CHAPTER 1

Introduction

This chapter begins with the introduction to concept of topology and its link to periodic systems in condensed matter theory. This is followed by thorough discussions highlighting the development of the subject and its contemporary status in terms of research and development. This chapter will clearly establish the motivation and objectives (which govern chapters 3, 4 and 5 of the thesis) with focus on the bulk and low dimensional materials, emphasising and identifying the existing caveats from the literature.

1.1 Concepts of Topology

Topological Insulators are a class of unconventional materials in condensed matter physics governed by the mathematical principles of Topology. Before we dwell deep into the thesis with our investigations of the topological materials, we would like to briefly introduce the concepts of Topology and how it translates into a governing principle in the investigation and exploration of topological materials.

Topology; is a branch of mathematics wherein objects are classified into spaces which are equivalent depending on the presence or absence of a *smooth* and *continuous* deformation between them.[1,2] From mathematical perspective, 'Homeomorphism' is one of the most common types of topological equivalence where, two spaces can transform into eachother without abrupt changes.[2] A trivial example is provided below (in illustrations 1.1, 1.2 and 1.3)

where, the english alphabets (A-Z) and different geometric shapes are grouped into equivalence sets/spaces based on the presence or absence of a continuous deformation amongst them.

$$\{A, R\}\{B\}\{C, G, I, J, L, M, N, S, U, V, W, Z\}\{D, O\}... \tag{1.1}$$

(1.2)

(1.3)

For example, it is evident from illustration 1.1 that, the alphabets 'A' and 'R' can be transformed into eachother through a smooth and continuous deformation making them topologically equivalent. However, 'A' or 'R' cannot be transformed under a smooth and continuous transformation into the alphabet 'B'. Similarly, we can observe the equivalence classes of different solid geometries presented in illustration 1.2 such as, circle, square, triangle etc. which can be transformed into eachother by varying the number of edges i.e., through smooth and continuous deformation. Such transformation is not possible between the solid objects (presented in illustration 1.2) and objects with hole (presented in illustration 1.3) which makes the two spaces topologically distinct.

This advanced mathematical method of topological distinction was implemented by David Thouless, Duncan Haldane, and Michael Kosterlitz to understand the physics in unconventional phases of matter such as, superconductivity, superfluidity and ultra-thin magnetic films.[3] This has had huge ramifications in the field of condensed matter physics opening up new avenues to explore matter in strange states for innovative applications, eventually earning them a Nobel prize in 2016.[4]

1.2 Topology in Condensed Matter

Explorations by Kosterlitz and Thouless were focused on the flat-lands so thin that they can be treated as two-dimensional matter whereas, Haldane focused on the edges where matter assumes the form of a thin thread which can be treated as one-dimensional.[4] Due to quantum confinement effects, the dynamics in these low-dimensional regimes is quite unusual. These regimes are quite unique, in the sense that, at macroscopic scales we are well versed with the phase transitions in matter as a function of temperature (for example,

phase transition of ice from solid > liquid > gas > plasma) however, in low-dimensional regimes these phase transitions were unexplored with matter assuming strange phases and unconventional behaviour (see Fig. 1.1 below).

For example, at absolute zero condition in low-dimensional regimes, unusual phenomena such as, unintrupted motion of particles and perpetually spinning vortices in fluid with zero viscosity crop-up which are associated with phenomena such as superconductivity and superfluidity respectively.[5–7] It was believed that, in low-dimensional matter even under conditions such as, ultra-cold temperatures of absolute zero, thermal fluctuations can give rise to disordered systems indicating towards the absence of phase transitions.[8] This understanding of matter and phase transition was challenged by Thouless and Kosterlitz in 1970s when they invented the *Kosterlitz-Thouless* (KT) transition which earned tremendous reputation for its novelty in the field of condensed matter physics.[9,10] This is a type of topological phase transition which is quite unique as compared to traditional phase transition observed in matter at macroscopic scales. Applying the concepts of topology to vortices in a thin layer of matter at ultra-cold temperatures, Kosterlitz and Thouless described a new phase transition. Under ultra-cold conditions, the vortices in a thin layer of matter form strongly correlated pairs and as the temperature increases, beyond certain critical temperature, these vortices drift apart from eachother in different directions (see Fig. 1.2 below). Such a phase transition in low-dimensional systems is known as the KT transition.[9,10] The underlying theory (which has been confirmed experimentally as well) is so versatile that it is applied in atomic and statistical physics as well making it a universal phenomena.

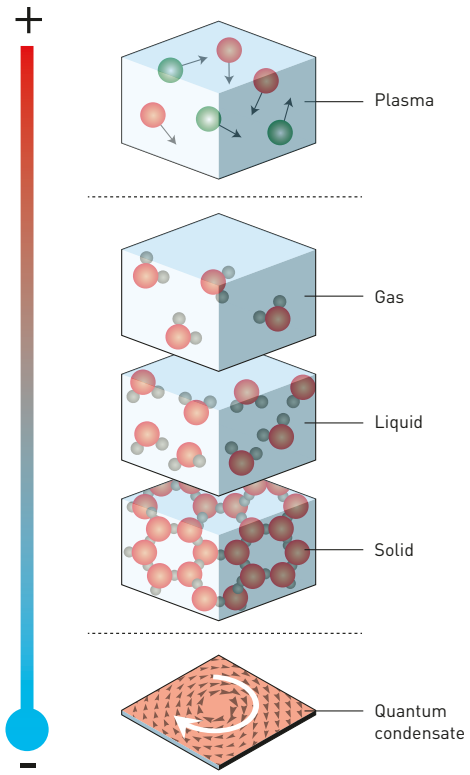

Figure 1.1: A schematic representation of phase transitions in matter at macroscopic scales as compared to the low-dimensional regimes as a function of temperature. *Adopted from The Royal Swedish Academy of Sciences, illustration by Johan Jarnestad.*

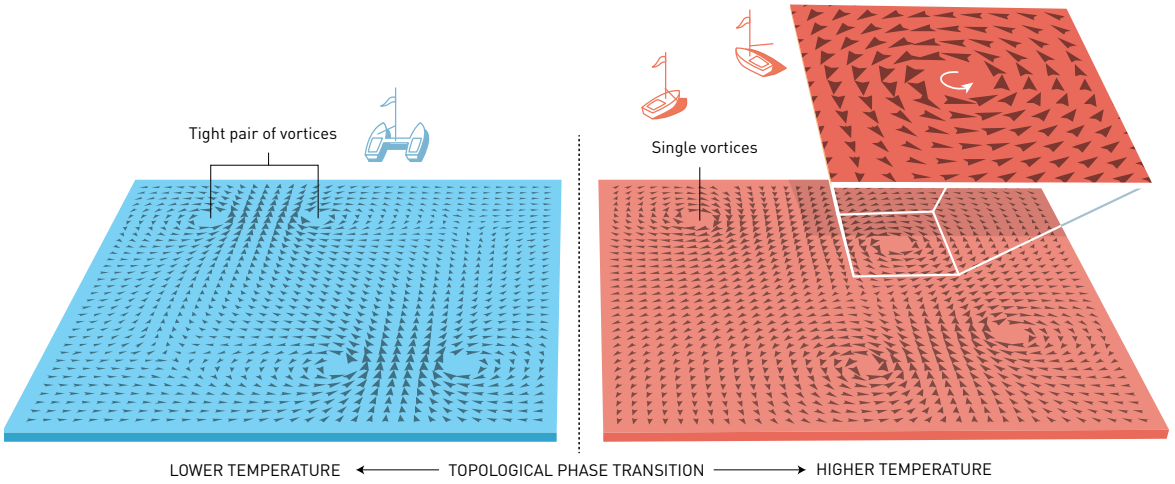

Figure 1.2: A schematic representation of the Kosterlitz-Thousless topological phase transitions as a function of temperature in thin layer of matter under ultra-cold conditions. *Adopted from The Royal Swedish Academy of Sciences, illustration by Johan Jarnestad.*

1.3 Topology and Quantum Hall Effect

Thouless and Haldane came together to developed a quantum mechanical theory which could be applied to determine the electrical conductivity of materials and understand phases of matter which cannot be identified by their pattern of symmetry breaking.[11–14] By mid 20^{th} century the scientific community in the field of condensed matter physics had a thorough understanding of the material properties such as electrical conductivity and its origin. However, there were certain unusual scanarios wherein the existing theories failed to provide a valid and logical explanation. For example, the discovery of quantum Hall effect by Klaus von Klitzing in 1980 generated a lot of curiosity amongst the physics community to understand the origin of the observed phenomena.[15] Klitzing investigated a sandwitch of thin conducting material between two semiconductors placed at ~ 2 K temperature and in a high magnetic field of the order of ~ 15 T. In such an arrangement, the electrical conductance assumed certain discrete integer values (n) with precision of the order of 10^{-9}, making it the most precise physical phenomena (as evident from Eq. 1.4).[15] The riddle was that, this phenomena existed irrespective of the variations in temperature, magnetic field and the impurities in semiconductor layers. Such physical phenomena could not be explained by the contemporary theories in 1980s.

$$\sigma_H = n\frac{e^2}{h} \tag{1.4}$$

Thouless applied the concepts of topology to address the unconventional phenomena of step-wise variation of electric conductivity at ultra-cold temperatures and under high magnetic

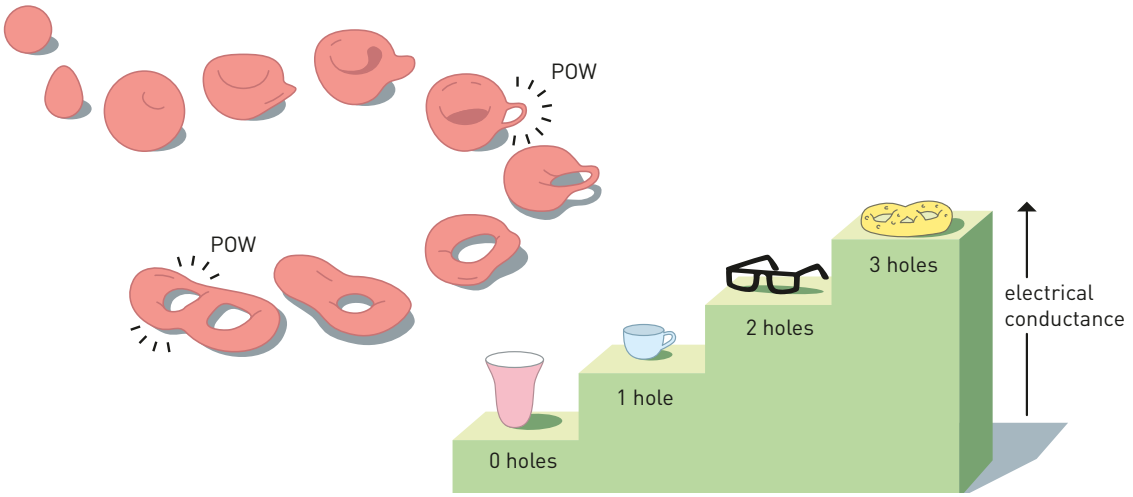

Figure 1.3: A schmatic representation of the analogy between the mathematical concept of topology and quantum Hall conductance where, the geometrical classification of object depends on the number of holes (which is necessarily an integer) and the electrical conductance which has integer dependence as evident from Eq. 1.4. *Adopted from The Royal Swedish Academy of Sciences, illustration by Johan Jarnestad.*

field observed in quantum Hall effect.[16–18] As discussed previously in section 1.1, topology pertains to equivalence between spaces wherein a smooth and continuous deformation persists amongst them. This analogy was applied to the experimentally observed quantum Hall effect which is schematically presented in Fig. 1.3 where the conductivity has integer variance. In other words, the topological quantum fluid of freely moving fermions in thin layer of material (which is sandwiched between two semiconductors) is quantised due to topology with unconventional behaviour along the boundaries. Eventually in 1988, Haldane proposed a model for graphene and discovered that, similar scenarios of topological quantum fuild can arise in thin layers of semiconductors even in the absence of magnetic field.[13]

Haldane investigated magnetic chain of atoms in certain materials and concluded that, these chains had distinct properties depending on the nature of atomic magnets i.e., odd or even depending on the spin.[12–14] He proposed and showed that, even and odd magnetic chains are topological and non-topological respectively. Similar to the topological quantum fluid, these properties exist along the edges where the terminals of a topological chain are governed by the spin along those sites which can be integer or half-integer in nature. This unraveled a novel phase of matter grouped as topological materials which were eventually observed not only in chains but also along the thin border layers and surfaces of bulk materials.

Over the years, collective efforts to investigate quantum flat-lands by Thouless, Haldane and Kosterlitz have led to the discovery and proliferation of topological materials into; topolo-

gical insulators, topological semi-metals, topological metals, topological superconductors etc.[3]

1.4 Topological Invariant

The highly precise nature of integer quantum hall effect motivated Robert Laughlin to explain the phenomena by using gauge invariance.[19] However, this did not give the complete understanding of the observed phenomena in real materials due to paradoxical results which was addressed by Thouless and colleagues.[11] This approach clearly established the role of topology in the observed physical phenomena. In case of quantum Hall effect, we have charged particles moving in a uniform magnetic field which is interpreted by neglecting the electron-electron interactions and by replacing the lattice potential with background positive charge. This scenario in materials was addressed by Landau who showed that, for a particular cyclotron frequency (as presented in Eq. 1.5), the energy of the system is quantized (as presented in Eq. 1.6) into degenerate states on macroscopic scales known as Landau levels such that, each state depends on the magnetic flux given in Eq. 1.7.[20,21] These Landau degeneracies are labelled in terms of crystal momentum since the translation symmetry in homogenous magnetic field is that of magnetic translations rather than the conventional transtional symmetry which breaks in a magnetic field. The resulting unit magnetic flux (presented in Eq. 1.7) persists in every lattice cell spanning the entire lattice of the material. Similar labelling can be done for eigenfunctions of an eigen state in the bandstructure i.e., the Landau levels can be associated with a vector in reciprocal lattice space. Therefore, the eigenfunction of n^{th} Landau state is presented as $u_{\vec{k},n}(\vec{r})$ in terms of the crystal momentum $\vec{k}$ in the irreducible brillouin zone.

$$\omega_c = \frac{eB}{m} \tag{1.5}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c \tag{1.6}$$

$$\phi_0 = \frac{h}{e} = \frac{2\pi}{e} \tag{1.7}$$

By using linear response theory an expression for conductance in terms of eigenfunctions can be obtained (as presented in Eq. 1.8) which depends on the *Berry* field strength ($\mathcal{B}$) (which can be expressed in terms of the *Berry* potential presented in Eq. 1.9 in terms of

eigenfunctions) with the integration being performed over the momentum space ($\vec{k}$) spanning the entire brillouin zone.

$$\sigma_H = \frac{e^2}{2\pi h} \sum_n \int_{\vec{k}\in BZ} d^2k \mathcal{B}(\vec{k}, n) \tag{1.8}$$

$$\mathcal{A}_i(\vec{k}, n) = i\langle u_{\vec{k},n} | \partial_{k_i} | u_{\vec{k},n} \rangle \tag{1.9}$$

Based on conventional theory of electromagnetism, such a vector potential (as in Eq. 1.9 above) is related to the *Berry* field strength as follows;

$$\mathcal{B}(\vec{k}, n) = \partial_{k_x} \mathcal{A}_y(\vec{k}, n) - \partial_{k_y} \mathcal{A}_x(\vec{k}, n) \tag{1.10}$$

Therefore, the integral presented in Eq. 1.8 represents a pseudo magnetic field over an enclosed geometry analogous to the case of a quantized magnetic monopole in electromagnetism. Eventually, it can be shown that, this *Berry* field strength has a finite value C_1 as presented in Eq. 1.11 which is known as the *first* Chern number (which happens to be an integer).[22]

$$\frac{1}{2\pi} \int_{\vec{k}\in BZ} \mathcal{B}(\vec{k}, n) = C_1(n) \tag{1.11}$$

This explicitly established the fact that, the extremely precise and robust nature of conductance observed in experiments originates from the mathematical condition presented in Eq. 1.11 which is independent of any sorts of perturbations, particle-particle interactions, magnetic impurities etc. This makes the Chern number a *topological invariant* which can only assume integer values owing to the mathematical constraints. As an extension to this, Thouless and his colleagues included the effects of lattice potential which was otherwise replaced by a smeared-out positive background charge. As a consequence, spliting of the Landau levels into sub-bands was observed which results in conductance same as that presented in Eq. 1.4. The major result of this effort by Thouless indicated towards the possibility of a quantum Hall effect in the absence of external magnetic field.[18]

Such a system was proposed by Haldane who realized that, on breaking the invariance under time-reversal symmetry can give rise to energy bands without Landau levels which are characterized by a non-zero *Chern* number.[13] This was implemented in graphene as a toy model where, the tight-binding approximation of fermions on a hexagonal lattice arrangement was

considered with inclusion of hopping between both; nearest and next-nearest neighbours of a sub-lattice position. In such a model, the magnetic flux is incorporated by making the hopping matrix elements complex in each unit cell. This breaks the invariance under time-reversal symmetry facilitating quantum Hall effect. This new phase of matter is known as *Chern* insulator wherein the quantized Hall effect was observed in absence of an external magnetic field. The first system to practically exhibit such a behaviour was Cr-doped $(Bi,Sb)_2Te_3$ wherein a plateau of Hall resistance ρ_{yx} was observed at a density corresponding to occupied bands.[23] One of the most important consequences of these investigations was the quantum spin Hall effect which is said to be akin to the quantum Hall effect because it does not require external magnetic field and, obeys charge-conservation and spin-S_z conservation symmetries.

1.5 Quantum Spin Hall Effect and Beyond

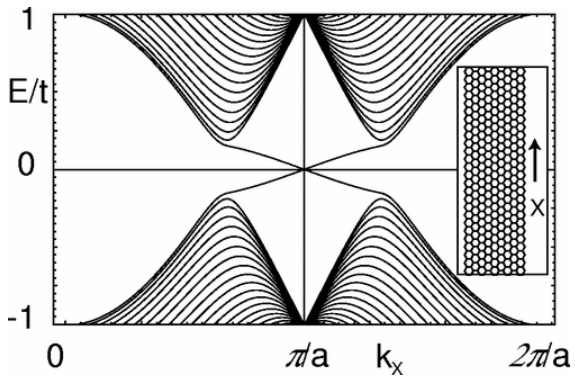

Figure 1.4: Spin filtered edge conducting energy bands in graphene (shown in inset). Adopted from Ref. *Phys Rev. Letts.*, **95**, 226801 (2005).

Inspired by Haldane's graphene model, Kane and Mele proposed the existance of quantum spin Hall effect in materials.[24] They investigated the effects of spin-orbit interactions in low energy electronic structures of graphene which could be experimentally realized (under cryogenic conditions) to exhibit symmetry protected transformation from an ideal semi-metallic nature to a quantum spin Hall insulator. Such a system would be insulating in $\mathcal{D}$ dimensions and conducting in $(\mathcal{D}-1)$ dimensions (as presented in Fig. 1.4). In case of graphene it was observed that the conducting states are non-chiral and insensitive to lattice disorders owing to their directional correlation with fermionic spin.

This model is now famously known as the Kane-Mele model which is a combination of two versions of Haldane's model with on version relevant to the spin-up fermions with chiral quantum spin Hall effect and the other version relevant to the spin-down fermions with anti-chiral quantum spin Hall effect. Based on the relativistic version of quantum spin Hall effect developed by Kaplan and colleagues (to perform numerical simulations of the

chiral gauge theories), it was observed that, quantum spin Hall systems consist, bulk fermions of opposite mass, massless Dirac mode and bulk currents which carry chirality rather than charge in a spin Hall current analogue.[25,26] These features are governed by the parity and time-reversal symmetry $U(1)$ gauge theory. This implies that the Kane-Mele model exhibits zero charge Hall conductance and non-zero spin Hall conductance (σ_{xy}^{spin}) in units of $\left(\frac{e}{4\pi}\right)$.

Similar investigations were performed independently by Bernevig and Zhang wherein, the spin-orbit interactions induced a momentum dependent magnetic field vector pointing upwards and downwards for spin-up and spin-down fermions respectively due to strong correlations under a strain configuration (as presented in Fig. 1.5).[27] Since the spin up and down fermions are not correlated, the Hall state remains invariant when the spin-spin scattering is introduced which otherwise destroys the quantum spin Hall effect.[28] This fact was established by Kane-Mele when they introduced a topological invariant ($\mathbb{Z}_2$) which is used to identify and classify trivial and non-trivial band insulators irrespective of the quantum spin Hall effects in the system.[28] This new phase of matter where, the edge conducting liquid is robust due to quantum spin Hall effect irrespective of the spin-spin and spin-orbital interactions is known as topological insulator. This exotic phase of matter is a type of symmetry protected topological order governed by the charge conservation and time-reversal symmetry. Hence, topological insulators and quantum spin Hall states are distinct states of matter owing to the symmetry protected topological order.

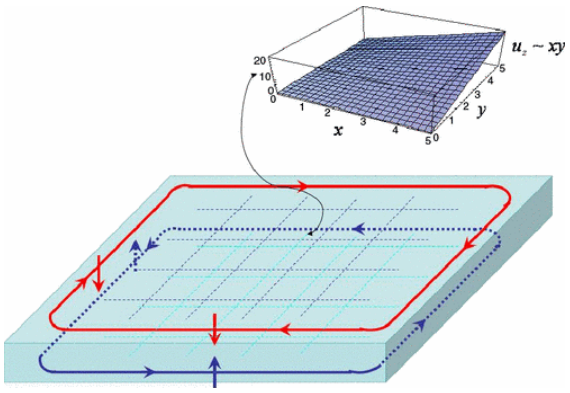

Figure 1.5: Spin-up and spin-down fermions with opposite chirality under opposite spin-orbit interaction force with the lattice displaced due to strain configuration. The net charge Hall conductance zero while the net spin Hall conductance is non-zero and quantized. Adopted from *Phys Rev. Letts.*, **96**, 106802 (2006).

Since the spin-orbit interactions induced splitting has a dependence on the effective nuclear charge Z as, $\Delta_{SO} \propto Z^4$, it implied that graphene would exhibit extremely weak spin-orbit effects; making it quite tough to realise quantum spin Hall effect experimentally. This was addressed by Bernevig, Hughes and Zhang who proposed that, the two-dimensional topological insulators can be realised in quantum wells made up of HgTe sandwiched between CdTe;

which was eventually observed in experimental conditions by the Molenkamp group.[29,30] When the thickness of HgTe in CdTe/HgTe/CdTe quantum well is small, the sandwich system behaves as an trivial insulator. However, when the thickness of the HgTe quantum well is increased beyond certain critical thickness the system CdTe/HgTe/CdTe undergoes a Lifshitz phase transition.[31,32] Such phase transitions correspond to change in the sign of gradient term in the Ginzburg-Landau free energy functional. This drives the quantum well system into a non-trivial topological phase transition wherein the bulk gap closes forming a Dirac cone at the critical point and then reopens into a quantum spin Hall insulator.

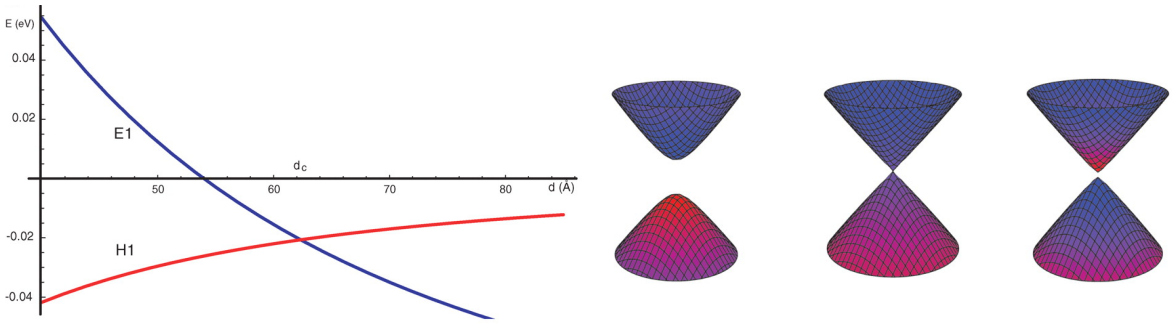

Figure 1.6: (left) Energy of sub-bands E_1 (blue) and H_1 (red) at Γ point in the momentum space as a function of the HgTe quantum well thickness (d). (right) Schematic energy dispersion relations of the energy sub-bands E_1 and H_1 at different HgTe quantum well thickness; $d = 40$, 63.5, and 70 Å (from left to right) indicating a Lifshitz phase transition. Illustrations adopted from *Science*, **314**, 1757-1761 (2006).

Figure 1.6(right) represents schematic energy dispersion relation $E(k_x,k_y)$ of the energy sub-bands E_1 and H_1 for different thickness of HgTe quantum well in momentum space. The red regions indicate dominant H_1 sub-band and the blue regions indicate dominant E_1 sub-band whereas the violet region indicates a uniform mixture of these sub-bands. At $d = 40$ Å the valence band is dominated by the H_1 sub-band and the conduction band is dominated by the E_1 sub-band (also evident from Fig. 1.6(left)). As the quantum well thickness is varied, at critical thickness (d_c) the sub-bands get mixed equally around the band crossings and beyond this critical thickness, the sub-band characters are reversed. The experimental success then led to the exploration of similar phenomena in bulk materials.

1.6 Topological Phenomena in Bulk Regime

Following the Lifshitz phase transitions and consequent measurement of edge channel dominant conductance (see Fig. 1.7) in the quantum Hall state of the CdTe/HgTe/CdTe

quantum wells; led to extensive research to realize similar phenomena in bulk materials. Prior to these investigations of quantum wells, in 1985-87, three dimensional topological insulators were predicted by Volkov, Pankratov and Pakhomov to exhibit Dirac fermions along the band inverted interface heterostructures of PbTe/SnTe and HgTe/CdTe.[33,34] However, the emphasis on topological character and the relevance of time-reversal symmetry was only realised in the early 21st century.

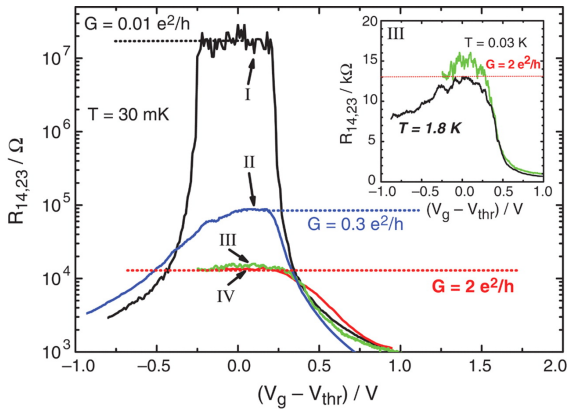

Figure 1.7: Longitudinal four-terminal resistance ($R_{14,23}$), when HgTe quantum well has thickness (d); 5.5 nm (I) before transition and 7.3 nm (II, III, IV) when the sub-band order is inverted, as a function of gate voltage in the absence of magnetic field and at 30 mK temperature. Adopted from *Science*, **318**, 766-770 (2007).

Three dimensional *strong* topological insulators were predicted to exist in binary compounds of Bismuth which would exhibit robust surface states which won't decay into multiple quantum spin Hall states.[35–37] The first three dimensional system to exhibit non-trivial topological insulating nature was an alloy of Bismuth and Antimony. Primarily, Bismuth (which natively exhibits a semi-metallic character with narrow band gap which results in high conductivity) is doped with varying concentrations of Antimony driving the system through a phase transition leading to an inverted band order similar to the one observed in the CdTe/HgTe/CdTe quantum wells.[36,38,39]

The energy difference between the valence band and conduction band of pure Bismuth reduces as the concentration 'x' of Antimony increases forming an alloy of the form $Bi_{(1-x)}Sb_x$. At a critical concentration of 4% (in this case) the valence band and conduction band intersect eachother forming a Dirac cone. Beyond this critical point, the energy of valence band increases and the energy of conduction band decreases resulting into an inverted band order (also known as band inversion) at a particular time-reversal invariant momenta (as presented schematically in Fig. 1.8). For concentrations of Antimony from 7% to 22% the inverted band order is retained wherein the alloy exhibits strong topological insulator nature with vanishing band gap on the surfaces leading to the robust surface states. Experimentally, through angle resolved photoemission

spectroscopy it was observed that, these surface states cross the Kramer degenerate points odd number of times featureing massive Dirac fermions hosting three dimensional Dirac particles which explains the observation of quantum Hall fractionalization in Bismuth.[24,38,40]

This was followed by similar experimental obervations in Bismuth and Antimony chalcogenides (which exhibit quintuple layered structures) as well as pure Antimony wherein robust surface states were observed protected by particle number conversion and time-reversal symmetries.[41–45] These were narrow gap semiconductors with strong spin-orbit interaction owing to the heavy elements such as Bismuth, Tellurium etc. Motivated by the non-trivial phenomena in these binary compounds, the focus of research moved onto a huge and diverse family of semiconductors known as the Heusler compounds.[48–51]

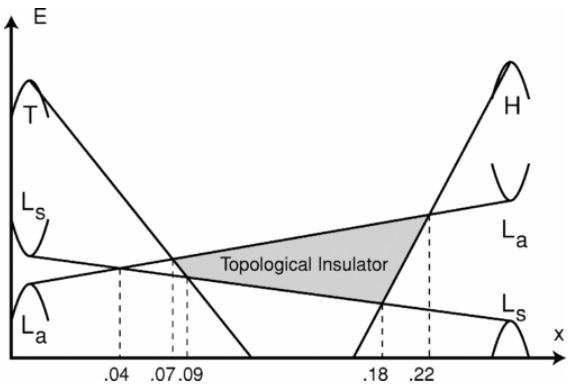

Figure 1.8: Schematic representation of band inversion as the concentration '*x*' of Antimony is varied in Bismuth forming the alloy $Bi_{(1-x)}Sb_x$. Adopted from *Phys. Rev. B*, **76**, 045302 (2007).

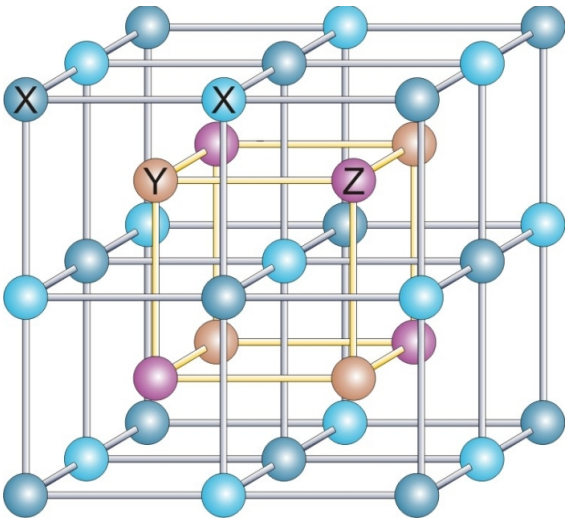

Figure 1.9: Structure of a Heusler compound, in full-Heusler; X_2 atoms form $L2_1$ structure and in half-Heusler with a vacant sublattice the structure is $C1_b$. Adopted from wikipedia.

These are compounds of type XYZ (half-Heusler) or X_2YZ (full-Heusler) which provide a large number of potential topological compounds hosting metallic surface states (also known as ideal two dimensional electron gas with spin-momentum locking and supressed Umklapp scattering) due to different permutation and combinations of the elements ocupying sites X, Y and Z.[42,46,47] Typically, the X and Y sites are occupied by the s-block/transition metal elements and the Z site is occupied by the p-block element forming a face centered cubic lattice arrangement. Natively, in some of these materials the Fermi level falls within the conduction

or valence band owing to the intrinsic imputirites which needs to be eliminated (pushing the Fermi level into the bulk gap) by employing methods such as, doping, gating, application of pressure/strain etc.[52–54] Also, some materials such as, ($Bi_{1.1}Sb_{0.9}Te_2S$) with mild Sn doping exhibit *intrisic* topological insulator phenomena with the Fermi level and the surface Dirac cone lying in the bulk gap which has been verified experimentally.[55]

1.7 Current Status

In real materials under practical conditions, things are a bit complicated and often deviate from the ideal scenario such as, homogenous crystals. However, inspite of such variations in practical scenarios, several physical phenomena have been explained theoretically by considering crystalline arrangement with the presence of minor impurities or defects. Branching out from such simple theories, especially the electronic band structure of materials gives us insights into the transport of electronic charge (which has lead to the classification of materials into insulators, semi-conductors and conductors) and the material response under different temperatures and external magnetic field. This was revolutionized with discovery of the quantum Hall and spin Hall effect which led to the development of the topological band theory of materials giving deeper insights into the unexplored exotic quantum phases of matter.[41,57] This has led to experimental discovery of topological insulators in two and three dimensional materials.[36,38,56] These phases of matter and also the topological superconductors are protected by symmetries; similar to those in Haldane's model. Recently, the 'Kitaev chain' has gained a lot of attention since they host Majorana modes which have applications as qubits, indicating towards the possibility of a topological quantum computer.[58,59] Also, it has been demonstrated that, topological insulators can be used to manipulate spin-torque computer memories due to metal-insulator transitions.[60] It was suggested that, topological insulators when placed in a magnetic field would behave as magnetoelectric materials with quantized magnetoelectric effect rather than surface conductors which was verified experimentaly in 2016.[61–63] In 2010, the Kondo effect (i.e., minima in electrical resistance as a function of temperature) was observed in Samarium Hexaboride (SmB_6) which led to the discovery of the topological Kondo insulators.[64,65] Guided by the proximity effects, superconductivity can be induced in topological insulators which would host symmetry protected and spin-momentum locked surface states made up of Majorana particles along the

interface.[66,67] The latest additions to the family of symmetry protected topological phases of matter are, Weyl semi-metals, Nodal-line semi-metals etc., which have been discovered experimentally in 2015.[68,69] This indicates that, topological materials can have several potential applications for example in, spintronics, valleytronics, dissipationless transistors, advanced magnetoelectronics, optoelectronics etc. Apart from these general applications, bulk topological insulators are known to exhibit excellent thermoelectric properties due to ultra-high mobility of the Dirac fermions on the surfaces and negligible scattering.[70,71] Recently a new field of topological quantum catalysis has been introduced wherein, the Fermi-arcs in topological semi-metals and surface/edge conducting Fermi liquids in topological insulators facilitate excellent catalytic reactions for applications in hydrogen evolution, oxygen evolution etc.[72]

1.8 Scope of the Thesis

Several methods (such as, application of strain/pressure, electric field etc.) to induce and enhance spin-orbit interactions in materials have been proposed to realise non-trivial topological insulators in bulk materials. These techniques were applied to a large number of bulk materials to realise the non-trivial topological phase transitions. Off these, half/full-Heusler compounds (introduced in section 1.6) stand out due to their multifunctional properties which involve; unconventional topologies, magnetic order, thermal transport properties, superconductivity etc. This is due to the unique valency (which is characteristic feature of Heusler compounds) which can be tuned by varying the chemical compositions under different permutations and combinations of elements from the *s*, *p* and *d* block of the periodic table. With an emphasis on strong spin-orbit interactions, the search for unconventional topologies has also extended to Heusler compounds with elements from the *f* block of the periodic table. Apart from ternary/quarternary Heusler compounds, binary compounds (which have inverted band order and are adiabatically connected to bulk HgTe) are also known to exhibit potential topological insulator nature subject to quantum topological phase transitions under strain/pressure.

From the perspective of two dimensional (low dimensional) materials, topological insulators are identified by the insulating bulk and conducting edges which lead to spin-charge accumulation along the edges giving rise to the quantum spin Hall effect. As established

in section 1.4, the magnetic field analogue governing two dimensional materials is the *Berry* curvature which exhibits sharp changes in the brillouin zone along the time-reversal invariant momenta which hosts the bulk gap. Due to promising room temperature applications (spintronic/valleytronic devices, ultra-fast switch etc.) two dimensional topological insulators have gained a lot of interest. However, a major criteria is the existence of a large non-trivial gap along a time-reversal momenta which is quite tough to be realised experimentally. To this effect, several efforts have been carried out to realise such materials at room temperature by, application of strain/pressure, electric field, hetero/homo-structures governed by interlayer van der Waals hybridizations, partial/complete functionalization etc.

With this background, we were motivated to explore the non-trivial topological phases and quantum phase transitions in some bulk and low-dimensional materials. We present a thorough and extensive investigation of the topological insulating nature in bulk and low dimensional materials alongwith their applications as thermoelectric and catalytic materials. We explored and predicted ternary half-Heusler compounds such as, LiMgX (X = Bi,Sb,As) and binary compound such as zincblende AuI for their potential applications as strong bulk topological insulators. Their non-trivial topological insulating nature are characterised in terms of band and orbital inversions (similar to those discussed in section 1.6) leading to topological phase transitions followed by classification of the topological class in terms of the $\mathbb{Z}_2$ invariants and angle resolved photoemission spectroscopy like surface plots. Low dimensional systems such as, LiMgAs (which is dimensionally engineered from the bulk half-Heusler parent LiMgAs), partially functionalized Tellurium and Selenium and AuI monolayer were explored and predicted for the first time. We found that, these low dimensional materials are large-gap topological insulators with potential room temperature applications. Finally, from multifunctional perspectives we explored, bulk AuI for thermoelectric applications at room temperature, low dimensional AuI for basal catalytic activity and low dimensional LiMgAs for topological quantum catalysis.

1.9 Objectives and Thesis Outline

With the scope of the thesis defined in previous section, we present the major objectives guiding the thesis and the computational investigations carried out thereof. Following are the major objectives addressed in this thesis:

1. To investigate Half-Heusler compounds; LiMgX (X = Bi, Sb, As) for non-trivial topological insulating properties.

2. To investigate non-trivial topological conducting and insulating nature in binary zincblende compound AuI.

3. To investigate dimensionally engineered two dimensional topological insulator from trivial bulk Half-Heusler compound.

4. To investigate dimensionally engineered AuI monolayer for non-triival topological insulating nature.

5. To explore and investigate the effects of partial functionlization of two dimensional monolayers of Tellurium and Selenium on non-tirvial topological insulating nature.

6. To investigate the thermoelectric properties of bulk topological insulator AuI.

7. To investigate the catalytic activity of basal plane of dimensionally engineered AuI monolayer towards hydrogen evolution reaction.

8. To investigate two dimensional topological insulator LiMgAs for topological quantum catalysis.

Overall, the thesis is divided into six chapters with three working chapters. With the objectives in place, we briefly discuss the thesis outline in terms of the three working chapters.

With **CHAPTER 1** setting the background motivation and objectives governing the thesis, we move onto **CHAPTER 2** wherein, we describe the computational formalisms employed as methods in the investigations carried out as part of this thesis. We begin with the description of the origin and various formalism which played a vital role in the development of density functional theory i.e., we present the eigen function based approximations and density based approximations which are used to solve the many-body time independent Schrödinger equation describing a periodic system. We then present various exchange correlations approximations and electronic approximations which govern the accuracy of the computational investigations carried out in this thesis. We then present, the formalisms defining lattice dynamics, elastic constants and abi-initio molecular dynamics simulations which are used to describe the structural stability of the proposed materials in this thesis. Also, we briefly discuss about the semi-classical approach of Botlzmann transport equations which are employed to compute

the thermoelctric transport properties of the bulk materials. We establish the methods such as, maximally localised wannier functions and tight-binding model which are used to compute the topological properties of various bulk and low dimensional materials. Finally, we discuss in short the codes used in our computational investigation of the bulk and low dimensional topological insulators.

In **CHAPTER 3**, we present our investigations on the topological quantum phase transitions in bulk materials. We begin with the description of our investigations on Half-Heusler family LiMgX (X = Bi, Sb, As) in the brackdrop of existing relevant literature. We then present our computations on pressure induced topological quantum phase transitions; driving the system from a trivial insulator to a non-trivial topological insulator. We point out the necessary and sufficient condition in realising a non-trivial topological insulator. We then present our work on bulk binary compound AuI wherein, on breaking the crystal cubic symmetry we find a transition from non-trivial topological conducting to topological insulating state. Prior to the discussions of non-trivial topological quantum phase transitions we discuss about structural stability. This is then followed by the qualitative (in terms of electronic band structures, density of states, orbital projected density of states etc.) and quantitative (in terms of surface states and $\mathbb{Z}_2$ invariants) investigations necessary to confirm the non-trivial topological properties.

In **CHAPTER 4**, we present our investigations on the topological quantum phase transitions in low dimensional materials. We begin with dimensional engineering of non-trivial low dimensional topological insulators from trivial bulk materials such as, Half-Heusler LiMgAs. We then present similar results wherein, the low dimensional AuI monolayer is dimensionally designed from bulk zincblende parent. In both the cases i.e., in LiMgAs and AuI monolayers we present non-trivial topological quantum phase transitions. We then present our investigations on the effects of partial functionalization on the topological properties of elemental monolayers made up of Tellurium and Selenium. Apart from the qualitative and quantitative analysis, we also study and present the Berry curvatures in these low dimensional materials which give further insights into the origin of the non-trivial topological chatacter. All the investigations in this chapter are presented with proper analysis of the structural stability of the proposed low dimensional materials in term of phonon dispersion curves and ab-initio molecular dynamics simulations.

In **CHAPTER 5**, we focus on the possibility of using topological insulators for potential

energy applications such as in, thermoelectrics and catalysis. We present the thermoelectric applications of bulk topological insulator AuI with an emphasis on the effects of band topologies on thermal transport properties. We then present our investigations on the catalytic activity of the basal plane of AuI monolayer (which was dimensionally engineered for non-trivial topological behaviour) towards hydrogen evolution reaction. This work further motivated us to explore the possibilities of highly efficient catalytic activity along the non-trivial edge states in a two dimensional topological insulator. We therefore present out computational investigations on the potential; topological quantum catalysis hosted by two dimensional topological insulator LiMgAs. The thermoelectric properties are analysed in terms of the thermoelectric transport parameters and the overall figure of merit. Whereas, the catalytic activity towards hydrogen evolution reaction is analysed in terms of various reaction mechanisms such as, Volmer, Volmer-Tafel and Volmer-Heyrovsky along with the computation of exchange current densitties.

Finally, in **CHAPTER 6**, we present the summary of all the investigations presented in the working chapters. Along with this, we also discuss the future scope of further research and exploration in topological materials.

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