined effect of strong crystal field and SOC in MoS$_2$. This large value of MAE will be of major interest for applications in which the axial states representing an information bit need to be protected from thermal fluctuations at room temperature.

Numerical Results

All numerical calculations have been carried out using DFT and with the use of Perdew-Burke-Ernzerh (PBE) generalized gradient (GGA) parametrization for exchange-correlation functional. Both spin-polarized and relativistic SOC calculations are performed. The sampling of the Brillouin zone was done for a supercell with the equivalent of a $35 \times 35 \times 1$ Monkhorst–Pack k-point grid for the MoS$_2$ primitive unit cell with a cutoff energy of 300 Ry. For all calculations, structures are first geometrically optimized with a force tolerance of 0.005 eV/Å. The calculations are implemented within Atomistic Toolkit [121]. We first obtain the results for the band structure and the density of states for pristine MoS$_2$, as shown in Fig. 5.1(c) and (d), respectively. Band gaps, SOC and lattice constant (3.161 Å) values for MoS$_2$ are in good agreement with previously reported values [13, 14]. The curves of DOS (Fig. 5.1(d)) for spin-up and spin-down electrons are totally symmetric and the Fermi level is located in the band gap region, suggesting that pristine MoS$_2$ is a nonmagnetic semiconductor.
For the MoS\textsubscript{2} defect calculations, we consider a 7×7×1 supercell with an edge length of 23.03 Å[see Fig. 5.2(a)]. The point group of MoS\textsubscript{2} with Mo\textsubscript{S} defect is C\textsubscript{3v} and it remains preserved after geometrical optimization. The magnetic energy gain $\Delta\varepsilon = 0.55$ eV, which is the difference in ground states energy $\Delta\varepsilon = \varepsilon_{NSP} - \varepsilon_{SP}$ between the non-spin-polarized (NSP) and spin-polarized (SP) calculations, indicates that the paramagnetic phase is stable well above room temperature. To visualize the magnetic properties resulting from the MoS\textsubscript{2} defect we plot the SP DOS (Fig. 5.2(b)) corresponding to the configuration shown in Fig. 5.2(a). Fig 5.2 (b) shows a significant change in the spin-up and spin-down total DOS (grey) as compared with pristine MoS\textsubscript{2} (Fig 5.1(d)). To understand the origin of this change, we plot the SP projected DOS at the MoS\textsubscript{2} atom (Fig. 5.2(b)), which shows that SP is induced mainly due to the MoS\textsubscript{2} defect. For further illustration we show the results for the SP isosurface and the Mulliken Population (MP) [192] analysis [Fig. 5.2 (c)]. Fig. 5.2(c) shows that magnetic moment resides mainly on the MoS\textsubscript{2} atom, decays sharply, and becomes negligibly small beyond a few lattice constants. Magnetic moment associated with MoS\textsubscript{2} defect in MoS\textsubscript{2} is found to be 2.04$\mu_B$. When an impurity atom is put into a crystal environment, crystal field effects break the orbital degeneracies of the impurity atom. An MoS\textsubscript{2} defect in MoS\textsubscript{2}
sees a trigonal crystal field [Fig. 5.3 (a)], for which the energy level diagram is shown in Fig. 5.3(b). The crystal field splitting associated with the $C_{3h}$ symmetry seen by the Mo$_S$ defect lifts the degeneracy of the d-orbitals of the Mo$_S$ defect and splits them into three multiplets $e'$ ($d_{x^2-y^2}$ and $d_{xy}$ orbitals), $e''$ ($d_{xz}$ and $d_{yz}$) and $a'_{1}$ ($d_{z^2}$). The exchange interaction then leads to further splitting for the states with the opposite spins. The total spin should be governed by the unpaired spin counts according to Hund’s rules. In solids the Fermi level plays a decisive role in populating or depopulating certain atomic levels. Hund’s rules together with the position of the Fermi level predict a magnetic moment of $2\mu_B$, which is an excellent agreement with the values obtained by means of our numerical results (Fig. 5.2(c)).

The 2D nature of MoS$_2$ provides the possibility of gating and thereby controlling both the electrical and magnetic properties by tuning the carrier density. The Fermi level of 2D materials can be shifted by changing the gate voltage or by doping. It has been shown that [12, 193] substitutional doping with the S atom replaced by a Cl (P) atom leads to n(p)-type doping in SL MoS$_2$. To develop a connection between magnetic moment and carrier density, we consider a $7\times 7\times 1$ supercell containing an Mo$_S$ defect and a substitutional Cl (P) atom as an n(p)-type dopant. We find that the magnetic moment due to an Mo$_S$ defect can be increased to $3\mu_B$ or decreased to $\sim 1\mu_B$ by raising or lowering the Fermi level, respectively. The tunability of the magnetic moment by electrical means is highly desirable from fundamental and technological perspectives, especially in view of recent developments in magnetoelectronics and spintronics [194, 195, 196, 197].

In Fig. 5.2 (d) we plot the magnetic moment vs various defect densities. It can be seen that the magnetic moment does not change for different concentrations of Mo$_S$ defects, which shows that the magnetic moment is localized and does not interact with neighboring defects. Therefore there is no ferromagnetic or antiferromagnetic ordering.

The MAE value is calculated by employing a two-step process. First, a Kohn-Sham based calculation with collinear electron density and without SOC corrections is performed in order to obtain a self-consistent ground state electronic charge density. In the second step, the obtained charge
density is used as an input for the non self-consistent SOC and non-collinear calculations with varying orientation of the magnetic moments. We consider two magnetization directions, i.e. in-plane (∥) and out-of-plane (⊥) to the 2D sheet of MoS_2. The energy difference $\epsilon_\parallel - \epsilon_\perp$ calculated by using SGGA+SOC calculations shows that the MAE can be as large as 550 meV ($S = 1$) per MoS defect, with highly preferential easy axis pointing out-of-plane. It is well known that higher values of magnetization lead to larger anisotropy. SGGA+SOC calculations for an n-doped MoS_2:Mo_S sample (Fig. 5.4(a)) show that the perpendicular MAE can be as large as 980 meV ($S = 3/2$). It is important to mention that our calculations show that there is no preferential in-plane orientations of the magnetization, which means that our system is described by an easy axis only. Zero field splitting Hamiltonian for a single atom magnet can be written as

$$\hat{H} = D(\hat{S}_z^2 - \frac{1}{3}S(S+1)), \quad (5.1)$$

where $D$ is related to the unquenched orbital angular momentum along the local axial direction of the magnetic ion. If $D < 0$ axial spin states are preferred over the planar ones, which means that the spin is aligned with respect to the $z$-axis, defining the easy axis. For $S = 1$ and $S = 3/2$ the corresponding level splittings are $|D|$ and $2|D|$, respectively. This simplified model fits the

Figure 5.3: Trigonal symmetry (left) seen by an antosite atom. Schematic representation of d level splittings of Mo_S atom (right) due to the crystal field with C_3(h) point symmetry and exchange interaction.
numerical results for a value of $D = -510$ meV with deviations of ±40 meV.

To investigate the effects of SOC on the magnetization direction, we plot band structures in the presence of SOC, with in-plane and out-of-plane magnetization directions in Fig. 5.5. Fig. 5.5(a) and (b) show that the influence of the SOC is significantly larger for $M\parallel \hat{z}$ than for $M\parallel \hat{x}$. More specifically, Kramers degeneracy, which arises due to time reversal symmetry, is preserved for $M\parallel \hat{x}$, while it is broken for $M\parallel \hat{z}$. This contrast in the band structures can be linked to the MAE of the Mo$_5$ atom. It is well known that magnetic ordering such as ferromagnetism or more related (in the context of single ion) superparamagnetism, breaks the time reversal symmetry, which in turn lifts the Kramers degeneracy. Our DFT calculations reveal that for $M\parallel \hat{x}$ Kramer doublets remain degenerate, indicating paramagnetism, while for $M\parallel \hat{z}$ Kramers degeneracy is lifted, which is due to superparamagnetism. The large energy barrier between out-of-plane and in-plane magnetization directions shows that superparamagnetism is more stable than paramagnetism well above room temperatures.

Figure 5.4: Electron difference density $\rho_\uparrow - \rho_\downarrow$ for n-doped (left) and p-doped (right) with a doping concentration of $32 \times 10^{12}$cm$^{-2}$. Green(red) circle shows Cl(P) atoms. MP values (numbers) are also shown.
Analytical Modeling

We see that SOC splits the electronic states for different orientations of the magnetization, thereby creating the large anisotropy. To understand up to what extent this can be explained analytically, we present a simple analytical model [198] that systematically considers all the essential factors contributing to the MAE, i.e. the crystal field effect $\hat{H}^{\text{cry}}$, the exchange field effect $\hat{H}^{\text{exch}}$, and the SOC $\hat{H}^{\text{SOC}}$. The simplified model Hamiltonian can be written as Appendix A

$$\hat{H} = \hat{H}^{\text{cry}} + \hat{H}^{\text{exch}} + \hat{H}^{\text{SOC}}. \quad (5.2)$$

To highlight the essential features, we only consider the d−orbitals of the Mo$_S$ atom. In crystal field theory the key factor is to find an expression for the field produced by point charges which possess a given symmetry. An Mo$_S$ atom sees a trigonal electrostatic environment due to the nearest neighbour (NN) Mo atoms of MoS$_2$. 

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Figure 5.5: Band structures of $7 \times 7 \times 1$ super cell of SL MoS$_2$ with Mo$_S$ defect including SOC with $M \parallel \hat{x}$ (left) and $M \parallel \hat{z}$ (right). Black lines show extended electronic states, colored lines show the localized defect states of Mo$_S$ atom.
The crystal field hamiltonian $\hat{H}^{\text{cry}}$ describing the electrostatic field produced by the NN Mo atoms, at Mo$_S$ site is $\sim Y_2^0$, where $l = 2$ and $m = 0$ are orbital and magnetic quantum numbers, respectively. The crystal field Hamiltonian lifts the d– orbital degeneracy of the Mo$_S$ atom by forming two doublets $d_{xy}/d_{x^2-y^2}(m = \pm 2)$, $d_{xz}/d_{yz}(m = \pm 1)$ and a singlet $d_{z^2}(m = 0)$, which is in agreement with our numerical results. Considering the fact that crystal field theory preserves the level splittings with respect to the degenerate d-orbitals of the isolated Mo atoms, i.e. $E_0 + 2E_1 + 2E_2 = 0$, the eigenenergies of the crystal field Hamiltonian can be written in the form of energy differences $\Delta_1$ and $\Delta_2$, as shown in Fig. 5.3.

For the exchange Hamiltonian we consider the spin quantization axis fixed (parallel to $\hat{z}$-axis). For magnetization $M || \hat{z}$

$$\hat{H}_{m'm's'ms}^{\text{exch}} = B_m, \quad m = m', \quad s = s' = 1/2,$$
$$\hat{H}_{m'm's'ms}^{\text{exch}} = -B_m, \quad m = m', \quad s = s' = -1/2,$$

(5.3)
where the subscript $m$ shows that the exchange splitting field $B_m$ depends on the magnetic quantum numbers (Fig. 5.3(b)). For $M \parallel \hat{x}$

$$\hat{H}^{exch}_{m'm's'ms} = B_m, \quad m = m', \quad s \neq s'.$$  \hfill (5.4)

The third contribution to the model Hamiltonian comes from the SOC. SOC is considered as the onsite interaction $\hat{H}^{SOC} = \xi \mathbf{L} \cdot \mathbf{S}$. The effect of the SOC inducing the splittings in energy levels can be obtained by diagonalizing the Hamiltonian (5.2) for $M \parallel \hat{x}$ and $M \parallel \hat{z}$. The values of the various parameters $\Delta_1, \Delta_2, B_0, B_1$ and $B_2$ are extracted from numerical calculations (Fig. 5.3), and the corresponding results are presented in Fig. 5.6. A pertinent feature of Fig. 5.6 is that the effect of $\xi$ is much weaker for in-plane magnetization $M \parallel \hat{x}$ than for the out-of-plane magnetization $M \parallel \hat{z}$, which is in agreement with our numerical results. Specifically, our simple analytical model shows that eigenenergies remain 2-fold degenerate (Kramers doublet) for sufficiently high values of SOC parameter $\xi$ for $M \parallel \hat{x}$, whereas degeneracy is completely lifted for $M \parallel \hat{z}$. The simple analytical model qualitatively explains the time reversal symmetry breaking for $M \parallel \hat{z}$, identifying the superparamagnetic state and also indicating that the MAE can be understood as the interplay between the crystal field, the exchange field, and SOC.

**Conclusion**

We have demonstrated that an Mo$_S$ defect in MoS$_2$ carries a magnetic moment of $\mu_B$, $2\mu_B$, and $3\mu_B$, which can be tuned by changing the position of Fermi level electrostatically. Remarkably, an Mo$_S$ defect in MoS$_2$ exhibits an exceptionally large MAE of 550 meV with out-of-plane easy axis. Our calculations reveal that this very large anisotropy is the combined effect of strong crystal field and SOC. We show that the MAE can be tuned up to $\sim 1$ eV with n-type doping, which allows for room-temperature operation of future magnetic memory devices based on single atomic defects.
CHAPTER 6: OPTICALLY ACTIVE POINT DEFECTS IN SL WSe\textsubscript{2}

Single photon emission lies at the heart of many applications in photonics, including optical quantum computing [199, 200] and quantum cryptography [201, 202, 203]. To make these applications practical, solid state single photon sources (SPSs), which can generate indistinguishable photons, are required. Efforts have been made to develop single photon sources based on single molecules [204], quantum dots and one dimensional materials [205]. SPS based on SL WSe\textsubscript{2} have been reported recently in a series of publications [77, 78, 79, 136]. It has been shown that long lived localized exciton states bound to defects [77] or impurities [136] in SL WSe\textsubscript{2} decay radiatively, thereby emitting antibunched single photons at constant time intervals due to the Pauli exclusion principle. The narrow line width of the emission spectra is a signature of the localized nature of the emission states. In single layer (SL) TMDCs, energetically favorable and most common types of defects are chalcogen (S, Se) vacancies [116, 206]. However, It has been observed [207] that in chemical vapor deposition (CVD) grown SL WSe\textsubscript{2}, the intrinsic defects are centered on the W sites instead of Se sites. This would indicate 4 possible defect structures: the W-vacancy (V\textsubscript{W}), the WSe\textsubscript{3} vacancy (V\textsubscript{WSe\textsubscript{3}}), the antisite defect with W being replaced by Se (Se\textsubscript{W}), and the Se\textsubscript{3} vacancy (V\textsubscript{Se\textsubscript{3}}) [207]. V\textsubscript{W} and Se\textsubscript{W} defects have D\textsubscript{3h} = C\textsubscript{3v} \otimes \sigma\textsubscript{h} symmetry whereas V\textsubscript{Se\textsubscript{3}} and V\textsubscript{WSe\textsubscript{3}} defects have C\textsubscript{3v} symmetry.

Here, by using density functional theory (DFT), we show that an antisite defect Se\textsubscript{W} (W replaced by Se) in WSe\textsubscript{2} leads to localized states within the band gap region, which in turn give rise to sharp optical transitions across the Fermi level and can be seen in the optical susceptibility. These transitions lie close in energy to the reported value [77]. We further obtain a radiative lifetime of 2.625 ns, which is in good agreement with observed value of 1.79 ns [77].

Our investigations also reveal that some transitions have exceptionally large radiative lifetimes of up to 1 ms.

Numerical Results

All numerical calculations have been carried out using DFT and with the use of local density approximation (LDA). The calculations are implemented within the Atomistic tool kit 2015.1 [121]. For all calculations, structures are first geometrically optimized to a force tolerance of 0.01 eV/Å. We first obtain the band structure and electric susceptibility of pristine WSe$_2$ and are shown in Fig. 6.1 (b) and (c), respectively. Band structures are calculated along the $\Gamma$ - M - K - $\Gamma$ path. It is well known that LDA underestimates the band gap for semiconductor materials. Our calculations reveal that for SL WSe$_2$ GGA gives an indirect band gap of 1.34 eV, which is contrary to experimental observations. That is why we work with LDA, which gives a direct band gap [208] of 1.62 eV with valence band splitting of 480 meV.
Figure 6.2: a) Defect structure, b) corresponding density of states and c) in-plane ($\chi_\parallel$) and out-of-plane ($\chi_\perp$) electric susceptibility of $V_W$, $Se_W$, $V_{Se_3}$ and $V_{WSe_3}$ defects in WSe$_2$. Shaded area in b) represents the density of states of pristine WSe$_2$. 

These values are found to be in good agreement with previously reported values [209]. Also, LDA is computationally less expensive and therefore allows us to perform DFT calculations on large supercells, corresponding to lower defect densities, which is desirable in order to suppress the inter-defect coupling between neighboring supercells. Bearing in mind the shortcomings of DFT in predicting the band gap of 2D materials, the theoretical value of the band gap through DFT is underestimated by 0.13 eV as compared with experimental value of 1.75 eV.

For defect calculations, we consider a $7 \times 7 \times 1$ supercell with an edge length of $\sim$23 Å, as shown in Fig. 6.1 (a). The Brillouin zone of the superlattice is sampled by a $5 \times 5 \times 1$ $k$-mesh grid.
Table 6.1: Transition rates (in units of sec$^{-1}$) between different localized defect states due to Se$_W$ defect in WSe$_2$.

| $\gamma$ | $|6\rangle$ | $|5\rangle$ | $|4\rangle$ | $|3\rangle$ | $|2\rangle$ | $|1\rangle$ |
|----------|--------------|--------------|--------------|--------------|--------------|--------------|
| $\langle -6 | 55.962      | $3.5091 \times 10^8$ | $1.0313 \times 10^{-3}$ | $5.3016 \times 10^8$ | $1.1029 \times 10^{-1}$ | $7.6916 \times 10^{-5}$ |
| $\langle -5 | 3.51 \times 10^8 | 55.968 | $5.30 \times 10^5$ | $1.03 \times 10^{-3}$ | $7.84 \times 10^{-5}$ | $1.11 \times 10^{-1}$ |
| $\langle -4 | 7.2 \times 10^{-2} | 8.15 \times 10^2 | 1.988 | $1.0287 \times 10^6$ | $1.2735 \times 10^5$ | $0.23467$ |
| $\langle -3 | 8.16 \times 10^2 | 7.199 \times 10^{-2} | 1.0288 \times 10^6 | 1.9883 | 0.3492 | $1.2733 \times 10^5$ |
| $\langle -2 | 26 | 1.6353 \times 10^5 | 1.9869 \times 10^{-4} | 9.3420 \times 10^{-4} | 3.9107 \times 10^5 | $8.7487 \times 10^{-5}$ |
| $\langle -1 | 1.64 \times 10^8 | 25.959 | 0.93790 | $2.0034 \times 10^{-4}$ | $8.75 \times 10^{-5}$ | $3.9054 \times 10^3$ |

It should be noted that the geometrical optimization preserves the trigonal symmetry associated with W-vacancy, W$_{Se3}$ and WSe$_3$ defects. However, C$_{3v}$ symmetry is broken for Se$_W$ defect, which relaxes to C$_{2v}$ symmetry after geometrical optimization. Later we will show that this symmetry breaking leads to important consequences. Our results are in agreement with the previously published results [207].

In fig. 6.2 we plot the imaginary part of the electric susceptibility of SL WSe$_2$ with V$_W$, Se$_W$, V$_{Se3}$ and V$_{WSe3}$ defects. It can be seen that the Se$_W$ defect leads to prominent sharp transition at 1.53eV in the in-plane component of the electric susceptibility, which lies close to the measured photon energy 1.67eV. The narrow line widths of optical transition for the Se$_W$ defect in WSe$_2$ indicates the presence of localized states. The other possible defects including V$_W$, V$_{Se3}$ and V$_{WSe3}$, do not any have significant optical response in the experimental wavelength regime. Thus our calculations suggest that the antisite Se$_W$ defect structure is most likely cause of the long lived excitonic states which leads to the single photon emission in WSe$_2$. To gain further insight into the nature of localized states, in Fig. 6.3, we plot the band structure of SL WSe$_2$ with Se$_W$ defect. It can be seen that localized states due to antisite Se$_W$ defect appear within the band gap region, which can gives rise to the subband gap optical absorptions or transitions across the Fermi level. Here we are interested in optical transition T between the localized states that lie close to
the band edges. this transition is alioed by the optical selection rules. The localized states staters transform according to the irreducible representations (IRs) of the symmetry group of the crystal in which defect resides, which is C\(_{2v}\) for Se\(_W\) defect. In-plane transition T is allowed by the electric dipole transistion rules, (A\(_1\)\(\otimes\)B\(_2\)\(\otimes\)B\(_2\) =A\(_1\)). It should be noted that localized defect states appear in the form of Kramer’s doublet due to the time reversal symmetry. The structural symmetry of the Se\(_W\) defect for relaxed structure is C\(_{2v}\), i.e., a two fold rotation along symmetry axis [010] and reflections about the perpendicular symmetry planes which contain the symmetry axis.

To further validate our findings we calculate the transition rates between different localized defect states across the Fermi level. Using Fermi’s golden rule for calculating the transition rate \(\gamma_{i\rightarrow f}^j\) between initial \(|i\rangle\) and final \(|f\rangle\) localized states, we obtain

\[
\gamma_{i\rightarrow f}^j = \frac{4\alpha}{3c^2m^2\hbar^2} \left| \langle i | p_j | f \rangle \right|^2,
\]

(details will be piublished somewhere else) where \(\varepsilon_i\) and \(\varepsilon_f\) are energies corresponding to the initial and final states \(|i\rangle\) and \(|f\rangle\), respectively. The matrix element \(\langle i | p_j | f \rangle\) is evaluated numerically by using the Bloch states obtained through DFT calculations. The transition rates \(\gamma^j\) are summerized in Table. 6.1. Here we use the notation \(\gamma^\parallel\) for in-plane (\(\gamma^x(y)\)) and \(\gamma^\perp\) (\(\gamma^z\)) for out-of-plane transition rates. The radiative lifetime \(\tau_{i\rightarrow f}\) between different localized states can be calculated as the inverse of transition rate, e.g. for transition T shown in Fig. 6.2, 6.3.

\[
\tau_{i\rightarrow f} = \frac{1}{\gamma_{|6\rangle\rightarrow|−5\rangle}} = 2.625 \times 10^{-9} \text{ s}
\]

This value is found to be quite close to the reported value of 1.79 ns [77]. Both the energy and the life time of optical transitioon T are in good agreement with reported values showing that antisite Se\(_W\) defect is responsible for single photon emission in SL WSe\(_2\).
Electron-hole exchange (EHE) interaction

In this section, we explain the co-linearly polarized biexcitonic decay observed in the photoluminescence (PL) spectra (with an energy difference of 45 meV) and exceptionally large decay time of 200 ns. The interband Coulomb exchange interaction, also known as the electron-hole exchange (EHE) interaction, leads to the fine structure splitting in the excitonic levels. EHE is stronger in SL materials due to confinement of the charge carriers [210]. This type of interaction has been widely used to explain the fine structure splittings observed in the optical spectra of quantum dots in GaAs/AlAs quantum wells. The EHE interaction depends on the geometry or symmetry of the defect structure and on external parameters such as the gate voltage. In particular the magnitude of the electron-hole exchange interaction can be reduced by increasing the gate voltage. For atomically thin semiconductors, sizeable electric field effects are also present due to interactions with the substrates. Charge carriers are usually accumulated at the semiconductor/insulator interfaces such as WSe$_2$/SiO$_2$ and WSe$_2$/hBN to equilibrate their chemical potential, resulting in significant modulation of PL emission spectra and the lifetimes of localized excitons [211, 212].
According to the methods of invariants the EHE interaction Hamiltonian describing the spin-spin coupling of electrons and holes is given by

\[
\hat{H}_{\text{exch}} = \sum_{x,y,z} (a_i J^e_i S^h_i + b_i (J^e_i)^3 S^h_i),
\]  

(6.3)

where \(a_i\) and \(b_i\) are coupling constants which depend on the symmetry of the structural defect, \(J^e_i\) and \(S^h_i\) are the total angular momentum of electrons and spin angular moment of holes, respectively.

Here we consider only the transition T between two-fold degenerate localized energy levels \(|\pm 3/2\rangle\) and \(|\pm 1/2\rangle\) with energies \(E_i\) and \(E_f\), respectively. Thus we have four degenerate excitonic states, \(|\pm 3/2, \pm 1/2\rangle\). Two of them are bright and two are dark exciton states. The EHE interaction lifts the degeneracy between these excitonic states. The EHE Hamiltonian in \(|3/2, -1/2\rangle, |3/2, 1/2\rangle, |3/2, 1/2\rangle\) and \(|-3/2, -1/2\rangle\) basis has the following form

\[
\hat{H}_{\text{exch}} = \begin{bmatrix}
\Delta_0 & \Delta_1 & 0 & 0 \\
\Delta_1 & \Delta_0 & 0 & 0 \\
0 & 0 & -\Delta_0 & \Delta_2 \\
0 & 0 & \Delta_2 & -\Delta_0
\end{bmatrix},
\]  

(6.4)

with real constants \(\Delta_0 = \frac{3}{4}a_z + \frac{27}{4}b_z\), \(\Delta_1 = -\frac{3}{8}(b_x - b_y)\) and \(\Delta_2 = -\frac{3}{8}(b_x + b_y)\). For rotational symmetry of the defect structure \(a_x = a_y\) and \(b_x = b_y\), so that the Hamiltonian \(\hat{H}_{\text{exch}}\) becomes diagonal for bright excitons. In contrast, dark excitons can still be mixed through \(\Delta_2\). In this case, the parameter \(\Delta_1\), which removes the degeneracy between the two bright exciton states, is zero. For Se\(_{14}\) defect which is asymmetrical in the xy plane \(b_x \neq b_y\) leads to a coupling of \(|\frac{3}{2}, -\frac{1}{2}\rangle\) and \(|-\frac{3}{2}, \frac{1}{2}\rangle\).

The new bright exciton states are linearly polarized exciton states \((|\frac{3}{2}, -\frac{1}{2}\rangle \pm |-\frac{3}{2}, \frac{1}{2}\rangle)/\sqrt{2}\) which are split by an energy difference of \(2\Delta_1\). It should be noted that EHE interaction is also dependent on external electric fields and can be compensated for charged excitons.
In Ref. [213] it has been shown that the exciton emission of WSe$_2$ on a h-BN substrate is 13 times greater than that of WSe$_2$ on a SiO$_2$. Since the exciton emission of atomically thin materials strongly depends on doping level so therefore it has been suggested that WSe$_2$ on a h-BN substrate becomes more charge neutral than that on SiO$_2$. Here, we propose that the EHE interaction, which leads to co-linearly polarized photons in WSe$_2$ on SiO$_2$ substrates, is suppressed due the presence of charge impurities which lead to trion states on the defect site.

Ultra-long lifetimes

Now we turn our attention to the dark exciton states, which lie close in energy to the bright excitons. An exciton for which electron and hole spins align (anti-) parallel to each other is called a (bright) dark excitons. Dark excitons have orders of magnitude longer recombination time than bright excitons, usually determined by a tiny essential coupling to optically active states. The key role played by the neutral dark excitons on the optical properties of SL TMDCs has been illustrated in various PL experiments [214, 215, 216]. In ref. [217] it has been shown that the lifetime of the
dark excitons is two orders of magnitude longer than the lifetime of the bright excitons in WSe$_2$.

We see a similar trend in our experimental results. Experimentally, two different radiative times can be seen, differing by two orders of magnitude, i.e. $\sim 2$ nsec and 200 nsec. In addition, long lived excitonic states are comparatively lower in count than short lived excitonic states. Lower count and longer lifetimes indicate that these transitions are mediated by dark excitons. Finally we present a simple toy model to model the experimental results. We consider a three level system, thus we have two exciton states, a bright (blue) and a dark exciton (green), as shown in Fig. 6.4. The radiative rate equations for this system can be written as

\begin{align*}
\dot{\rho}_g &= \Gamma_{bg}\rho_b \quad (6.5) \\
\dot{\rho}_d &= \Gamma_{bd}\rho_b - \Gamma_{db}\rho_d \quad (6.6) \\
\dot{\rho}_b &= -\Gamma_{db}\rho_b - \Gamma_{dg}\rho_b + \Gamma_{db}\rho_d \quad (6.7)
\end{align*}

where different $\rho$'s are normalized level populations so that at any given instant of time $\rho_b + \rho_d + \rho_g = 1$, and $\Gamma$'s are decay rates, as shown in Fig. 6.4 (a). We solve Eq. 6.5 with initial conditions $\rho_b(0) = 2/3, \rho_d(0) = 1/3, \rho_g(0) = 0$. The ground state population as a function of time is shown in Fig. 6.4(b).

Conclusion

We conclude on the basis of the DFT results and semi empirical modelling that the antisite defect Se$_{1W}$ is the possible origin of single photon emission in SL WSe$_2$. Our findings show sufficient agreement with the observed results. Specifically, we are able to reproduce approximately the energy levels corresponding to the observed absorption and also the life time of single photon emitters. Lastly, we present a simple toy model based on rate equations which correctly reproduces
the observed two different life times for photon emission, giving rise to the observed biexponential decay. Our findings will open up the possibility for a wide range of optical quantum computing applications on a single material platform.
APPENDIX A: CRYSTAL FIELD HAMILTONIAN (TRIGONAL SYMMETRY)
We derive here the crystal field Hamiltonian for trigonal symmetry (Fig. A.1). The contribution of the surroundings point charges (Mo atoms, Fig. A.1) to the electron potential energy at Mo\textsubscript{S} site can be expressed as

\[ V_{CF} = \sum_{i=1}^{3} \frac{Z e^2}{|\vec{r} - \vec{R}_i|} \]  

(A.1)

where \( \vec{r} \) is the electron coordinate and \( \vec{R}_i \) are the position vectors of the neighboring point charges. With the help of Mathematica [218] we can write down the expression for the crystal field Hamiltonian

\[ V_{CF} = C_0 + C_1 \rho Y_1^0 + C_2 \rho^2 Y_2^0 + \rho^3 [C_3 Y_3^0 + C_3' (Y_3^{-3} + Y_3^3)] + \rho^4 [C_4 Y_4^0 + C_4' ((Y_4^{-3} + Y_4^3))] + ..., \]

(A.2)

where \( \rho = r/\sqrt{R^2 + P^2} \) and \( Y_{lm} \) are the spherical harmonics with orbital angular momentum quantum numbers \( l \) and \( m \). The expansion coefficients \( C_j, j = 0, 1, 2, ... \) can be adjusted to fit the DFT results. Here we use \( d \)-orbitals of the Mo\textsubscript{S} atom, i.e. \( d_{x^2-y^2} = (Y_2^{-2} + Y_2^2)/\sqrt{2}, d_{xy} = i(Y_2^{-2} - Y_2^2)/\sqrt{2}, d_{z^2} = Y_0^0, d_{xz} = (Y_2^{-1} + Y_2^1)/\sqrt{2} \) and \( d_{yz} = i(Y_2^{-1} - Y_2^1)/\sqrt{2} \).

Figure A.1: Trigonal symmetry seen by the Mo\textsubscript{S} atom. The origin is set at the Mo\textsubscript{S} atom. One of the Mo atom is set at x-axis and the coordinates of the 2 and 3 atoms are obtained through rotation of coordintes.
Spherical harmonics with odd magnetic quantum numbers do not contribute, thus $V_{CF} \sim \rho^2 Y_2^0$ in lowest order. The matrix elements of the $V_{CF}$ between different $d$-orbitals may be written as

$$
\hat{H}^{\text{cry}}_{mm'} \sim \int \psi^*_{nl}(r) \rho^2 \psi_{nl}(r) r^2 dr \int d_m(\theta, \phi) Y_2^0 d_{m'}(\theta, \phi) d\theta d\phi
$$

(A.3)

where $\psi_{nl}(r)$ is the radial function for MoS atom ($n = 4, l = 2$) and subscripts $m$ and $m'$ stand for different $d$-orbitals of the MoS atom. In this work we are able to omit the radial parts by fitting the appearing integrals, this spatial distribution may be omitted, which allows to simplify the treatment with any loss of accuracy. The diagonal matrix elements are given by

$$
\langle d_{z^2} | Y_2^0 | d_{z^2} \rangle = 145 \sqrt{5\pi}/512 = E_0,
\langle d_{x^2-y^2} | Y_2^0 | d_{x^2-y^2} \rangle = -45 \sqrt{5\pi}/1024 = E_2,
\langle d_{xy} | Y_2^0 | d_{xy} \rangle = -45 \sqrt{5\pi}/1024 = E_2,
\langle d_{xz} | Y_2^0 | d_{xz} \rangle = -15 \sqrt{5\pi}/256 = E_1,
\langle d_{yz} | Y_2^0 | d_{yz} \rangle = -15 \sqrt{5\pi}/256 = E_1.
$$

(A.4)

It should be noted that all the diagonal terms are zero with in the lowest approximation ($V_{CF} \sim Y_2^0$). Eq. (A.4) correctly reproduces the numerical results, i.e. two doublets $d_{x^2-y^2}/d_{xy}, d_{xz}/d_{yz}$ and a singlet $d_{z^2}$ with the correct energy sequence $E_0 > E_2 > E_1$.

Considering the fact that crystal field theory preserves the level splittings with respect to the degenerate $d$-orbitals of the isolated Mo atoms, i.e. $E_0 + 2E_1 + 2E_2 = 0$, the eigenenergies of the crystal field Hamiltonian can be written in the form of energy differences $\Delta_1 = E_2 - E_1$ and $\Delta_2 = E_0 - E_2$ with $E_0 > 0, E_1 < 0, E_2 > 0$, as shown in Fig. 5.3. The crystal field Hamiltonian may be written as
SOC is considered as the onsite interaction $\hat{H}^{SOC} = \xi L \cdot S$. Using the d-orbital bases $|d_{x^2-y^2}, \uparrow\rangle$, $|d_{xy}, \uparrow\rangle$, $|d_{xz}, \uparrow\rangle$, $|d_{yz}, \uparrow\rangle$ and $|d_{x^2-y^2}, \downarrow\rangle$, $|d_{xy}, \downarrow\rangle$, $|d_{xz}, \downarrow\rangle$, $|d_{yz}, \downarrow\rangle$, we get the SOC contribution to the Hamiltonians $\hat{H}^{SOC}(\vec{M} \parallel \hat{z})$ and $\hat{H}^{SOC}(\vec{M} \parallel \hat{x})$ as

$$
\hat{H}_{\text{cry}} = \begin{pmatrix}
\frac{1}{5}(2\Delta_1 - \Delta_2) & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{5}(2\Delta_1 - \Delta_2) & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{2}{5}(\Delta_1 + 2\Delta_2) & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{1}{5}(3\Delta_1 + \Delta_2) & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{5}(3\Delta_1 + \Delta_2)
\end{pmatrix},
$$
(A.5)

$$
\hat{H}^{SOC}(\vec{M} \parallel \hat{z}) = \begin{pmatrix}
0 & -2i\xi & 0 & 0 & 0 & 0 & 0 & \frac{\xi}{2} & i\frac{\xi}{2} \\
2i\xi & 0 & 0 & 0 & 0 & 0 & 0 & -i\frac{\xi}{2} & \frac{\xi}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}\xi}{2} & -i\frac{\sqrt{3}\xi}{2} \\
0 & 0 & 0 & -i\xi & \frac{\xi}{2} & -i\frac{\xi}{2} & \frac{\sqrt{3}\xi}{2} & 0 & 0 \\
0 & 0 & i\xi & 0 & i\frac{\xi}{2} & \frac{\xi}{2} & -i\frac{\sqrt{3}\xi}{2} & 0 & 0 \\
0 & 0 & \frac{\xi}{2} & -i\frac{\xi}{2} & 0 & -2i\xi & 0 & 0 & 0 \\
0 & 0 & 0 & i\frac{\xi}{2} & \frac{\xi}{2} & 2i\xi & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{\sqrt{3}\xi}{2} & i\frac{\sqrt{3}\xi}{2} & 0 & 0 & 0 & 0 \\
\frac{\xi}{2} & i\frac{\xi}{2} & \frac{\sqrt{3}\xi}{2} & 0 & 0 & 0 & 0 & 0 & -i\xi \\
-i\frac{\xi}{2} & \frac{\xi}{2} & i\frac{\sqrt{3}\xi}{2} & 0 & 0 & 0 & 0 & i\xi & 0
\end{pmatrix},
$$
(A.6)
\[
\hat{H}_{SOC}^{\text{SOC}}(\vec{M} \parallel \hat{x}) = \begin{pmatrix}
0 & 0 & 0 & \xi & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \xi & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{3}\xi & 0 & 0 & 0 & 0 & 0 \\
\xi & 0 & \sqrt{3}\xi & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \xi & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \xi \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{3}\xi & 0 \\
0 & 0 & 0 & 0 & \xi & 0 & \sqrt{3}\xi & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \xi & 0 & 0 & 0
\end{pmatrix}, \quad (A.7)
\]

respectively.
APPENDIX B: SPONTANEOUS EMISSION IN WSe$_2$
In this section we will drive the expressions for the transition rates between different localized defect states. Starting from Fermi’s Golden rule, the expression for the transition rate $\Gamma$ between initial $|i\rangle$ and final $|f\rangle$ states, can be written as

$$\Gamma = \frac{2\pi}{\hbar} \sum_{k,\sigma} |\langle f | \mathcal{H}_{ep} | i \rangle|^2 \delta(E_f - E_i)$$  \hspace{1cm} (B.1)

where $E_f$ and $E_i$ are energies of $|f\rangle$ and $|i\rangle$ states, respectively. $\mathcal{H}_{ep}$ is the light matter interaction hamiltonian

$$\mathcal{H}_{ep} = -\frac{e}{m} \hat{A} \cdot \hat{p}$$  \hspace{1cm} (B.2)

where, $\hat{p}$ is the momentum operator and $\hat{A}(\mathbf{r},t)$ is the vector potential. Working in Coulomb gauge i.e. $\nabla \cdot \mathbf{A} = 0$, $\mathbf{A}(\mathbf{r},t)$ can be written as

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{\sqrt{\varepsilon_0 V}} \sum_{\mathbf{r},s, q} \left[ u_{q,s}(t) e^{i\mathbf{q} \cdot \mathbf{r}} \mathbf{e}_q + u^*_{q,s}(t) e^{-i\mathbf{q} \cdot \mathbf{r}} \mathbf{e}_q^* \right]$$  \hspace{1cm} (B.3)

where $u_{q,s}(t) = A_q e^{-i\omega t}$ is the complex conjugate.

Quantization of Electromagnetic Field

Introducing the real canonical variables:

$$Q_{q,s}(t) = u_{q,s}(t) + u^*_{q,s}(t)$$

$$P_{q,s}(t) = -i\omega_q(u_{q,s}(t) - u^*_{q,s}(t))$$  \hspace{1cm} (B.4)
\[ \Rightarrow \mathcal{H}_{EM} = \frac{1}{2} \sum_{q,s} [P_{q,s}^2(t) + \omega_q^2 Q_{q,s}^2(t)] \]

\[ \Rightarrow A(r,t) = \frac{1}{2\sqrt{\varepsilon_0 V}} \sum_{q,s} [(P_{q,s}(t) + \frac{i}{\omega_q} Q_{q,s}(t))e^{iqr}e^{qs} + c.c] \]  

(B.5)

where, the operators \( \hat{Q}_{q,s}(t) \) and \( \hat{P}_{q,s}(t) \) satisfy the following commutation relations

\[ [\hat{Q}_{q,s}(t), \hat{P}_{q',s'}(t)] = i\hbar \delta_{qq'}\delta_{ss'} \]

\[ [\hat{Q}_{q,s}(t), \hat{Q}_{q',s'}(t)] = 0, [\hat{P}_{q,s}(t), \hat{P}_{q',s'}(t)] = 0 \]  

(B.6)

Defining creation and annihilation operators

\[ \hat{a}_{q,s}(t) = \frac{1}{\sqrt{2\hbar \omega_q}} [\omega_q \hat{Q}_{q,s}(t) + i \hat{P}_{q,s}(t)] = \hat{a}_{q,s}(0)e^{-i\omega qt} \]

\[ \hat{a}_{q,s}^\dagger(t) = \frac{1}{\sqrt{2\hbar \omega_q}} [\omega_q \hat{Q}_{q,s}(t) - i \hat{P}_{q,s}(t)] = \hat{a}_{q,s}^\dagger(0)e^{i\omega qt} \]  

(B.7)

with

\[ [\hat{a}_{q,s}(t), \hat{a}_{q',s'}^\dagger(t)] = \delta_{qq'}\delta_{ss'} \]

\[ [\hat{a}_{q,s}(t), \hat{a}_{q',s'}(t)] = [\hat{a}_{q,s}^\dagger(t), \hat{a}_{q',s'}^\dagger(t)] = 0 \]  

(B.8)

\[ \Rightarrow \mathcal{H} = \sum_{q,s} \hbar \omega_q (\hat{a}_{q,s}^\dagger(t)\hat{a}_{q',s'}(t) + \frac{1}{2}) \]  

(B.9)

and

\[ A(r,t) \cdot \hat{p} = \sum_{q,s} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_q V}} [\hat{a}_{q,s}e^{iqr}e^{qs} \cdot \hat{p} + \hat{a}_{q,s}^\dagger e^{-iqr}e^{qs} \cdot \hat{p}] \]  

(B.10)
using electric dipole approximation

\[ e^{-i\mathbf{q} \cdot \mathbf{r}} = 1 + i\mathbf{q} \cdot \mathbf{r} + \ldots \]  
\[ e^{-i\mathbf{q} \cdot \mathbf{r}} \approx 1 \]  
(B.11)

so that the matrix element can be written as

\[
\langle f | \mathcal{H}_{ep} | i \rangle = -\frac{e}{m} \langle \psi_f, n_{q \sigma} \sum_{q', s'} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega_q V}} [\hat{a}_{q', s'} \hat{e}_{q' s'} + \hat{a}^\dagger_{q', s'} \hat{e}^*_{q' s'}] \cdot \hat{p} | \psi_i, n_{q \sigma} \rangle
\]

(B.12)

Here, first term on the right in curly braces is for absorption while the second term is for emission. For spontaneous emission \( n_{q \sigma} = 0 \), so that eq. B.1 becomes

\[
\Gamma = \frac{2\pi}{\hbar} \left( \frac{e}{m} \right)^2 \sum_{k, \sigma} \frac{1}{\omega_q} | \hat{e}_{q \sigma} \cdot \langle \psi_f | \hat{p} | \psi_i \rangle |^2 \delta(E_f - E_i + \hbar \omega_q)
\]

(B.13)

Different directions are defined in fig. B.1, using fig. B.1 one can write

\[
\sum_{\sigma = 1, 2} | \hat{e}_{q \sigma} \cdot \langle \psi_f | \hat{p} | \psi_i \rangle |^2 = | \langle \psi_f | \hat{p} | \psi_i \rangle |^2 \sin^2 \theta
\]

(B.14)

Since here we are considering the transitions between localized states only, \( \psi_{f(i)} \) are localized defect states (LDS). Expanding LDS in terms of Bloch states:

\[
\psi_{nk} = \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(\mathbf{r})
\]

(B.15)

In the continuum limit i.e.

\[
\sum_q \rightarrow \frac{V}{(2\pi)^3} \int d^3q
\]

(B.16)
so that,

$$\Gamma = \frac{4\alpha}{3c^2m^2} \left| \varepsilon_i - \varepsilon_f \right| \left| \langle \psi_f | \hat{p} | \psi_i \rangle \right|^2$$  \hspace{1cm} (B.17)

Here $\alpha$ is the fine structure constant, $c$ is velocity of light and $m$ is the mass of electron.
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