Topological Insulating Phase In Some Bulk And Low Dimensional Materials

*A **Synopsis** Submitted by*

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1 Introduction:

In the year 2016, David Thouless, Duncan Haldane, and Michael Kosterlitz shared the prestigious Nobel prize for their exceptional and seminal contributions to the field of condensed matter physics wherein they introduced and applied the concepts of topology to periodic systems.[1] They pioneered a different approach to acurately predict ordered phases and phase transitions in thin layered periodic systems.[2–6] This has had far reaching implications in research pertaining to topological insulators (TI), superconductors and other materials with applications in quantum computers, new generations of electronics and superconductors. This mechanism has attained the status of a fundamental theory in condensed matter physics with topological phases identified in chain of atoms (1D), thin layers of atoms (2D) and bulk (3D) periodic systems.[1] Eversince, several materials have been identified to exhibit topological behaviour wherein the material is insulating D dimension and conducting in $(D-1)$ dimensions.[7–10]

Initially, the topological properties were theoretically explored in graphene however, it was tough to realise such non-trivial phase at room temperature owing to the weak spin-orbit coupling (SOC) induced band-gap in graphene. Eventually, the first TI material with unconventional topological properties was identified in a system made up of quintuple layered arrangement of atoms, $Bi_{(1-x)}Sb_x$ (with the phase transitions governed by the concentration idex 'x').[11] This was followed by observation of unconventional topologies in 2D material made of HgTe/CdTe quantum wells (with the phase transitions governed by the thickness of quantum well).[12] Inspired by these initial investigations, several materials were eventually explored and discovered to exhibit unconventional topological phases. This established a fact that, irrespective of the material class (i.e., 3D or 2D), non-trivial topologies can be realised intrinsically due strong SOC effects which can be expected from heavier elements of the periodic table.

Apart from strong SOC effects, several approaches were introduced to realise the non-trivial phase in 3D materials such as, application of strain/pressure, electric field, doping

etc.[13–15] These techniques were applied to a large number of 3D materials to realise the non-trivial phase/phase transitions. Off these, Half/Full-Heusler compounds stood out due to their multifunctional properties which involved; 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.[16–19] With an emphasis on strong SOC effects, the search for unconventional topologies was also extended to Heusler compounds with elements from the f block of the periodic table.[20] 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 TI nature subject to quantum topological phase transitions under strain/pressure.[21]

From the perspective of 2D materials, TI nature is identified by the insulating bulk and conducting edges. Such unconventional behaviour of spin-charge accumulation along the edges is known as the quantum spin hall effect. However, instead of the strong magnetic field (as in quantum Hall effect) the SOC gives rise to quantum spin Hall effect. The magnetic field analogue governing 2D systems is the Berry curvature which indicates sharp changes in the Brillouin Zone (BZ) along the non-trivial bulk gap. 2D TI have promissing room temperature applications as spintronic/valleytronic material, ultra-fast switch etc. subject to existence of large non-trivial bandgap in the entire BZ while the edge is conducting. Systems which exhibit large non-trivial gap have been quite tough to be realised experimentally. However, several efforts have been carried out to realise such materials at room temperature such as, application of strain/pressure, electric field, hetero/homo-structures governed by interlayer van der Waals hybridizations, partial/complete functionalization etc.[22–25]

With this background, we were motivated to explore the non-trivial topological phases and quantum phase transitions in some bulk and low-dimensional materials. In this thesis, we present a thorough and extensive investigation of the TI nature in 3D and 2D

materials along with their applications as thermoelectrics and catalysis. We explored and predicted ternary Half-Heusler (HH) compounds such as, LiMgX (X = Bi,Sb,As) and binary compound such as zincblende AuI for their potential applications as strong 3D TI.[26–29] Their non-trivial TI nature are characterised in terms of band and orbital inversions leading to topological phase transitions followed by classification of the topological class in terms of the $\mathbb{Z}_2$ invariants and ARPES like surface state plots. 2D systems such as, LiMgAs (dimensionally engineered from bulk HH LiMgAs), partially functionalized Tellurium and Selenium and AuI monolayer were explored and predicted for the first time. We found these 2D systems to be large-gap TI systems with potential applications at room temperature.[30, 31] From multifunctional perspectives, we explored bulk AuI (for thermoelectric applications at room temperature) and 2D AuI (for catalytic activity) and LiMgAs (for topological quantum catalysis) for the first time.[29, 31, 32] The results presented in this thesis are quite exciting since we have predicted four large-gap 2D TI and three robust 3D TI materials.

2 Objectives:

1. To investigate HH compounds; LiMgX (X = Bi,Sb,As) for TI applications.
2. To dimensionally engineer 2D TI from bulk HH LiMgAs.
3. To investigate TI nature and thermoelectric properties of binary zincblende compound AuI.
4. To explore and investigate the effects of partial functionlization of 2D Tellurium and Selenium with respect to TI nature.
5. To investigate dimensionally engineered AuI monolayer for 2D TI nature and catalyic activity.
6. To investigate topological quantum catalysis in 2D TI LiMgAs.

3 Thesis Outline

Broadly, the thesis is divided into six chapters with the introduction, literature survey, objectives, motivation and methodology discussed in chapters I,II. This is followed by chapters III-V wherein the results of the research are presented in complete detail covering all the aspects in its length and breadth. The brief details of the chapter contents are provided in the following sub-sections.

Chapter I: 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 III-V of the thesis) with focus on the bulk and low dimensional materials, emphasising and identifying the existing caveats from the literature.

Chapter II: Methodology

This chapter discusses the origin and development of *first-principles* based density functional theory (DFT) which is the primary tool of investigation employed in this thesis. We begin with the fundamental formulations pertaining to the Kohn-Sham equations which are at the heart of DFT and employed in our computations using Quantum ESPRESSO code.[34] The ground state of a material is computed by employing a typical self-consistency loop presented in Fig. 3.1 below wherein,[33] we begin with an initial guess n(r) of the electronic density and then calculate the corresponding effective/Kohn-Sham potential ($V_{KS}[n]$) which is used in the reduced Schrödinger equation (also known as Kohn Sham equation) to calculate the actual electronic density. This loop continues until a reasonable accuracy is achieved known as self-consistency. We will also discuss in brief other methods such as, density functional perturbation theory (DFPT) (used to

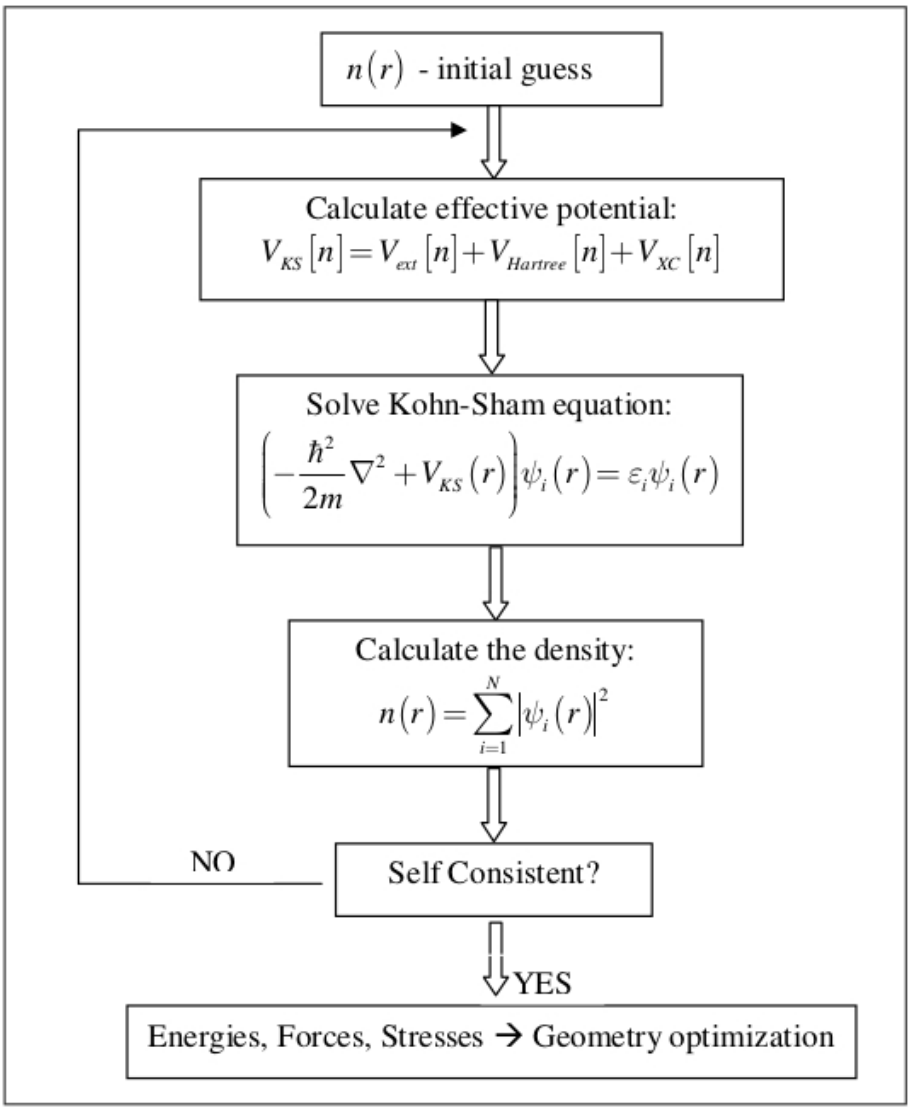

Figure 3.1: A typical self-consistency loop implemented in Quantum ESPRESSO code to compute the ground state of a material by solving the Kohn-Sham equations.[33]

compute and analyse the phonon dynamics), *ab-initio* molecular dynamics simulations (AIMD) (used to assess the structural stability of predicted materials at room temperature), ElaStic code (used to compute the elastic stress tensors to assess the mechanical stability of materials),[35] BoltzTrap code and the ShenBTE code (used to compute the thermoelctric properties of the predicted materials),[36,37] and, maximally localised wannier functions (MLWF) (used to create tight-binding model to investigate TI properties such as, $\mathbb{Z}_2$ invaraints (wherein, for systems without inversion symmetry, the invariants are calculated in terms of the Wanier Charge Centers in the vicinity of the Fermi level

along the two momentum planes in the BZ using Eq. 1 and 2), ARPES-like surface/edge spectra (using the imaginary part of the surface Green's functions (for a semi-infinite system and a dual surface presented in Eq. 3 and 4 respectively) which is calculated using the surface spectrum function $A(k_{||}, \omega)$ presented in Eq. 5), slab band structures etc.) using Wannier90 and WannierTools code.[38, 39]

$$\nu_0 = \Big[\big(\mathbb{Z}_2\big)_{(k_i=0)} + \big(\mathbb{Z}_2\big)_{(k_i=0.5)}\Big]\big(mod2\big) \tag{1}$$

$$\nu_i = \big(\mathbb{Z}_2\big)_{(k_i=0.5)} \tag{2}$$

$$G_s(k_{||}, \omega) \simeq (\omega - \epsilon_n^s)^{-1} \tag{3}$$

$$\tilde{G}_s(k_{||}, \omega) \simeq (\omega - \tilde{\epsilon}_n^s)^{-1} \tag{4}$$

$$A(k_{||}, \omega) = -\frac{1}{\pi} \lim_{\eta \to 0^+} ImTrG_s(k_{||}, \omega + i\eta) \tag{5}$$

Chapter III: Topological Insulating Phase in Bulk Materials

We discuss the origin and background of the topological phases and phase transitions in 3D materials in this chapter. Specifically, we will discuss about HH compounds and present the results of our investigation on TI nature of HH's LiMgX (X=Bi,Sb,As) in the brackdrop of existing relevant literature. We will discuss the effects strain fields in realising non-trivial TI nature in HH. Also, we will discuss the different mechanisms by which TI nature can be realised in binary compound such as AuI. The topological phase transitions will also be qualitatively discussed in terms of the band order and orbital character inversions which are charactertistic to quantum transitions. This will be followed by the quantitative analysis in terms of the $\mathbb{Z}_2$ invariants ($= \nu_0, \nu_1\nu_2\nu_3$) and

ARPES-like surface spectra. Also, we will present and discuss about the stability of the proposed materials in terms of phonon dispersion curves etc.

Chapter IV: Topological Insulating Phase In Low-Dimensional Materials

In this chapter we will discuss the origin of TI nature in 2D quantum materials. We will emphasise and discuss effects arising in 2D TI materials in terms of the Berry and spin-Berry curvatures alongside their relevance as an analogue to the magnetic field in quantum spin hall effect. We will discuss in brief; different methods from literature by which non-trivial TI nature can be explored in 2D materials. With this background we will discuss three methods (such as, dimensional engineering, application of stress/strain and partial functionalization) by which non-trivial TI nature is realised in 2D materials LiMgAs, AuI, Tellurene and Selenene. We will discuss the TI nature in terms of the qualitative and quantitative analysis (similar to that in chapter III) wherein we will present the non-trivial band and orbital inversions, unconventinaly Berry and spin-Berry curvature behaviour (at specific points in the BZ), quantum conductivity, $\mathbb{Z}_2$ invariant (ν), ARPES-like egde state spectra and slab band structures. Apart from this, we will also discuss in short various routes to synthesize the proposed 2D materials. Also, we will present and discuss about the stability of the proposed materials in terms of phonon dispersion curves, AIMD etc.

Chapter V: Energy Applications of Topological Materials

This chapter will focus on multifunctional applications of the 3D and 2D materials proposed in chapters III and IV. We will begin with brief dicussions on the background of the thermoelectric applications of 3D TI materials (specifically in terms of ternary HH compounds) and the implications of their non-trivial topologies on the thermoelectric transport properties. Followed by this, we will discuss the results of the investigation of thermoelectric properties of binary zincblende compound AuI. We will next discuss in brief the catalytic activity of quantum materials towards Hydrogen evolution reac-

tions (HER) in terms of different mechanisms of HER such as Volmer, Volmer-Tafel and Volmer-Heyrovsky. This will be followed by the qualitative and quantitative anaylsis of the catalytic activity of AuI towards HER. We will then establish the relation between the non-trivial topologies and catalysis. The relevant results will be discussed in terms of the qualitative and quantitative analysis of the topological quantum catalysis in 2D LiMgAs.

Chapter VI: Conclusion and Future Prospects

This chapter will summarise and culminate the results and discussions done in previous chapters in backdrop of the motivation and objectives presented at the onset of this thesis in chapter I. We will metion 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. This summary will be succeeded with discussions on 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.

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