Chapter 7

Electronic Structure, Topological and Optical Properties of PbS Nano-sheets

7.1 Introduction

Two dimensional materials which are atomically thin, have been studied extensively in the recent years due to their unique properties like high mechanical strength, high charge carrier density, piezoelectricity\(^1\) etc. Other important applications of two dimensional (2D) systems are in thin film solar cells, dye sensitized solar cells, photonic crystals, negative refractive index materials, light emitting devices, optical switching devices, quantum cascade lasers and thermoelectric devices. Though in the earlier time, it was thought that two dimensional systems are thermodynamically unstable, the discovery of graphene\(^2\) not only introduced new synthesis techniques for 2D systems based on chemical and mechanical exfoliation but also introduced a new area of research in material science, namely Dirac materials. These novel synthesis technique are explored to prepare other
anallogues of graphene, e.g. silicene,\textsuperscript{3,4} germanene,\textsuperscript{5} stanene,\textsuperscript{5} transition metal di chalcogenides (TMD),\textsuperscript{6} maxene,\textsuperscript{7} phosphorene\textsuperscript{8} and many others. Some of these 2D materials are free-standing (e.g. graphene, Mxene, TMDs) and others require a substrate (e.g. silicene). These systems can be metallic or semiconducting. A new class of insulating state, namely topological insulating state is hosted by some of these systems. "Topological insulators (TI)" are those where bulk is insulating and surface states are conducting. In these materials, conducting surface states are protected by time reversal symmetry (TRS) which are called as "$Z_2$ TI". Later Fu\textsuperscript{9} proposed a new phase of matter called as "topological crystalline insulator (TCI)"; where space group symmetry of the crystals replaces the role of TRS and protect the surface states. These systems must possesses four fold ($C_4$) or six fold ($C_6$) rotational symmetry as well as the mirror symmetry at the special high symmetry points in the Brilliouin Zone.

Recently lead chalcogenides have attracted attention due to their interesting properties. The carrier multiplication is an interesting phenomena where photo-excited hot charge carrier with excess energy larger than the band gap may also relax by exciting another electron across the band gap observed in quantum dots, nanorods of lead chalcogenides.\textsuperscript{10} M. Aerts \textit{et. al.}\textsuperscript{11} have reported that carrier multiplication is more effective in PbS nanosheets compared to quantum dots, nanorods and bulk lead chalcogenides materials. These lead chalcogenides are not only promising candidates for solar cell, but also have interesting properties like high permitivities, high carrier densities and play important role in many other applications. Wrasse and Schmidt\textsuperscript{12} have revealed that monolayer of [100] flat plane of PbSe shows TCI behavior due to the combined effect of crystalline symmetry and strong spin-orbit coupling.
Very recently it has been shown lead chalcogenide nanosheets, specially PbS nanosheets can be prepared by controlling the anisotropy by maintaining the precursor concentrations, synthesis temperature and in this process the shape of colloidal lead sulfide nanostructures can be tuned from spheres to stripes and finally into sheets. Monolayer of PbS also has been synthesized\textsuperscript{13} and it is shown that when PbS nanowires are assembled, they form nanosheet\textsuperscript{14} and the absorption spectra display step like behavior typical for 2-D materials. Though bulk PbS is a narrow gap semiconductor but for the reduced dimensions (1-D, 2-D) of PbS, band gap will enhance due to the quantum confinement effect. Experimentally\textsuperscript{14} it has been seen that absorption spectra of 2-D PbS sheet is in the visible region so it may be useful in optoelectronic devices. Recently S. Acharya et. al.\textsuperscript{14} have reported the synthesis of PbS nanosheets where [100] planes are flat and [110] planes are corrugated or buckled. There are only very few theoretical works on PbS. In a study\textsuperscript{15} of the electronic structure of PbS nanosheet using effective mass model it was shown that exciton binding energy in nanosheets is smaller than that of nanowires in agreement with experiment. Recently topological, valleytronic, and optical properties of (001) monolayer of PbS has been reported.\textsuperscript{16}

In view of the above we have systematically studied the electronic structure and optical properties with and without including spin-orbit coupling (SOC) for [100] and [110] surfaces of PbS. We have discussed topological band structure for these planes. We have further shown the relative stability between [100] and [110] planes and identified the probable reason for buckling of [110] plane of rock-salt PbS. Further we have studied the electronic structure for more than one layer of PbS, where the reduction of band gap upon increasing the thickness of the sheet is observed and we have also calculated the absorption spectra
7.2 Computational Method

Electronic-structure calculations are carried out in the framework of density functional theory (DFT) as implemented in Vienna \textit{ab-initio} simulation package (VASP).\textsuperscript{17,18} We have used plane-wave basis set with energy cutoff of 500 eV along with the projector augmented wave (PAW) method. Our calculations are performed with generalized gradient approximation with Perdew-Burke-Ernzerhof (PBE) functional.\textsuperscript{19} We have used Γ-centered k-mesh (8x8x1) for the Brillouin zone integration. Sufficient vacuum (24 Å) is introduced in the z direction to get rid of the periodic image in that direction. We have relaxed the atomic positions to minimize the Hellman-Feynman forces on each atom with the tolerance value of 0.01 eV/Å. In order to obtain insight about the topological band structure we have calculated the hopping parameters and onsite energies of the low-energy tight binding model of PbS retaining Pb-p and S-p states in the basis using the Nth order muffin-tin orbital (NMTO) downfolding method as implemented in the Stuttgart code.\textsuperscript{20–22}

7.2.1 Structural Details

For our study we have constructed two planes \([100]\) and \([110]\) from rock-salt bulk PbS with lattice constant \(a = 5.9362\ \text{Å}\). These planes are made periodic along x and y directions and confined along the z direction. It is to be noted that \([110]\) plane is corrugated or buckled and \([100]\) is flat as shown in Fig. 7.1, where the unit cell of both the planes contain 2 Pb and 2 S atoms.
7.3 Results and Discussions

To begin with, we have calculated the electronic structure of bulk rock-salt PbS. The band gap is calculated to be 0.35 eV using GGA-PBE exchange-correlation functional which is close to the experimental value (0.41 eV). It is to be noted that the band gap is direct at high symmetry "L" point in its first Brillouin zone as shown in Fig. 7.2(a). Pb is a heavy element, so it is pertinent that spin-orbit coupling (SOC) will play an important role. The band structure for bulk PbS including SOC is displayed in Fig. 7.2(b) and it is observed that due to the presence of SOC there is a splitting of the degenerate conduction bands. As a consequence the conduction bands (CBs) some closer to the valence bands (VBs) resulting in the reduction of band gap to a value of 0.02 eV. In the following we have investigated the electronic structure of [100] and [110] PbS monolayer.
7.3.1 Electronic and topological properties of [100] and [110] monolayer of PbS

[100] Monolayer of PbS

The structure of [100] monolayer of PbS is displayed in Fig. 7.1(a). This [100] plane is a flat plane and band structure of [100] without and with SOC are shown in Fig. 7.3(a) and (b) respectively. It is observed that [100] plane has direct band gap at the high symmetry "M" point having the value 0.57 eV without SOC. To know the character of valence and conduction band we have plotted the orbital projected band structure (fat bands) for [100] plane as shown in Fig. 7.4. The plot of the fat bands reveal that the valence band is primarily composed of S-p states, while the conduction band is dominated by Pb-p states. In the presence of SOC (see Fig. 7.3(b)), the direct band gap shrinks to 0.1 eV. From this observation it is expected that upon increasing the strength of SOC there can be band inversion and PbS may display topological crystalline insulator behavior similar to PbSe.\(^{12}\)

To investigate the topological properties of band structure for the [100] plane of PbS we have constructed a tight binding model Hamiltonian including the effect of SOC only in

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Figure 7.2: Band structure of bulk rock-salt PbS, (a) without SOC and (b) with SOC.
Figure 7.3: Band structure of monolayer of [100] PbS, (a) without SOC and (b) with SOC the Pb atoms. The Hamiltonian may be written as,

$$H_{\text{total}} = H_{\text{Kinetic}} + H_{\text{SOC}}$$

Where, $H_{\text{Kinetic}} = - \sum t_{ij} c_{i\sigma}^\dagger c_{j\sigma}$ and $H_{\text{SOC}} = \lambda \vec{L} \cdot \vec{S}$.

Suffix denotes corresponding part of the Hamiltonian. The $t_{ij}$, $c_{i\sigma}^\dagger$, $c_{j\sigma}$ are hopping parameter between i-th and j-th sites with spin $\sigma$, creation and annihilation operators respectively. $\lambda$ is the spin-orbit coupling parameter and $\vec{L}$, $\vec{S}$ are the orbital and spin momenta respectively.

The unit cell of monolayer of [100] plane of PbS is a square lattice (See Fig. 7.1) and it contains two inequivalent Pb atoms and two equivalent S atoms. The first Brillouin Zone is also a square and there exists four time-reversal invariant momenta (TRIM) points for the square lattice, which are "Γ" point (0,0), "M" point ($\frac{\pi}{a}$, $\frac{\pi}{a}$), and "X" points [($\frac{\pi}{a}$,0) or (0,$\frac{\pi}{a}$)]. It is observed from band structure for [100] plane that it has direct band gap at "M" point. The VBM and CBM have the contribution from S-3p and Pb-6p orbitals respectively. The plot of fat bands for [100] plane reveal that Pb-p$_z$ has the main contribution in CBM and S-p$_x$, S-p$_y$ have the contribution in VBM. So, the minimal basis set for the tight
Figure 7.4: Fat band of monolayer of [100] PbS. Circles and tri-angles describe the contribution Pb and S respectively.

The binding Hamiltonian consisted of Pb-\(p_y\), Pb-\(p_z\), Pb-\(p_x\), S-\(p_y\), S-\(p_z\), S-\(p_x\). The dimension of the Hamiltonian becomes 24×24 taking spin into account. The onsite SOC term takes the following form:

\[
\begin{array}{cccccccc}
\hat{S} & p_y \uparrow & p_z \uparrow & p_x \uparrow & p_y \downarrow & p_z \downarrow & p_x \downarrow \\
p_y \uparrow & 0 & 0 & i\frac{\lambda}{2} & 0 & -i\frac{\lambda}{2} & 0 \\
p_z \uparrow & 0 & 0 & 0 & i\frac{\lambda}{2} & 0 & -\frac{\lambda}{2} \\
p_x \uparrow & -i\frac{\lambda}{2} & 0 & 0 & 0 & i\lambda & 0 \\
p_y \downarrow & 0 & -i\frac{\lambda}{2} & 0 & 0 & 0 & -i\frac{\lambda}{2} \\
p_z \downarrow & i\frac{\lambda}{2} & 0 & \frac{\lambda}{2} & 0 & 0 & 0 \\
p_x \downarrow & 0 & -\frac{\lambda}{2} & 0 & i\frac{\lambda}{2} & 0 & 0 \\
\end{array}
\]

Such a model allows us to vary the strength of SOC for Pb atoms and examine whether there is band inversion upon increasing the strength of SOC by changing the value of \(\lambda\).

The results of our calculations are presented in Fig. 7.5. Fig. 7.5 reveals that with inclusion of SOC with different fraction, the band gap decreases and at a critical value of the SOC parameter when \(\lambda_c\) equals to 0.9 eV the VBM and CBM touches each other and when \(\frac{\lambda}{\lambda_c} \sim 1.10\) band inversion take place as shown in Fig. 7.5 and further increase of \(\lambda\) value
opens up a gap. This band inversion occur at the M point and we have an even number

![Band structure for different value of λ for monolayer of [100] sheet of PbS. Red circles and blue circles denote S-p and Pb-p contributions respectively.](image)

Figure 7.5: Band structure for different value of $\lambda$ for monolayer of [100] sheet of PbS. Red circles and blue circles denote S-p and Pb-p contributions respectively.

of M points on the 2D first BZ. In view of the fact this system cannot present protected edge states by time reversal symmetry because the band inversion are at momentum space mirror planes, so PbS [100] monolayer in the presence of substantial SOC behave as a topological crystalline insulator (TCI). So, we can say that monolayer of [100] plane of PbS is a topological crystalline insulator (TCI) similar to PbSe\textsuperscript{12} due to its crystalline ($C_4$) symmetry.

**[110] Monolayer of PbS**

We have next considered [110] monolayer of rock-salt PbS. Monolayer of [110] plane of PbS is a buckled plane as shown in Fig. 7.1. The band gap for [110] sheet is calculated to be 2.01 eV which is larger than bulk PbS due to the effect of quantum confinement. The band gap for [110] plane is also higher in comparison to [100] plane. The band structure of monolayer of [110] plane is depicted in Fig. 7.6 and it is observed that there is indirect band gap in between "M" to "Γ" point. From the plot of orbital projected band
structure (fat bands) as displayed in Fig. 7.7, it is observed that similar to [100], here also VBM and CBM are from S-p and Pb-p respectively. It is important to note that the band structure of [110] plane has less dispersion compared to [100] plane. Due to the reduction of dispersion the effective mass of the carriers enhances. Inclusion of SOC into [110] plane splits the degeneracy of the bands resulting in reduction of band gap to a value 1.80 eV as the conduction bands are placed close to the valence bands as shown in Fig. 7.6(b). In the same way as we did for [100] plane we have also calculated the band structure of [110] plane from a low energy tight binding Hamiltonian with different value of SOC parameter and it is observed that there is no sign of band inversion in the electronic structure for the [110] plane.

To investigate the origin of buckling of the [110] plane, we have calculated the electron localization function (ELF). The ELF is defined as follows.

\[ ELF = (1 + \left( \frac{D}{D_h} \right)^2)^{-1}. \]
where, \( D = \frac{1}{2} \sum |\nabla \phi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho} \) and \( D_h = \frac{3}{10} (3\pi^2)^{\frac{5}{3}} \rho^{\frac{5}{3}} \).

Where \( \rho \) and \( \phi_i \) are the electron density and Kohn-Sham wavefunctions. The iso-surface of ELF for [110] and [100] planes are shown in Fig. 7.8 (a) and (b) respectively. It is observed that symmetric distribution of ELF in [100] plane but asymmetric distribution of ELF in [110] plane. It is known that there is a lone pair of electrons in Pb atoms. It is observed from Fig. 7.8(a) that for [110] plane lone pair are directed perpendicular to the plane similar to (CsCl) structure of PbO and alpha-PbO structure as described by Watson et. al.\(^{23} \). In [110] plane, due to the displacement of Pb atoms in perpendicular direction, Pb-p\(_z\) orbitals interact with S-p orbital producing the asymmetric electron density around the Pb. In contrast, in [100] plane S-p orbitals interact with Pb-s orbitals only because symmetry does not allow for an interaction with Pb-p\(_z\). For this reason [110] is a buckled but [100] is a flat one. Further we have calculated the total energy per pair of PbS [100] and...
Figure 7.8: Iso-surface of electron localization function for (a) [110] and (b) [100] sheet. Pb and S atoms are indicated by grey and yellow colors respectively.

[110] plane (see TABLE 7.1). It is observed that [110] is energetically stable compared to [100] further confirming the stability of the [110] plane.

Table 7.1: Band gap and energy per pair of PbS for bulk, and, monolayer [110] and [100] sheets.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Relative Energy per pair of PbS (eV)</th>
<th>Band gap (eV)</th>
</tr>
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<tbody>
<tr>
<td>Bulk PbS</td>
<td>0.0</td>
<td>0.35</td>
</tr>
<tr>
<td>[110] sheet</td>
<td>+0.23</td>
<td>2.01</td>
</tr>
<tr>
<td>[100] sheet</td>
<td>+0.89</td>
<td>0.57</td>
</tr>
</tbody>
</table>

7.3.2 Role of Defects

We have also studied the electronic structure in presence of defects such as neutral vacancies of Pb, S, and doping of Sn at Pb sites in the most stable [110] monolayer of PbS. It is observed that in the presence of Pb vacancy (12.5 %), S-p bands are unoccupied and the value of band gap is decreased to 0.75 eV. The band gap remain indirect and it is from 'M'
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to 'Γ’ point which is however different from the pristine nanosheet. In case of S vacancy (12.5 %), band gap (0.587 eV) decreases further as some Pb-p states become occupied. Also, band gap become indirect from 'M' to 'Γ’ point. It is important to note that bulk PbS is a direct band gap semiconductor. We have substituted Sn for Pb atoms belonging to the same group as Pb in the periodic table from 12.5 % to 50 %, it is observed that we can tune the band gap within 2.1 eV to 1.87 eV by just doping Sn in these nanosheets which is also observed for PbS quantum dots.

7.3.3 Optical properties of mono-layer and multi-layers of PbS nano-sheets

Finally we have studied the optical properties of monolayer as well as bilayer and four layers of [100] and [110] plane of PbS. It is to be noted that the band gap of bilayers and four layers decreases with increasing thickness, which is due to the reduction of the confinement as the system is approaching to the bulk regime. This trend is in agreement with the earlier studies of PbS nanosheets. We have calculated absorption intensity (see

Figure 7.9: Band structure of [110] sheet (a) with Pb vacancy, (b) S vacancy.
Fig. 7.10) for the monolayer, bilayer and four layers of [100] and [110] planes of PbS. It is observed that absorption edges for mono to four layers of PbS are red-shifted due to the reduction of band gap due to the effect of quantum confinement. Here the most interesting fact is that absorption spectra (see Fig. 7.10) exhibits step like feature as one move from mono to four layers. The step like behavior is attributed to the 2D like constant DOS for the [110], [100] planes. The discontinuity between two constant energies seen in the steps occur due to the inter-subband transition. These transition follows the optical selection rule ($\delta n = 0$, n is the index of energy levels). Such step like feature is also seen in experiments confirming the 2D nature of the PbS sheets.

![Figure 7.10: Absorption Co-efficient of monolayer and multi-layers of [100] and [110] plane of PbS.](image)
7.4 Summary

We have studied the electronic structure and optical properties of [100] and [110] nanosheets using DFT within the GGA approximation. We have shown that monolayer of [100] plane of PbS is a topological crystalline insulator in presence of strong spin-orbit coupling and crystalline mirror symmetry. Further from our total energy calculations it is observed that monolayers of [110] are more favorable compared to monolayers of [100] with the former having larger band gap. We have found that asymmetric distribution of electron localization function is the probable reason for the buckling of [110] plane. We have also explored the electronic structure in the presence of defects in stable [110] plane and it is observed that due to the introduction of Pb and S vacancies the band gap reduces and become indirect. Further due to the doping of Sn in Pb site, we can tune the band gap in a wide range that was also shown earlier for PbS quantum dot. From the absorption spectra it is observed that absorption edges are red shifted from monolayer to bilayer to four layer of PbS nanosheets due to reduction of band gap. The optical absorption spectra display step like feature as expected for two-dimensional materials.


