CHAPTER 6

Summary and Future Prospects

This chapter summarises the results and discussions done in previous chapters in the backdrop of the motivation and objectives presented at the onset of this thesis in chapter 1. We mention in brief the key and outstanding features of this thesis accompanied with emphasis and reiteration of the unconventional/exceptional results obtained from our first-principles investigations. Also we briefly discuss the future prospects and scope for further explorations which might branch-out from the results presented and discussed in this thesis along-side my plans to further explore and investigate topological materials.

The revelations discovered by Thouless, Kosterlitz and Haldande by the end of 19^{th} century, gave birth to a new branch in condensed matter physics. By the start of 21^{st} century, Kane and Mele extended the Haldane's approach to realise a more generalised picture. On extending the graphene model to bulk materials the field of topological insulators in bulk and low dimensional materials was established. These materials exhibit insulating nature in D dimensions and conducting nature in $(D-1)$ dimensions. This excited the scientific community due to numerous potential applications of such materials. For example, the conduction in $(D-1)$ dimensions are robust against material impurities and external perturbations such as stress or temperatures. This implied that, these conducting states would host dissipationless transport of Fermions robust against back-scattering. Such materials would be extremely useful in realising room temperature quantum computers (which are currently only operated under cryogenic conditions), spintronic materials, valleytronic materials, sensors, ultra-fast switches for memory devices etc. The numerous possibilities attracted us to explore the

topological insulating phase in some bulk and low dimensional materials. Although, by the time we began our investigations using first-principles method, numerous materials in bulk as well as low dimensional phase were already explored either experimentally or theoretically. However, there was lots of scope to fill in the gap and also to generate material repository which would guide experimental explorations. With this motivation we streamlined the objectives mentioned in chapter 1 of this thesis.

By employing state-of-the-art density functional theory approach, we predicted novel bulk and low dimensional materials in this thesis. Also, we established a necessary and sufficient condition to realise a non-trivial bulk topological insulator. We proposed methods by which we can realise a topological insulator from a topological conductor in bulk materials. We established that, trivial bulk materials can be used to realised non-trivial low dimensional materials by imposing quantum confinement effects. To further enhance the topological insulating character in low dimensional materials we presented the orbital filtering effects which can be realised by performing partial or complete functionalization of two dimensional materials. Once we predicted the non-trivial materials in bulk and low dimensional phase, we also explored them for energy applications. We began with the application of bulk AuI in thermoelectrics and then we explored the low dimensional phase of AuI for catalysis. We finally proposed novel technique to realise a topological quantum catalyst from a two dimensional topological insulator. We summarise the results obtained in this thesis in brief detail below.

In **CHAPTER 3**, we presented our investigations of topological quantum phase transitions in bulk materials. We began with Half-Heusler compounds LiMgX (X = Bi, Sb, As); governed by $F\bar{4}3m$ space group with face centered cubic structures. LiMgBi was found to be dynamically stable with a direct global gap in the electronic band structure. On applying volume expansion pressure, we observed that at a critical pressure of 4.5% LiMgBi undergoes a topological quantum phase transition governed by *s-p* orbital band inversions with, spin-orbit coupling interactions induced gap of 1.10 meV. The closing and opening of the band gap was verified by using hybrid functional approach apart from the generalised gradient approach. The non-trivial character was verified by computing the surface state spectra which exhibit conducting nature. Also, we computed the $\mathbb{Z}_2$ invariants which were $(\nu_0, \nu_1\nu_2\nu_3) = (1, 0\ 0\ 0)$ which indicated that, LiMgBi is a strong topological insulator. We then presented similar phase transitions in LiMgSb, however, we observed that although LiMgSb presented band gap closing and

reopening alongwith exchange of orbitals across Fermi level and conducting surface state spectra but, on computing the $\mathbb{Z}_2$ invariants we found it to be a trivial insulator. Similarly, LiMgAs which was another direct band gap semi-conductor was subjected to pressure. Similar to LiMgSb, this system also presented band gap closing and reopening with exchange of orbital characters across Fermi level and conducting surface state spectra, but on computing the $\mathbb{Z}_2$ invariants we found it to be a trivial insulator like LiMgSb. Although the site 'X' in LiMgX were replaced with members of pnictogen family but, we observed contradicting topological properties. With this we established the necessary and sufficient condition for realising a non-trivial topological insulator i.e., apart from band gap closing and reopening, orbital inversion across Fermi level and conducting surface state spectra, the system should *necessarily* exhibit non-trivial $\mathbb{Z}_2$ invariants. Further, since these systems (LiMgSb, and LiMgAs) presented topological phase transitions at very high pressures we proposed that, dimensionally engineered monolayers can be realised using these bulk materials to facilitate non-trivial topological quantum phase transitions at relatively lower pressures.

Another problem in the topological insulator LiMgBi was that, the conduction bands crossed the Fermi level during the topological phase transitions. We addressed this issue by breaking the cubic symmetry and converting the material from a topological conductor to a topological insulator. We presented this phenomena in binary zincblende compound AuI. Although the stability of such a compound has been debated but, on computing phonon dispersion curves, formation energy and elastic tensors we found that, AuI is dynamically, energetically and mechanically stable. We followed two approaches to realise non-trivial topological properties in this binary compound, (i) application of isotropic compression and (ii) application of uni-axial compressive pressure along [001] crystal direction. We observed semi-metal to topological conductor and topological insulator transitions respectively under the said approaches. We observed that, due to the bulk inversion asymmetry, AuI exhibits Dresselhauss-like band-spin splittings characterized by unconventional *s*, *p*-*d* orbital band inversions. The non-trivial nature was confirmed by computing the conducting surface state spectra and the principle $\mathbb{Z}_2$ invariant which was $\nu_0 = 1$ (when cubic symmetry was retained and broken).

In **CHAPTER 4**, we presented our investigations on the dimensional engineering of non-trivial two dimensional topological insulator LiMgAs from trivial bulk parent. As expected, this system presented non-trivial topological quantum phase transitions at low

pressure due to quantum confinement effects and large surface-volume ratio. The proposed monolayer of LiMgAs was found to be dynamically stable with absence of negative phonon frequencies in the entire brillouin zone. Also, the non-trivial phase of LiMgAs monolayer exhibits unconventional Fermion velocities along different directions of the brillouin zone. The non-trivial topological phase transition in this system is characterised by *s-p* orbital inversions across the Fermi level accompanying the inversion in band dispersions. This system is proposed to exhibit room temperature applications owing to large-gap induced by spin-orbit interactions. Also, we compared the band inversion strength which is stronger as compared to the bulk parent, indicating towards the underlying quantum confinement effects. We finally confirmed the non-trivial nature by computing the $\mathbb{Z}_2$ invariant which was $\nu = 1$ and edge state spectra indicating a conducting Dirac dispersion along the edge brillouin zone path.

To further increase the non-trivial gap solely due to spin-orbit interactions i.e., without applying strain, we explored functionalization technique. We presented, elemental monolayers of Tellurium and Selenium for the first time. According to previous reports in literature, we too observed that, the free-standing elemental monolayers are dynamically unstable. However, on partially functionalizing these monolayers with oxygen and sulphur (since, they would form bonds due to mutually favourable electronic configurations) we observed that TeO, SeS and SeS were dynamically stable except TeS. These stable monolayers were then explored for their electronic properties and we found that both, TeO and SeS present a large-gap under the influence of spin-orbit interactions. On inclusion of spin-orbit interactions we observed *s-p* orbital inversions across the Fermi indicating towards potential non-trivial character of TeO and SeS. The effect was attributed to orbital filtering effects which saturate the dangle bonds (originating from the *pz*-orbitals) in z-direction giving rise to extra degrees of freedom to the electrons. This was confirmed by plotting the π and σ orbital projected band structures. We performed in-depth analysis of TeO since it exhibited highest non-trivial gap under spin-orbit interactions of 0.365 eV. We presented the Berry curvature and spin-Berry curvature analysis of TeO in the non-trivial regime under the influence of spin-orbit interactions. From the analysis we observed that, TeO can be used for spintronic and valleytronic applications, due to the opposite Lorentz forces acting on the electrons which leads to the spin-charge accumulation along the edges. This was presented in terms of the spin-projected electronic band structure along the two valleys points in the brillouin zone. The large-gap induced due

to spin-orbit interactions also leads to unconventionally high spin Hall conductivity in the global gap (which was observed to be superior to several other materials). From experimental perspective, we also presented the investigations of quantum well *h*BN/TeO/*h*BN which was found to retain the large-gap due to spin-orbit interactions under a tensile strain of 14%. These computations were followed by computing the edge state spectra of TeO and SeS. Clearly, TeO and SeS presented Dirac dispersions along the edge brillouin zone path. Also, we presented that the spin channels along the edges of SeS traverse in opposite directions by plotting the edge spectra along the [100] and [010] crystal directions. Ultimately, we presented the $\mathbb{Z}_2$ invariant which was found to be $\nu = 1$ indicating that, the non-trivial charcters are indeed topological in nature and that, TeO and SeS are two dimensional topological insulators.

Similar to the dimensional engineering of LiMgAs from bulk parent, we presented the dimensionally engineered AuI monolayer. We saw that, due to quantum confinement effects, the low dimensional phase exhibits a narrow gap as compared to the bulk parent which exhibits semi-metallic character. The ground state of this system was found to exhibit buckled structure governed by the P3m1 space group rather than $P6_3mmc$ space group. However, in the P3m1 phase, AuI monolayer presented a gap of 14.4 meV, from here we subjected the system to compressive and tensile pressures to mark the topological quantum phase transition boundaries. We found that, the lower boundary was at -2% and the upper boundary was at 4%, within this region, AuI presented non-trivial topological insulating phase in two different structural phases of P3m1 and $P6_3mmc$ with the non-trivial gap as high as 0.113 eV under spin-orbit interactions. The underlying mechanism was found to be unconventional *s*, *p*-*d* orbital inversion mechanism alongwith the inverted band dispersions. Also, we presented the inversion mechanism in terms of the exchange of charge densities or electron localisation functions across the Fermi level. To ascertain that, the non-trivial nature persists at the pressure of 3% (where the spin-orbit interactions induced gap is 0.113 eV) we computed the slab band structures and the edge state spectra both of which clearly host the non-trivial Dirac like edge dispersion in the edge brillouin zone. Finally we present the $\mathbb{Z}_2$ invariant and find that it is $\nu = 1$ in the region of -2% to 4% strain.

Finally, in **CHAPTER 5**, we presented our computational results wherein, topological insulators were explored for potential energy applications such as, thermoelectrics and catalysis. We presented our computations of thermoelectric transport properties for bulk AuI due to the dense states across the Fermi level and the semi-metallic band dispersion. Due to semi-

metallic nature, the electronic mobility was found to be high resulting in a high power factor. Also, we observed strong phonon-phonon scattering which lead to smaller lattice thermal conductivity. We employed the semi-classical Botlzmann transport equations to compute the thermoelectric transport coefficients. We explored the thermoelectric parameters at various temperatures and carrier concentrations. We found that, contrary to several thermoelectric materials which exhibit high figure of merit at higher temperatures, AuI exhibits excellent figure of merit of 0.55 at room temperature which is more useful from practical purposes.

We also presented our investigations on the catalytic activity of AuI monolayer towards hydrogen evolution reaction. The dimensionally engineered AuI monolayer exposes the basal plane containing Au which is a transition metal known for superior catalytic activities. We therefore presented the hydrogen evolution reactions along the basal plane of the two dimensional topological insulator AuI. The basal plane was preferred over the edge sites because, under pristine conditions (i.e., without any strain) the non-trivial gap was found to be 14.4 meV which is far less than the thermal energy at room temperature. Hence, the edge conducting states wont be prominent which implied that, there wont be significant difference in the catalytic response of the basal plane as compared to the edge plane. We presented various mechanisms by which a hydrogen evolution reaction could occur on the basal plane of two dimensional topological insulator AuI. Based on the adsorption energy and Gibb's free energy values, we conclude that, the basal plane of AuI favours Volmer-Heyrovsky over Volmer-Tafel reaction. Also, we found that, the preferred site of interaction would be over Au rather than I since at I the hydrogen atom interacts too strongly. We cofirmed the evolution of hydrogen molecule by plotting the charge density profiles in 3D.

Similarly, inspired by the latest developments in the field of topological quantum catalysis, we explored two dimensional LiMgAs for topological catalysis favouring hydrogen evolution reaction. We presented the transformation of the hexagonal unit cell into an orthorhombic unit celll by using a rotation transformation matrix. The stability of the proposed system was confirmed by computing ab-initio molecular dynamics simulations. We reiterated the, non-trivial topological quantum phase transitions by presenting the exchange of charge density profiles of bands near the Fermi level. Also, we presented the electronic slab band structure which indicated the edge Dirac semi-metallic nature. This was confirmed by plotting the edge charge densities in for the zig-zag and planar-like nanoribbon configurations wherein, we observed distinct egde charge accumulations. We begin with the computation of catalytic

activity on the basal plane of LiMgAs monolayer and found that the system would be ineffecient due to large adsorption energies and Gibb's free energy. However, we observed that, the catalytic activity along the edges was excellent with Gibb's free energy as low as -0.02 eV. This places two dimensional topological insulator LiMgAs into the Sabartiers optimum i.e., near the top of the volcano plot with high exchange current densities. Also, we explored various mechanisms of hydrogen evolution reactions such as, Volmer, Volmer-Tafel and Volmer-Heyrovsky. Off the planar and zig-zag nanoribbon termimantions, we found that, the zig-zag nanoribbon configuration facilitated both the mechanisms of hydrogen evolution reaction (i.e., Volmer-Tafel and Volmer-Heyrovsky) whereas, the planar-like nanoribbon configuration facilitates only Volmer-Heyrovsky reaction. In order to confirm that, such superior catalytic activity is originating from the conducting edge states (due to the topoogical insulating nature of LiMgAs), we investigated the catalytic activity along the middle regions of the nanoribbon. We found that, the superior catalytic activity is indeed originating due to the conducting edge states and that the results are not a numerical artifact.

With this, we conclude the findings presented in our thesis. We now briefly present some future prospects. The versatility of topological materials makes them materials of choice for various potential applications apart from countable few which were discussed in this thesis. Recently, topological semi-metals hosting Fermi arcs across the surfaces have gained a lot of attention. Also, topological superconductors have attained significant attention over the past few years due to the topologically protected superconducting character which would be robust against external perturbations. Apart from these usual proliferations, topological materials have also found applications in, photodetectors, high energy particle physics, at the interface of topological insulator and superconductor (governed by Majorana Fermions), magnetic devices, field-effect transistors, gas-sensors, bio-sensors, batteries, memory cells, photonics, topological quantum catalysis, floquent topological insulators, interferometers, magnetic field detectors, photo-luminesence, lasers etc. This indicates that, the work presented in this thesis and the results obtained thereoff are timely. Hence, significantly contributing further research and development in the field of topological materials, inspiring experimental investigations.