

**IMPLICATIONS OF THE ANISOTROPIC
MEXICAN-HAT BAND STRUCTURE IN 2D
MATERIALS ON THEIR
THERMOELECTRIC PROPERTIES: AN
ANALYTICAL AND COMPUTATIONAL
INVESTIGATION**

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Implications of the Anisotropic Mexican-Hat Band Structure in 2D
Materials on their Thermoelectric Properties: An Analytical and
Computational Investigation
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We certify that we have read this dissertation and that in our opinion it is fully
adequate, in scope and in quality, as a dissertation for the degree of Doctor of
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ABSTRACT

IMPLICATIONS OF THE ANISOTROPIC MEXICAN-HAT BAND STRUCTURE IN 2D MATERIALS ON THEIR THERMOELECTRIC PROPERTIES: AN ANALYTICAL AND COMPUTATIONAL INVESTIGATION

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The electronic band structures of two-dimensional (2D) materials often exhibit non-parabolic, highly anisotropic features near the valence band edge. A particularly intriguing case is the Mexican-hat-like dispersion, characterized by a ring-shaped energy extremum in momentum space. This topology gives rise to a van Hove singularity in the 2D density of states (DOS) and a sharp onset in the electronic transmission spectrum, both of which can significantly enhance thermoelectric performance. However, realistic materials frequently exhibit angular anisotropy in these dispersions, shifting the DOS singularity and degrading transport efficiency. In this thesis, we investigate the interplay between anisotropy in Mexican-hat-like band structures and thermoelectric properties across a family of 2D materials.

Using first-principles density functional theory (DFT) and density functional perturbation theory (DFPT), we systematically study seven monolayer compounds, including PbBrF, PbClF, PbIF, BaHI, BiOCl, CaHBr, and SrHI. For each material, we perform structural optimization, electronic band structure analysis, and phonon stability checks. Thermoelectric transport coefficients are computed using the semi-classical Boltzmann transport equation via BoltzTraP, incorporating spin-orbit coupling (SOC) for the PbXF compounds. Phonon-limited lattice thermal conductivity is evaluated through third-order force constants obtained from `thirdorder.py` and `ShengBTE`. To analytically interpret the Mexican-hat features, we develop a tight-binding model parameterized by the ratio of next-nearest to nearest-neighbor hopping amplitudes ($\xi = t_2/t_1$) and an angular anisotropy term β . We demonstrate how ξ and β jointly control the curvature and shape of the band edge, thus tuning the thermoelectric response.

Across the PbXF series, SOC suppresses the valence-edge singularity and tends to lower the p -type performance while modestly enhancing the n -type response by sharpening conduction edges. Phonon calculations (second- and third-order force constants; ShengBTE) reveal intrinsically low lattice thermal conductivities due to soft optical modes and strong three-phonon scattering.

As a case study in band-structure engineering, we apply *biaxial tensile* strain (0–6%) to SrHI and show that strain reduces the Mexican-hat anisotropy, slightly decreases the hat height and ring radius, and sharpens the DOS onset. Consistent with the Mott relation, p -type S and the power factor improve (with a mild trade-off in conductivity). In contrast, the lattice thermal conductivity decreases as strain softens modes and enlarges anharmonic phase space. Taken together, the results establish clear descriptors and knobs— ξ , β , hat height, and strain—for designing high-performance 2D thermoelectrics.

Keywords: Thermoelectrics, 2D Materials, Mexican-Hat band structure, First principles, Density functional theory (DFT), Density functional perturbation theory (DFPT).

ÖZET

İKİ BOYUTLU (2B) MALZEMELERDE ANİZOTROPİK MEKSİKA-ŞAPKASI BANT YAPISININ TERMOELEKTRİK ÖZELLİKLERİ ÜZERİNDEKİ ETKİLERİ: ANALİTİK VE HESAPLAMALI BİR İNCELEME

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İki boyutlu (2D) malzemelerin elektronik bant yapıları, değerlik bandı kenarı yakınında çoğu zaman parabolikten saparak belirgin biçimde anizotropik özellikler sergiler. Momentum uzayında halka biçimli bir enerji ekstremumu ile karakterize edilen Meksika-şapka benzeri dağılım, özellikle ilgi çekici bir durum. Bu topoloji, 2D durum yoğunluğunda (DOS) bir van Hove tekilliği ve elektronik iletim spektrumunda keskin bir eşik oluşturur; her ikisi de termoelektrik performansı önemli ölçüde artırılabilir. Ancak gerçek malzemelerde bu dağılımlar sıklıkla açısız anizotropi gösterir; bu da DOS tekilliğini kaydırır ve taşınım verimini düşürür. Bu tezde, Meksika-şapka benzeri bant yapılarındaki anizotropi ile termoelektrik özellikler arasındaki etkileşimi bir 2D malzeme ailesi genelinde inceliyoruz.

Birinci ilke yoğunluk fonksiyonel teorisi (DFT) ve yoğunluk fonksiyonel pertürbasyon teorisi (DFPT) hesaplamalarını kullanarak, PbBrF , PbClF , PbIF , BaHI , BiOCl , CaHBr ve SrHI olmak üzere yedi tek katmanlı bileşiği sistematik biçimde inceliyoruz. Her malzeme için yapısal optimizasyon, elektronik bant yapısı analizi ve fonon kararlılık denetimleri gerçekleştiriyoruz. Termoelektrik taşınım katsayıları, yarı-klasik Boltzmann taşınım denklemi çerçevesinde BOLTZ-TRAP aracılığıyla hesaplanmakta ve PbXF bileşikleri için spin-yörünge etkileşimi (SOC) dâhil edilmektedir. Örgü (fonon sınırlı) ısı iletkenliği, `thirdorder.py` ile elde edilen üçüncü mertebe kuvvet sabitleri ve `SHENGBTE` kullanılarak değerlendirilmektedir. Meksika-şapka özelliklerini analitik olarak yorumlamak amacıyla, en yakın ve ikinci en yakın komşu zıplama genliklerinin oranı ($\xi = t_2/t_1$) ve açısız anizotropi terimi β ile parametrelenen bir sıkı-bağ modelini kullanıyoruz. ξ ve β 'nin bant kenarının eğriliğini ve şeklini birlikte nasıl denetlediğini ve böylece termoelektrik yanıtı nasıl ayarladığını gösteriyoruz.

PbXF serisi genelinde SOC, değerlik kenarı tekilliğini bastırır ve p -tip performansı düşürme eğilimindeyken, iletim kenarını keskinleştirerek n -tip yanıtı ılımlı biçimde artırabilir. Fonon hesapları (ikinci ve üçüncü merteye kuvvet sabitleri; SHENGBTE), yumuşak optik modlar ve güçlü üç-fonon saçılmaları nedeniyle örgü ısı iletkenliğinin doğası gereği düşük olduğunu ortaya koymaktadır.

Bant yapısı mühendisliğine bir örnek olarak, SrHI'ye 0–6% aralığında *çift eksenli çekme* gerinimi uyguluyor ve gerinimin Meksika-şapkası anizotropisini azalttığını, şapka yüksekliği ile halka yarıçapını bir miktar düşürdüğünü ve DOS eşiğini keskinleştirdiğini gösteriyoruz. Mott ilişkisiyle uyumlu olarak, p -tip S ve güç faktörü (iletkenlikte hafif bir ödün pahasına) iyileşmektedir. Buna karşılık, modların yumuşaması ve anharmonik faz uzayının genişlemesiyle örgü ısı iletkenliği azalır. Sonuçlar bir arada değerlendirildiğinde, yüksek performanslı 2D termoelektriklerin tasarımı için açık tanımlayıcılar ve ayar düğmeleri— ξ , β , şapka yüksekliği ve gerinim—ortaya konmaktadır.

Anahtar sözcükler: Termoelektrik, İki boyutlu (2B) malzemeler, Meksika-şapkası bant yapısı, Birinci ilkelere dayalı, Yoğunluk Fonksiyoneli Kuramı (YFK), Yoğunluk Fonksiyoneli Pertürbasyon Kuramı (YFPK).

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Chapter 1

Introduction

As the global demand for renewable and sustainable energy sources increases, research into alternative energy conversion technologies has also increased. Among these, thermoelectric (TE) materials have attracted attention due to their ability to directly convert waste heat into electricity through the Seebeck effect and vice versa through the Peltier effect. The efficiency of a thermoelectric material is measured with the figure of merit, ZT . It is represented by ($ZT = \frac{S^2\sigma T}{\kappa}$); where (S) represents the Seebeck coefficient, (σ) is the electrical conductivity, (T) denotes temperature, and (κ) is the total thermal conductivity. Improving the ZT value presents a challenge, as the optimization of competing parameters becomes necessary. That is, enhancing the power factor ($S^2\sigma$) while simultaneously reducing (κ).

Thermoelectric materials have a wide range of potential applications across different sectors. These materials are actively used in many industries, including radioisotope thermoelectric generators for deep-space exploration, solid-state Peltier cooling systems in electronics, and compact waste-heat recovery units [1]. The solid-state nature of these materials offers advantages such as increased longevity, reduced noise, and the potential to miniaturize, as they do not rely on moving parts. This makes them particularly suitable for remote, wearable, and embedded energy harvesting devices.

Since the pioneering theoretical work by Hicks and Dresselhaus [2, 3], low-dimensional systems have demonstrated a significant enhancement in thermoelectric efficiency compared to their bulk counterparts. This improvement is mainly attributed to the quantum confinement of charge carriers, which alters the electronic density of states (DOS), along with increased phonon-boundary scattering that lowers lattice thermal conductivity. Recent advancements in the fabrication of atomically thin layers of materials, such as graphene, transition metal dichalcogenides (TMDs) [4, 5], group-IV monochalcogenides [6], and halide/oxyhalide monolayers, have opened avenues for discovering new thermoelectric material options [7, 8]. These materials have beneficial electronic properties and offer tunability for band structures through chemical functionalization, strain, or heterostructure engineering. As a result, there is an increasing interest in band engineering approaches that focus on van Hove singularities, flat bands, and specific dispersion features like Mexican-hat shapes. Mexican-hat-like dispersions, seen in materials such as GaSe [9], InSe [10], and functionalized PbI₂ [11], are particularly promising due to the associated van Hove singularities in the DOS, which can result in enhanced Seebeck coefficients and power factors [12].

1.1 2D Materials

Two-dimensional (2D) materials have attracted significant attention in recent years. The reduced dimensionality of these materials introduces quantum confinement effects, significantly altering the electronic band structure and the density of states (DOS) near the Fermi level. Specifically, quantum confinement leads to sharper features in the DOS [13], which can enhance the Seebeck coefficient (S) and power factor ($S^2\sigma$). Both of these factors are critical for achieving adequate thermoelectric (TE) performance.

In a hypothesis proposed by Hicks and Dresselhaus [2, 3], they suggested that low-dimensional systems could surpass bulk materials in thermoelectric efficiency. Extensive theoretical and experimental studies have supported this idea. The improvement in thermoelectric (TE) properties is attributed to several factors,

including an increased density of states (DOS) near the band edges, reduced lattice thermal conductivity due to heightened phonon-boundary scattering, and the tunability of band structures.

A wide range of two-dimensional (2D) materials has demonstrated promising thermoelectric properties. For instance, Bi_2Te_3 monolayers exhibit improved ZT values due to their low thermal conductivity and favorable band alignments [14]. MoS_2 , a transition metal dichalcogenide (TMD), shows tunable band gaps and anisotropic carrier transport under strain, making it particularly attractive for thermoelectric devices [5]. Similarly, SnSe and black phosphorus (BP) monolayers have been found to achieve high ZT values due to their anisotropic electronic dispersion and low phonon group velocities [4, 15]. InSe monolayers have drawn attention for their high mobility and large density of states (DOS) near the valence band edge [10]. Additionally, functionalized 2D halides and oxyhalides exhibit unique band features, such as Mexican-hat-like dispersions, which contribute to DOS singularities that are beneficial for thermoelectric performance [8, 7].

2D materials are highly advantageous because they allow for the manipulation of electronic band structures through external parameters, enabling precise control over transport properties. Additionally, they offer opportunities for exploring fundamental physics and optimizing devices in thermoelectrics.

1.2 Mexican-Hat Band Structure: Origin, Relevance, and Anisotropy

The Mexican-hat-like dispersion among the band topologies of interest in two-dimensional (2D) materials significantly impacts thermoelectric performance. This dispersion describes a quartic energy-momentum relationship near the valence or conduction band edge, resulting in a ring-shaped energy extremum in momentum (k) space. Unlike a simple parabolic band edge, the Mexican-hat

structure features a nearly degenerate set of k -states arranged along a finite-radius ring in reciprocal space. This degeneracy leads to a van Hove singularity in the 2D density of states (DOS) [16, 17], which sharply increases the number of electronic states near the band edge.

The origin of the Mexican-hat dispersion in two-dimensional (2D) systems primarily stems from a combination of crystal symmetry, orbital hybridization, and spin-orbit coupling effects. This band structure can emerge when anti-bonding interactions between p or d orbitals at neighboring atomic sites create an energy extremum displaced from the Γ point, resulting in a local maximum or minimum that forms a circular ridge [17]. Such scenarios are frequently observed in materials with layered or buckled geometries, where the in-plane and out-of-plane orbital overlaps are imbalanced due to symmetry breaking or vertical asymmetry. For example, in materials such as GaSe or InSe, the interaction between p_z and p_x/p_y orbitals under crystal field effects leads to non-parabolic dispersion near the band edges [9, 10]. Additionally, in some cases, strong spin-orbit coupling, especially in heavy elements like Pb or Bi, further modifies the band curvature and can enhance the quartic-like dispersion through mechanisms like band inversion or splitting [7, 11]. External factors, including electric fields, chemical functionalization, or strain, can also modify the Mexican-hat features by adjusting the relative energies and curvatures of competing electronic states.

The singularity enhances the Seebeck coefficient and the power factor by concentrating carrier transport within a narrow energy range near the Fermi level [12, 18]. Consequently, materials that exhibit this feature—such as GaSe, InSe, BiOCl, and Pb-based halides—are regarded as promising candidates for thermoelectric applications [9, 10, 8]. In ideal scenarios, the Mexican-hat dispersion is isotropic, meaning the energy minimum (or maximum) along the ring remains constant across all angular directions in k -space. However, in real materials, this ring-shaped extremum often becomes distorted due to factors like crystal field asymmetry, spin-orbit coupling, or orbital hybridization.

This deviation from perfect isotropy introduces angular anisotropy, which mathematically appears as a modulation resembling $\cos(n\theta)$ around the Fermi

ring [17]. Here, θ represents the polar angle in k -space, and the crystal's symmetry determines the value of n . As a result, the energy band edge ceases to maintain a uniform depth or radius, instead varying with angle. Consequently, the density of states (DOS) singularity broadens and shifts to lower energy levels [16], reducing its steepness near the Fermi level. This suppression leads to a weakened Seebeck coefficient and blurs the distinct features in the transport distribution function, ultimately lowering both the power factor and the figure of merit (ZT).

Anisotropy also influences the group velocity distribution of charge carriers, which can create a directional dependence in electrical conductivity and make the optimization of thermoelectric properties more complex. These effects cause challenges in using isotropic models to estimate transport coefficients, as they may result in overestimating performance.

Several strategies can be implemented to manage angular anisotropy. One is, applying mechanical strain to symmetrize the electronic structure. This strain can modulate orbital overlaps and band curvature, effectively minimizing the anisotropic components of the dispersion. For instance, compressive biaxial strain in certain halide monolayers has been shown to restore more isotropic Mexican-hat-like bands [7, 9]. Another method is chemically functionalizing the surface or introducing symmetry-restoring dopants [19], which can flatten the angular variations in the band edge. Additionally, constructing heterostructures with a higher-symmetry substrate may impose more uniform boundary conditions on the electronic wavefunctions [20].

In this thesis, the impact of anisotropy in the Mexican-hat-like band structure is analyzed through both first-principles calculations and a parameterized tight-binding model. An angular modulation term is introduced to the model to simulate varying degrees of anisotropy. This allows correlating between symmetry breaking and transport degradation. In addition, investigation of strain engineering in the 2D SrHI system demonstrates that reducing anisotropy can directly enhance thermoelectric efficiency.

1.3 Research Objectives and Material Selection

The primary objective of this research is to explore the role of anisotropy in Mexican-hat-like band structures and how it affects the thermoelectric performance of two-dimensional materials. We concentrate on seven monolayer compounds: PbBrF, PbClF, PbIF, BaHI, BiOCl, CaHBr, and SrHI; which display quartic or near-quartic valence band dispersions with varying degrees of anisotropy. For six of these materials, we conduct systematic first-principles calculations that include structural optimization, electronic band structure analysis (with and without spin-orbit coupling for Pb-based compounds), phonon stability assessment (using Density Functional Perturbation Theory and Phonopy), and thermoelectric transport evaluation (via BoltzTraP). The lattice thermal conductivity is calculated using third-order force constants and ShengBTE. An analytical tight-binding model is created to represent the shape and anisotropy of the band edges. For the 2D SrHI compound, biaxial strain is applied to investigate how reducing band-edge anisotropy influences its thermoelectric properties.

1.4 Thesis Structure

This thesis is organized into five chapters. Chapter 2 presents the computational techniques used; such as Density Functional Theory (DFT), Density Functional Perturbation Theory (DFPT), the Boltzmann Transport Equation (BTE), phonon transport, and lattice thermal conductivity. Chapter 3 discusses the construction of the tight-binding model and presents the results derived from it, comparing the effects of isotropic and anisotropic Mexican hat band structures on thermoelectric properties. Chapter 4 covers the results of structural optimization, along with electronic and phonon properties, thermoelectric transport, and spin-orbit interaction. Chapter 5 examines the effects of biaxial strain on the anisotropic Mexican hat band structure and discusses its implications for thermoelectric properties. Finally, Chapter 6 outlines the main conclusions of the study, addresses implications for the future design of thermoelectric materials,

and suggests possible directions for future research.



Chapter 2

Computational Methods

In this chapter, the necessary theoretical framework of electronic and thermoelectric properties is investigated, providing a foundation for the relevant information needed in the thesis. The chapter includes an overview of Density Functional theory (DFT), thermoelectric transport theory, and essential elements of electronic band structure that capture the key features of the Mexican-hat-like dispersion observed in various two-dimensional (2D) materials.

2.1 Density Functional Theory (DFT)

One of the widely used quantum mechanical approaches for investigating the electronic structure of matter is Density Functional Theory (DFT). Within the context of materials science, it provides a structure to calculate ground-state properties of many-electron systems with a manageable computational cost, while maintaining a balance in accuracy. As opposed to directly solving the complex many-body Schrödinger equation, using DFT to construct the problem in terms of electron density reduces computational complexity.

In thermoelectric material research, DFT plays a crucial role in predicting and understanding electronic band structures, density of states (DOS), and structural

stability. Due to their effect on Seebeck coefficient, electrical conductivity, and phonon transport, these properties are critical to evaluate thermoelectric performance. Although it relies on approximations, DFT provides a reliable framework for initial screening and analysis of candidate materials.

The core idea of Density Functional Theory (DFT) is that the ground-state properties of a many-electron system are uniquely determined by its electron density $\rho(\mathbf{r})$, rather than the much more complex many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ [21]. This fundamental insight, rooted in the Hohenberg-Kohn theorems [22], significantly simplifies the formidable task of solving the quantum mechanical problem for interacting electrons, transforming it from a $3N$ -dimensional problem, where N is the number of electrons, to a more manageable 3-dimensional problem focused on the electron density.

2.1.1 Hohenberg–Kohn Theorems

The theoretical foundation of DFT rests on two key theorems proposed by Hohenberg and Kohn [22]:

1. **First theorem:** The external potential $V_{\text{ext}}(\mathbf{r})$, and consequently the total energy, is a unique functional of the electron density $\rho(\mathbf{r})$.
2. **Second theorem:** The ground-state energy of the system is minimized by the correct ground-state density.

These theorems justify the use of a variational principle in terms of the electron density, leading to a functional $E[\rho]$ which might be minimized to find the true ground-state density and energy.

2.1.2 Kohn–Sham Equations

To make DFT practically attainable, Kohn and Sham proposed a hypothetical system of non-interacting particles that have the same ground-state density as the real interacting system. This leads to the Kohn–Sham equations [23]:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2.1)$$

Here, $V_{\text{eff}}(\mathbf{r})$ includes the external potential, Hartree potential, and the exchange-correlation potential. The electron density is reconstructed from the Kohn–Sham orbitals as [23]:

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2 \quad (2.2)$$

Although the exact form of the exchange-correlation functional $E_{\text{xc}}[\rho]$ is not known, practical approximations such as Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) have shown adequate results in various applications [24]. The accuracy of the KS scheme mainly depends on the approximation used for the exchange-correlation (XC) potential.

2.1.3 Exchange–Correlation Functionals

One of the main approximations in DFT is in the treatment of the exchange–correlation (XC) energy functional, $E_{\text{xc}}[\rho]$. Since the exact form of this functional is unknown, various approximations were developed:

2.1.4 Local Density Approximation (LDA)

One of the first and most widely used approximations for exchange–correlation (XC) energy functional in Density Functional Theory (DFT) is the Local Density Approximation (LDA). In LDA, exchange–correlation energy at each point in space is approximated by using the value of a homogeneous electron gas (HEG) of the same local density.

The total exchange–correlation energy in LDA can be found by [25]:

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{HEG}}[\rho(\mathbf{r})] d\mathbf{r}, \quad (2.3)$$

where $\rho(\mathbf{r})$ is the electron density at position $\mathbf{r}$, and $\varepsilon_{\text{xc}}^{\text{HEG}}[\rho]$ is the exchange–correlation energy per particle for a uniform electron gas of density ρ .

This can be separated into exchange and correlation components:

$$\varepsilon_{\text{xc}}^{\text{HEG}}[\rho] = \varepsilon_{\text{x}}[\rho] + \varepsilon_{\text{c}}[\rho], \quad (2.4)$$

where $\varepsilon_{\text{x}}[\rho]$ is the exchange energy per electron and $\varepsilon_{\text{c}}[\rho]$ gives the correlation part of the expression.

For the exchange part, the analytical expression for a spin-unpolarized homogeneous electron gas can be written as:

$$\varepsilon_{\text{x}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3}. \quad (2.5)$$

The exchange potential $v_{\text{x}}^{\text{LDA}}(\mathbf{r})$ is obtained by functional differentiation:

$$v_{\text{x}}^{\text{LDA}}(\mathbf{r}) = \frac{\partial E_{\text{x}}[\rho]}{\partial \rho(\mathbf{r})} = - \left(\frac{3}{\pi} \right)^{1/3} \rho(\mathbf{r})^{1/3}. \quad (2.6)$$

Correlation contributions $\varepsilon_{\text{c}}[\rho]$ are usually obtained from quantum Monte Carlo simulations (e.g., Ceperley–Alder) and parameterized (e.g., by Perdew–Zunger).

Although LDA tends to overestimate binding energies and underestimate band gaps, it performs well for systems with slowly varying electron densities, such as

metals and bulk semiconductors [26]. It is computationally efficient and still widely used in large-scale simulations, especially for initial structure relaxations.

2.1.5 Generalized Gradient Approximation (GGA)

By including not only the local electron density $\rho(\mathbf{r})$ but also its gradient $\nabla\rho(\mathbf{r})$ in the formulation of the exchange–correlation (XC) energy, GGA improves upon the Local Density Approximation (LDA). This inclusion allows GGA to better describe systems with rapidly varying densities, such as molecules, surfaces, and low-dimensional materials. Thus, GGA usually has better structural properties and lower cohesive energies than LDA.

The general form of XC energy in GGA is [24]:

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})) d\mathbf{r}$$

where $\varepsilon_{\text{xc}}^{\text{GGA}}$ is a function depending on the local density and its gradient.

One of the most widely used GGA functionals is the Perdew–Burke–Ernzerhof (PBE) functional [27], which balances accuracy and computational efficiency for many materials. The exchange part of PBE modifies the LDA exchange by introducing an enhancement factor $F_x(s)$ that depends on the reduced density gradient:

$$s = \frac{|\nabla\rho|}{2k_F\rho}, \quad \text{where} \quad k_F = (3\pi^2\rho)^{1/3}$$

The PBE exchange energy density is given by:

$$\varepsilon_x^{\text{PBE}}(\rho, \nabla\rho) = \varepsilon_x^{\text{LDA}}(\rho) \cdot F_x(s)$$

This approach systematically improves the treatment of exchange interactions in non-homogeneous electron systems, making it a practical choice for thermoelectric materials where anisotropy and bonding variations are prominent.

2.1.6 Hybrid Functionals

Hybrid functionals improve DFT approximations by combining a part of the exact exchange energy from Hartree–Fock (HF) theory into the exchange–correlation (XC) energy functional [28]. This helps reduce self-interaction errors inherent in local and semi-local DFT approximations, such as LDA and GGA, and helps improve accuracy for electronic properties—specifically band gaps and charge localization in insulators and semiconductors.

The general form of a hybrid XC functional is [29]:

$$E_{\text{xc}}^{\text{hybrid}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{DFT}} + E_c^{\text{DFT}}$$

where:

- E_x^{HF} is the non-local exact exchange from Hartree–Fock theory,
- E_x^{DFT} and E_c^{DFT} are the exchange and correlation components from a GGA-type functional (e.g., PBE),
- α is the mixing parameter (typically around 0.25).

The two broadly used hybrid functionals are [30]:

- **PBE0:** Global hybrid functional, combining 25% exact exchange with 75% PBE exchange, and the full PBE correlation:

$$E_{\text{xc}}^{\text{PBE0}} = \frac{1}{4} E_x^{\text{HF}} + \frac{3}{4} E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

- **HSE06:** Range-separated hybrid functional that screens Coulomb interaction, using exact exchange only in the short range. This reduces the cost of computation while preserving accuracy:

$$E_x^{\text{HSE06}} = \alpha E_x^{\text{HF},\text{SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE},\text{SR}}(\omega) + E_x^{\text{PBE},\text{LR}}(\omega)$$

where ω is the screening parameter, *SR* is the short-range component, and *LR* is the long-range component.

Hybrid functionals excel at predicting crucial electronic properties such as band gaps, defect levels, and charge transfer phenomena [28, 30]. This accuracy makes them particularly valuable for modeling the electronic structure of thermoelectric materials. However, their significant computational cost often restricts their use to smaller, specific configurations or for generating high-accuracy reference data to validate more efficient GGA (Generalized Gradient Approximation) calculations.

2.1.7 Practical Choices for Thermoelectric Materials

GGA functionals are often used in studying thermoelectric materials due to their accuracy in predicting structural and electronic properties at low computational cost. However, hybrid functionals like HSE06 may be employed to correct the underestimation typical of LDA/GGA in materials where accurate band gaps are essential.

2.1.8 From Kohn–Sham Eigenvalues to Band Structures

The Kohn–Sham equations give a set of single-particle eigenvalues and eigenfunctions which describes the effective non-interacting system corresponding to the real interacting many-electron system [31]. These eigenvalues are widely used to construct the electronic band structure of materials. The band structure demonstrates which energy levels of electrons are allowed as a function of crystal momentum. It is crucial for understanding transport, optical, and magnetic properties.

2.1.9 Brillouin-Zone Sampling

In crystalline solids, electrons experience a periodic potential due to the lattice, and their wavefunctions are characterized by Bloch’s theorem. Thus, electronic

states can be labeled by a crystal momentum vector $\mathbf{k}$ limited to the first Brillouin zone (BZ) of the reciprocal lattice.

In order to compute physical quantities such as total energy, charge density, or transport coefficients; it is necessary to integrate over the Brillouin zone. However, this integration must be discretized using a finite set of $\mathbf{k}$ -points; because the BZ is a continuous space. The choice and density of the $\mathbf{k}$ -point grid affects the accuracy of DFT calculations greatly.

The most common approach is to use a *Monkhorst-Pack* grid [32], which distributes $\mathbf{k}$ -points uniformly over the BZ:

$$\mathbf{k}_{ijk} = \frac{i}{N_1}\mathbf{b}_1 + \frac{j}{N_2}\mathbf{b}_2 + \frac{k}{N_3}\mathbf{b}_3$$

where $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are the reciprocal lattice vectors, and N_1 , N_2 , N_3 are the number of divisions along each direction.

In systems which have reduced dimensionality (such as two-dimensional materials), the $\mathbf{k}$ -point mesh must be chosen carefully to reflect the reduced periodicity accurately. For instance, in a monolayer with periodicity in the x and y directions only, a dense k_x - k_y grid with a single point along k_z is used.

2.1.10 Density of States (DOS)

Electronic density of states (DOS), $D(E)$, is a quantity to measure carrier concentrations, Fermi level positioning, and thermoelectric transport. It quantifies the number of electronic states per unit energy at each energy level E .

For a system with energy eigenvalues $E_{n\mathbf{k}}$ obtained from Density Functional Theory (DFT), the DOS is fundamentally defined as [33]:

$$D(E) = \sum_{n,\mathbf{k}} \delta(E - E_{n\mathbf{k}})$$

where the summation extends over all energy bands n and wavevectors $\mathbf{k}$ in the Brillouin zone. In practical numerical evaluations, the ideal Dirac delta function

is approximated by a smearing function with a finite width. A commonly used approximation is the Gaussian function [34]:

$$D(E) \approx \sum_{n,\mathbf{k}} \frac{1}{\sqrt{2\pi}\eta} \exp \left[-\frac{(E - E_{n\mathbf{k}})^2}{2\eta^2} \right]$$

Here, η represents the smearing parameter, which controls the width of the Gaussian and effectively broadens the discrete energy levels into a continuous distribution, allowing for a smooth and computationally tractable representation of the DOS.

The total DOS gives a comprehensive view of the electronic structure; whereas the projected DOS (PDOS) gives the contributions of specific atomic orbitals or elements. Peaks in the DOS near the Fermi level may indicate van Hove singularities; they can strongly influence properties like the Seebeck coefficient.

In this thesis, band structures and DOS for each material are calculated by the Kohn-Sham eigenvalues obtained using DFT.

2.1.11 Density Functional Perturbation Theory (DFPT)

While Density Functional Theory (DFT) offers a framework for calculating a material's ground-state properties, many crucial physical quantities are instead derived from the system's response to subtle external perturbations. Density Functional Perturbation Theory (DFPT) provides an elegant and computationally efficient method to calculate these response properties. Instead of performing a separate, costly ground-state calculation for each slightly perturbed configuration, DFPT directly solves for the first-order change in the Kohn-Sham wavefunctions and electron density in response to a perturbation, thus enabling the calculation of second-order derivatives of the total energy.

The core of DFPT lies in the chain rule, which allows for the calculation of the second-order derivative of the total energy with respect to a perturbation parameter, λ . A key quantity is the first-order change in the Kohn-Sham potential,

$\partial V_{KS}^{(1)}$, which depends on the perturbation itself and the first-order change in the electron density, $\partial n^{(1)}$. The first-order change in the electron density is, in turn, a function of the first-order changes in the Kohn–Sham wavefunctions, $\partial \psi_i^{(1)}$. The central task of a DFPT calculation is to solve a linear system of equations, commonly known as the **Sternheimer equation**, to determine these perturbed wavefunctions:

$$\left(H_{KS}^{(0)} - \varepsilon_i^{(0)} \right) \partial \psi_i^{(1)} = - \left(\partial V_{KS}^{(1)} + \partial H_{XC} \right) \psi_i^{(0)}$$

Here, $H_{KS}^{(0)}$ and $\varepsilon_i^{(0)}$ are the unperturbed Kohn–Sham Hamiltonian and eigenvalues, and δH_{XC} represents the change in the exchange–correlation potential. By solving this equation for all occupied states, the perturbed wavefunctions $\partial \psi_i^{(1)}$ are obtained. These are then used to compute the second-order total energy, from which response properties can be derived.

A primary application of DFPT is the calculation of phonon dispersion relations. Phonons, the quanta of lattice vibrations, are determined by the interatomic force constants (IFCs), which are the second derivatives of the total energy with respect to atomic displacements [35]. DFPT provides a highly accurate way to calculate these IFCs by treating atomic displacements as perturbations. This approach is generally more efficient and numerically stable than the finite-difference method, especially for large supercells, as it requires only one self-consistent calculation for each non-equivalent displacement. The calculated IFCs can then be used to construct the dynamical matrix and solve for the phonon frequencies and vibrational modes.

Beyond phonons, DFPT is also the workhorse for computing a wide range of other material properties, including:

- **Dielectric properties:** By considering an applied electric field as a perturbation, DFPT can be used to calculate dielectric constants and Born effective charges.
- **Elastic properties:** Stress and strain can be treated as perturbations to determine elastic constants.

- **Raman and Infrared spectra:** DFPT is used to compute the polarizability and effective charges that govern the intensity of these vibrational modes.

2.2 Thermoelectric Effects

Thermoelectric effects illustrate the relationship between thermal and electrical phenomena in materials; they enable direct conversion between heat and electricity. Increase in the effectiveness of thermoelectric materials and devices requires optimizing the three main thermoelectric effects, which are Seebeck, Peltier, and Thomson.

2.2.1 Seebeck Effect

The Seebeck effect is defined as the formation of an electric potential difference (voltage) in response to a temperature gradient across the material. This occurs due to diffusion of charge carriers from higher thermal energy (hot side) to lower thermal energy (cold side) in the material, named as the Seebeck effect.

As the charge carriers move, they transport both charge and entropy. As a result, they produce an internal electric field that eventually starts to oppose further carrier diffusion. This results in a steady-state voltage difference ΔV which depends on the temperature difference ΔT across the material.

The proportionality constant between the generated voltage and the temperature difference is known as the Seebeck coefficient, denoted by S :

$$S = -\frac{\Delta V}{\Delta T}. \quad (2.7)$$

where ΔV is the voltage difference and ΔT is the temperature difference across the material. A large Seebeck coefficient is feasible, as it is an indicator of efficiency in thermoelectric energy conversion. The negative sign indicates that

voltage develops in the direction opposite to the temperature gradient for electrons. In other words, the magnitude and sign of the Seebeck coefficient depend on the type of charge carriers and electronic band structure.

Materials with a sharp energy dependence of the density of states (DOS) near the Fermi level usually have a large Seebeck coefficient. Specifically, low-dimensional materials with van Hove singularities or flat bands, such as those with Mexican-hat-like dispersion, can lead to enhanced S values.

A large Seebeck coefficient contributes positively to the thermoelectric figure of merit ZT and is critical for designing efficient thermoelectric materials. However, it must be balanced with electrical conductivity, as both enter the power factor $S^2\sigma$.

In this thesis, the Seebeck coefficient is computed using the Boltzmann transport equation under the relaxation-time approximation, allowing for a detailed investigation of how band structure features, especially anisotropic Mexican-hat dispersions, influence thermoelectric performance.

2.2.2 Peltier Effect

When an electric current passes through the junction of two different materials, it causes heat to be absorbed/released at the junction, depending on the direction of the current and the nature of the materials [36]. This is defined as the Peltier effect. The Peltier coefficient, Π , represents the amount of heat transported per unit electric current:

$$\dot{Q} = \Pi I, \quad (2.8)$$

where $\dot{Q}$ is the heat flow and I is the electric current.

The Peltier and Seebeck coefficients are related to each other in a Kelvin relation:

$$\Pi = ST, \quad (2.9)$$

where T is the absolute temperature.

It is important to note here that the Peltier effect can be defined as the inverse of the Seebeck effect.

2.2.3 Thomson Effect

The Thomson effect describes a conducting material that heats/cool when an electric current flows through, while there is a temperature gradient present. Unlike the Seebeck effect or the Peltier effect, the Thomson effect is seen within a single homogeneous material.

The rate of heat generation per unit length due to the Thomson effect is given by [37]:

$$\dot{q} = \tau I \frac{dT}{dx}, \quad (2.10)$$

where τ is the Thomson coefficient, I is the current, and dT/dx is the temperature gradient.

The Thomson coefficient is related to the Peltier coefficient as:

$$\tau = \frac{d\Pi}{dT} = T \frac{dS}{dT}. \quad (2.11)$$

2.2.4 Figure of Merit

The efficiency of a thermoelectric material is characterized by its dimensionless figure of merit ZT , defined as [38]:

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}}, \quad (2.12)$$

where:

- S is the Seebeck coefficient,
- σ is the electrical conductivity,

- T is the absolute temperature,
- κ_e is the electronic thermal conductivity,
- κ_{ph} is the lattice (phonon) thermal conductivity.

To achieve a high ZT , a large power factor $S^2\sigma$ and a low total thermal conductivity are necessary. However, these quantities depend on each other. For instance, increasing carrier concentration improves σ ; but it also reduces S and increases κ_e . Thus, optimizing ZT becomes a complex problem.

One guiding principle is the phonon-glass electron-crystal (PGEC) concept: a good thermoelectric material should conduct electricity like a crystal (high σ) but scatter heat like a glass (low κ_{ph}). Achieving such behavior often requires band engineering, nanostructuring, and control over phonon scattering mechanisms.

2.3 Boltzmann Transport Equation (BTE) for Electrons

The Boltzmann Transport Equation (BTE) offers a powerful semiclassical structure that helps describe carrier transport in solids. In thermoelectric transport analysis, it explains the theoretical background, making it essential in connecting microscopic carrier dynamics to macroscopic quantities such as electrical conductivity, thermal conductivity, and the Seebeck coefficient. For weaker external fields and/or smaller temperature gradients, the BTE can be solved within the relaxation-time approximation (RTA) to yield analytically tractable expressions for transport coefficients.

2.3.1 Semiclassical BTE in Relaxation-Time Approximation

The semiclassical BTE describes the evolution of the carrier distribution function $f(\mathbf{k}, \mathbf{r}, t)$ in phase space [39]:

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}. \quad (2.13)$$

In steady-state and spatially uniform conditions, under external electric field $\mathbf{E}$ and temperature gradient ∇T , this can be reduced to:

$$-e\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{k}} - \nabla T \cdot \frac{\partial f}{\partial T} = \frac{f_0 - f}{\tau(\mathbf{k})}, \quad (2.14)$$

where f_0 is the equilibrium Fermi–Dirac distribution and $\tau(\mathbf{k})$ is the momentum-dependent relaxation time. This linearized BTE allows perturbative treatment of f around f_0 due to small external driving forces.

2.3.2 Electrical Conductivity and Seebeck Coefficient from BTE

Transport coefficients can be derived from moments of the distribution function weighted by group velocities and relaxation times. Within the constant relaxation-time approximation, the electrical conductivity tensor $\sigma_{\alpha\beta}$ and Seebeck coefficient tensor $S_{\alpha\beta}$ are given by [40]:

$$\sigma_{\alpha\beta} = e^2 \int \frac{d\mathbf{k}}{(2\pi)^3} \tau(\mathbf{k}) v_{\alpha}(\mathbf{k}) v_{\beta}(\mathbf{k}) \left(-\frac{\partial f_0}{\partial \varepsilon} \right), \quad (2.15)$$

$$S_{\alpha\beta} = \frac{1}{eT} \frac{L_{\alpha\beta}^{(1)}}{L_{\alpha\beta}^{(0)}}, \quad (2.16)$$

where $v_{\alpha}(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(\mathbf{k})}{\partial k_{\alpha}}$ is the group velocity, and $L_{\alpha\beta}^{(n)}$ are the transport integrals:

$$L_{\alpha\beta}^{(n)} = \int \frac{d\mathbf{k}}{(2\pi)^3} \tau(\mathbf{k}) v_{\alpha}(\mathbf{k}) v_{\beta}(\mathbf{k}) (\varepsilon_{\mathbf{k}} - \mu)^n \left(-\frac{\partial f_0}{\partial \varepsilon} \right). \quad (2.17)$$

These integrals display the contribution of all states near the Fermi level to transport coefficients, weighted by how strongly they are affected by external gradients.

2.3.3 Numerical Implementation

In practice, evaluating the transport integrals requires knowledge of the whole electronic band structure $\varepsilon_{n\mathbf{k}}$ and corresponding group velocities. The steps involved in this process are as follows:

- **Band interpolation:** The discrete DFT-calculated eigenvalues, interpolated over a dense $\mathbf{k}$ -mesh using schemes like Fourier interpolation or maximally localized Wannier functions (MLWFs).
- **Group velocities:** Calculated numerically, the gradient of energy bands with respect to $\mathbf{k}$:

$$v_{n\alpha}(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial k_\alpha} \quad (2.18)$$

- **Energy and $\mathbf{k}$ -space integration:** Transport integrals $L^{(n)}$, evaluated by summing over the interpolated $\mathbf{k}$ -points with appropriate smearing (e.g., Fermi–Dirac window at temperature T).

This procedure is implemented in codes such as BoltzTraP and BoltzTraP2, which take the band structure as an input; calculate σ , S , and the electronic contribution to thermal conductivity κ_e as a function of temperature and carrier concentration. These quantities are central for evaluating the thermoelectric figure of merit ZT .

2.4 Phonon Transport and Lattice Thermal Conductivity

Understanding lattice thermal conductivity (κ_{ph}) is essential to evaluate thermoelectric efficiency, since it influences the denominator in the figure of merit $ZT = S^2\sigma T/(\kappa_{el} + \kappa_{ph})$ directly. In 2D materials, reducing κ_{ph} is a key strategy to maximize ZT .

2.4.1 Phonon Dispersion from Harmonic DFT

Phonon transport originates from the lattice vibrations of atoms in a crystal [41]. The vibrational frequencies and modes are derived from the harmonic approximation of the interatomic potential, using Density Functional Perturbation Theory (DFPT) or the finite displacement method. By solving the dynamical matrix, phonon dispersion relations are found. They are derived from the second-order harmonic interatomic force constants (IFCs). These force constants describe how atoms respond to small displacements. They are calculated using the finite-displacement method or density-functional perturbation theory (DFPT).

The elements of the dynamical matrix $D_{\alpha\beta}^{pq}(\mathbf{q})$ for wavevector $\mathbf{q}$ are given by:

$$D_{\alpha\beta}^{pq}(\mathbf{q}) = \frac{1}{\sqrt{m_p m_q}} \sum_l \Phi_{\alpha\beta}^{pq}(l) e^{i\mathbf{q} \cdot \mathbf{r}_l}, \quad (2.19)$$

where $\Phi_{\alpha\beta}^{pq}(l)$ is the second-order force constant between atom p and atom q in cell l , m_p and m_q are the atomic masses, and α, β denote Cartesian components. Diagonalizing this matrix yields phonon frequencies $\omega_\lambda(\mathbf{q})$ and eigenvectors for each mode λ .

$$D(\mathbf{q})\mathbf{e}_\lambda(\mathbf{q}) = \omega_\lambda^2(\mathbf{q})\mathbf{e}_\lambda(\mathbf{q}), \quad (2.20)$$

The dispersion curves distinguish between acoustic and optical branches.

Acoustic modes correspond to collective motion of atoms (long-wavelength lattice vibrations) and exhibit linear behavior near the Γ -point. Optical modes arise from the relative motion of atoms within the unit cell, involve out-of-phase movements between atoms in the basis, and generally occur at higher frequencies [42].

2.4.2 Boltzmann Transport for Phonons

The phonon contribution to the thermal conductivity in the relaxation-time approximation (RTA) is given by [43]:

$$\kappa_{\text{ph}} = \frac{1}{NV} \sum_{\lambda} C_{\lambda} v_{\lambda}^2 \tau_{\lambda}, \quad (2.21)$$

where N is the number of $\mathbf{q}$ -points in the Brillouin zone, V is the crystal volume, C_{λ} is the mode-specific heat capacity, v_{λ} is the group velocity, and τ_{λ} is the phonon lifetime [44].

The heat capacity C_{λ} of mode λ at temperature T is:

$$C_{\lambda} = k_B \left(\frac{\hbar \omega_{\lambda}}{k_B T} \right)^2 \frac{e^{\hbar \omega_{\lambda}/k_B T}}{(e^{\hbar \omega_{\lambda}/k_B T} - 1)^2}, \quad (2.22)$$

where $\hbar$ is the reduced Planck constant and k_B is Boltzmann's constant.

The group velocity v_{λ} is obtained as the gradient of the phonon dispersion:

$$v_{\lambda}(\mathbf{q}) = \nabla_{\mathbf{q}} \omega_{\lambda}(\mathbf{q}). \quad (2.23)$$

The lifetime τ_{λ} accounts for all scattering mechanisms and is primarily governed by three-phonon interactions. These anharmonic processes include both absorption and emission:

- $\lambda + \lambda' \rightarrow \lambda''$ (collision)
- $\lambda \rightarrow \lambda' + \lambda''$ (decay)

2.4.3 Anharmonic Scattering and Boundary Effects

The anharmonic phonon scattering rates are derived from third-order interatomic force constants, which account for interactions among triplets of atoms. The transition rate for three-phonon processes can be found by Fermi's Golden Rule [45]:

$$\Gamma_{\lambda\lambda'\rightarrow\lambda''} = \frac{\pi\hbar}{4} |V_{\lambda\lambda'\lambda''}|^2 \delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''}) (n_\lambda + 1) (n_{\lambda'} + 1) n_{\lambda''}, \quad (2.24)$$

where $V_{\lambda\lambda'\lambda''}$ is the three-phonon interaction matrix element and n_λ is the phonon occupation number.

Boundary and isotope scattering also contribute to the total phonon lifetime:

$$\frac{1}{\tau_\lambda^{\text{tot}}} = \frac{1}{\tau_\lambda^{\text{anh}}} + \frac{1}{\tau_\lambda^{\text{boundary}}} + \frac{1}{\tau_\lambda^{\text{isotope}}}. \quad (2.25)$$

Nanostructuring, such as embedding grain boundaries or interfaces and alloying techniques, introduces mass disorder in the crystal, which in turn causes elastic scattering due to mass fluctuations that can suppress lattice thermal conductivity by introducing additional scattering channels, effectively reducing phonon mean free paths. This enhances ZT by minimizing κ_{ph} without affecting electronic transport.

The solution of the phonon Boltzmann Transport Equation (BTE) beyond the RTA involves self-consistently computing the deviation from equilibrium distribution f_λ under a thermal gradient. The full BTE reads:

$$\frac{\partial f_\lambda}{\partial t} + \mathbf{v}_\lambda \cdot \nabla T \frac{\partial f_\lambda^{(0)}}{\partial T} = - \sum_{\lambda'} (f_\lambda - f_{\lambda'}) \Gamma_{\lambda\rightarrow\lambda'}. \quad (2.26)$$

Solving this equation provides a more accurate picture of phonon transport, especially in systems with strong anisotropy or long phonon lifetimes. It is essential for predicting thermal transport in low-dimensional materials, alloys, and nanostructured systems where classical models are unable to provide accurate results.

Chapter 3

Analytical Model

This chapter presents results from a parameterized analytical model based on the tight-binding representation of two-dimensional materials with a Mexican-hat-like valence band. Building on the theoretical formalism developed in Chapter 2, we now apply the model, which systematically evaluates the electronic and thermoelectric properties of isotropic and anisotropic Mexican-hat band structures. Analytical models allow high flexibility in tuning parameters such as curvature, Fermi ring radius, and anisotropy strength, providing insight into how these band features affect the Seebeck coefficient, electrical conductivity, power factor, and figure of merit ZT .

3.1 Mexican-Hat Band Structures

The *Mexican-hat band structure* is an energy dispersion profile with a local extremum forming a ring in momentum space, rather than a single point [46]. The shape resembles the cross-section of a sombrero, with a flat central region and a raised rim, hence the name Mexican Hat. In two-dimensional (2D) materials, such dispersions are due to mechanisms such as broken inversion symmetry,

strong spin-orbit coupling, or specific orbital hybridizations. These effects flatten the energy bands near the valence/conduction band edges and give rise to a characteristic ring-shaped constant-energy contour, referred to as the Fermi ring [17]. This ring occurs at a finite momentum value, ($k = k_c$), around the Brillouin zone center.

The formation of a Fermi ring in momentum space leads to a van Hove like singularity in the density of states (DOS) and a step-like onset in the transmission spectrum [47]. The sharp peak in the density of states (DOS) near the band extremum arises from the ring of degenerate states and the flat energy surface. A high DOS peak indicates the presence of a large number of available electronic states near the band edge [16, 48]. The transmission spectrum's step-like onset at the valence band edge reflects the DOS singularity. This step-like transmission onset and sharp DOS peak enhance the Seebeck coefficient by increasing carrier occupation asymmetry near the chemical potential, without significantly reducing electrical conductivity. Modifying the band shape in such 2D materials through chemical doping, strain engineering, or heterostructure design offers a promising approach to optimizing thermoelectric performance.

The Mexican-hat dispersion enables enhanced energy filtering, which selectively allows carriers near the band edge to contribute to electrical transport. This dispersion also promotes band convergence and potential carrier localization, as flat bands inherently lead to a high effective mass [49]. These characteristics collectively make the rational design of high-efficiency thermoelectric materials particularly appealing. Consequently, the Mexican-hat band structure provides a modifiable and adjustable design platform for efficient 2D thermoelectric materials, further supported by its associated van Hove singularity and a step-like transmission function.

3.2 Tight Binding model

To investigate the thermoelectric properties of 2D materials that exhibit a Mexican-hat-like band dispersion, we begin by modeling the electronic structure using a tight-binding Hamiltonian. This model captures both nearest-neighbor (t_1) and next-nearest-neighbor (t_2) hopping processes and is given by [50]:

$$H = -t_1 \sum_{\langle i,j \rangle} (c_i^\dagger c_j + \text{h.c.}) - t_2 \sum_{\langle\langle i,j \rangle\rangle} (c_i^\dagger c_j + \text{h.c.}) \quad (3.1)$$

Where $c_i^\dagger$ and c_j are electronic creation and annihilation operators, respectively. The corresponding energy dispersion in momentum space becomes:

$$E_{\pm}(\mathbf{k}) = \pm t_1 \sqrt{3 + f(\mathbf{k})} - t_2 f(\mathbf{k}) \quad (3.2)$$

where $f(\mathbf{k})$ is a lattice-dependent structure factor:

$$f(\mathbf{k}) = 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\cos\left(\frac{3}{2}k_x a\right) \quad (3.3)$$

The shape of the band structure and, in particular, the emergence of Mexican-hat-like features such as the radius of the Fermi ring k_c and the height of the Mexican-hat ϵ_0 near the valence band edge is controlled by the dimensionless ratio $\xi = t_2/t_1$. Physically, ξ reflects the relative importance of next-nearest-neighbor hopping, which can be tuned by strain, gating, or chemical doping [17].

3.2.1 Low-Energy Analytical Model

We use a low-energy approximation of the valence band near its extremum to gain analytical insight into the Mexican-hat-like dispersion. In the isotropic case, the band structure is modeled using a quartic dispersion relation given by [51]:

$$\varepsilon(\mathbf{k}) = \varepsilon_v - \alpha(k^2 - k_c^2)^2 \quad (3.4)$$

where ε_v represents the energy at the band edge, α is a prefactor related to curvature, and k_c is the radius in $\mathbf{k}$ -space at which the valence band maximum occurs, forming the Fermi ring.

The radius k_c can be expressed explicitly as:

$$k_c = \frac{2}{3a} \cos^{-1} \left(\frac{1}{16\xi^2} - \frac{5}{4} \right), \quad (3.5)$$

Where a is the lattice constant, and $\xi = t_2/t_1$ is the hopping ratio between next-nearest and nearest neighbors.

The energy at the valence band edge is given by [52]:

$$\varepsilon_v = \frac{1}{4\xi} + 3\xi, \quad (3.6)$$

The band curvature parameter, denoted as α , is expressed as follows:

$$\alpha = \frac{1}{k_c^4} \left(\frac{1}{4\xi} - 3 + 9\xi \right) \quad (3.7)$$

The energy at the valence band edge is given by:

$$\varepsilon_v = \frac{1}{4\xi} + 3\xi \quad (3.8)$$

The band curvature parameter α becomes:

$$\alpha = \frac{1}{k_c^4} \left(\frac{1}{4\xi} - 3 + 9\xi \right). \quad (3.9)$$

The energy at the Γ point (where $k = 0$) is given by:

$$\varepsilon_0 = \varepsilon_v - \alpha k_c^4. \quad (3.10)$$

The hopping ratio ξ plays a critical role in defining the geometric profile of the Mexican-hat-like band structure of a material. Adjusting ξ directly modifies the depth of the central valley and the radius of the Fermi ring [53]. These modifications substantially affect critical properties, including the density of states (DOS) near the band edge, which subsequently determine the material's thermoelectric performance.

In real materials, the hopping ratio, $\xi = t_2/t_1$, can be changed through several mechanisms. These include applying external electric fields, as seen in layered heterostructures, substrate-induced symmetry breaking, mechanical strain, which changes bond lengths and orbital overlap, and chemical functionalization or alloying [54]. This ability to tune the hopping ratio makes the Mexican-hat band topology a versatile target for electronic and thermoelectric engineering.

The resulting band structure behavior is illustrated in Figure 3.1, where Figure 3.1 (a) shows the 3D surface of the analytical dispersion at a representative value of ξ , showing the ring-like energy extremum. Figure 3.1 (b) presents the 1D band dispersion for various values of ξ , showing how both the valley height ε_0 and Fermi ring radius k_c evolve. The plots demonstrate that increasing the parameter ξ produces a flatter electronic band structure and increases the degeneracy of electronic states at the valence band maximum. These features are known to enhance thermoelectric performance by increasing the Seebeck coefficient and electrical conductivity.

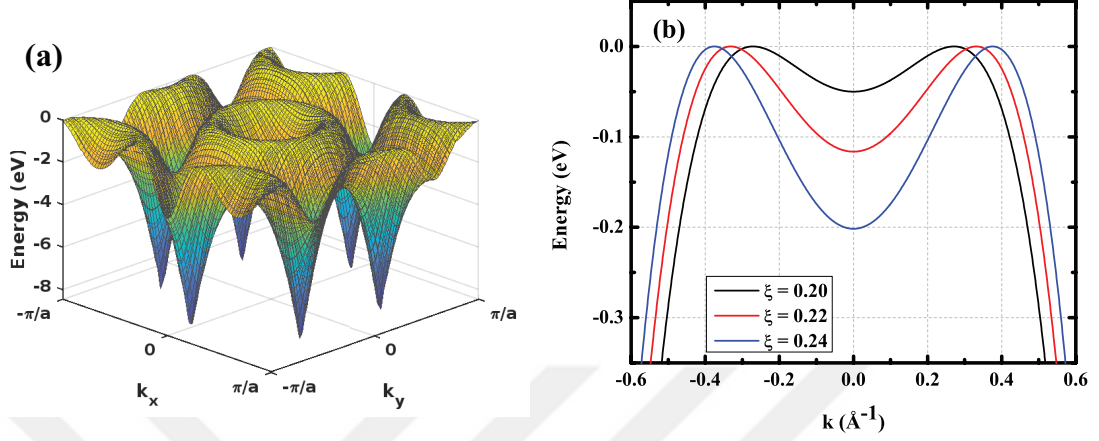


Figure 3.1: (a) 2D surface plot of the Mexican-hat-like valence band showing a ring extremum at radius k_c . (b) Band dispersions for different hopping ratios $\xi = t_2/t_1$; increasing ξ flattens the band and deepens the Mexican-hat profile.

This isotropic model preserves the ring-like extremum and captures key features such as the step-like density of states (DOS) at the band edge:

$$g(\varepsilon) = \frac{\pi}{2} \sqrt{\frac{\alpha}{\varepsilon_v - \varepsilon}} [1 + \theta(\varepsilon - \varepsilon_v + \alpha k_c^4)] \quad (3.11)$$

where θ is the Heaviside step function. This analytical form shows a sharp increase in DOS as the energy approaches ε_v from below. The square-root divergence reflects a quasi-1D character in the DOS due to the ring of extrema, known as a van Hove singularity. Such a singularity enhances the Seebeck coefficient by amplifying energy-dependent carrier asymmetry, especially in narrow energy windows near the Fermi level.

The Mexican-hat geometry profoundly affects the transmission spectrum $T(\varepsilon)$, quantifying the number of propagating modes at each energy level. From the quartic dispersion, we derive:

$$T(\varepsilon) = \theta(\varepsilon_v - \varepsilon)(k_1 + k_2) \frac{a}{\pi} \quad (3.12)$$

where k_1 and k_2 are the wavevector solutions to the equation

$\varepsilon(k) = \varepsilon_v - \alpha(k^2 - k_c^2)^2$, obtained by inverting the quartic dispersion. These values account for the number of conduction channels contributing to transport at energy ε .

For an explicit analytical approximation near the band edge, $T(\varepsilon)$ simplifies to:

$$T(\varepsilon) = \frac{k_c a}{\pi} \left[\left(1 + \sqrt{\frac{\varepsilon - \varepsilon_v}{\alpha k_c^4}} \right)^{1/2} + \left(1 - \sqrt{\frac{\varepsilon - \varepsilon_v}{\alpha k_c^4}} \right)^{1/2} \right] \theta(\varepsilon_v - \varepsilon) \quad (3.13)$$

which shows $T(\varepsilon)$ grows sharply as ε drops below ε_v . This step-like behavior indicates a sudden onset of multiple transport channels, stemming from the nearly degenerate k -states along the Fermi ring.

At the lowest-order approximation, the transmission becomes:

$$T(\varepsilon) = \theta(\varepsilon_v - \varepsilon) \cdot \frac{2k_c a}{\pi} \quad (3.14)$$

This reveals the stabilized transmission that occurs immediately below the band edge, which is an essential trait for enhancing thermoelectric efficiency.

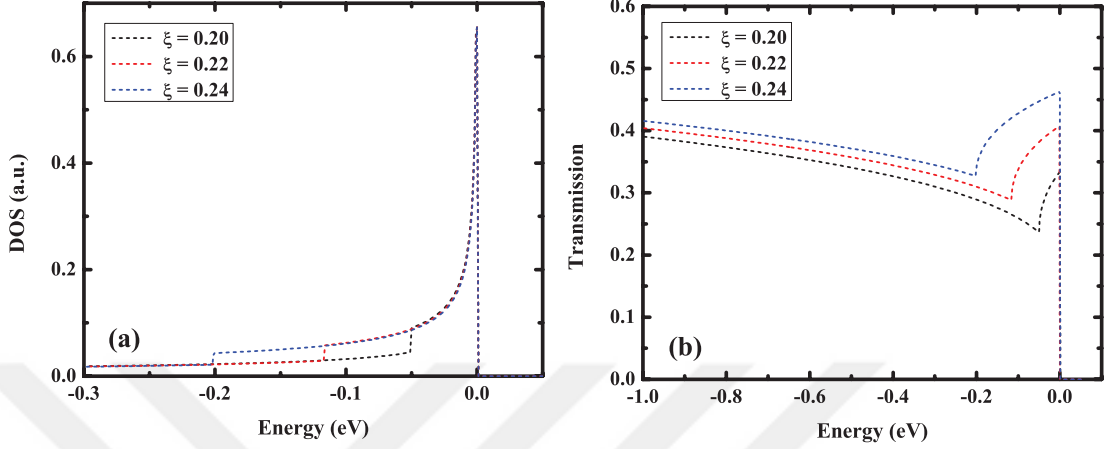


Figure 3.2: (a) Density of states (DOS) and (b) transmission spectrum $T(E)$ obtained from the *isotropic* Mexican-hat dispersion for various hopping ratios $\xi = t_2/t_1$. Increasing ξ sharpens the near-edge DOS and steepens the transmission onset.

The plots in Figure 3.2 validate the theoretical predictions. As ξ increases, the DOS and transmission spectra exhibit more dramatic features. The DOS divergence becomes sharper, indicating more substantial energy filtering effects. Simultaneously, the transmission spectrum shows an increasingly step-like rise below ε_v , corresponding to a larger number of propagating modes. Together, these characteristics point to a higher power factor ($PF = S^2\sigma$) and an improved thermoelectric figure of merit (ZT).

3.2.2 Anisotropic Mexican-Hat Band Structure

The anisotropy in the Mexican-hat band structure occurs when energy dispersion around the valence band maximum diverges from circular symmetry [55, 56]. This is usually caused by angular variations in the electronic structure, which may originate from crystal field effects, spin-orbit interactions, strain, or anisotropic hopping between orbitals in the tight-binding model. While an isotropic Mexican-hat dispersion exhibits a degenerate energy contour forming a perfect ring (Fermi ring) in k -space, the anisotropic variant distorts this ring into an angular-dependent shape where the energy extrema no longer lie on a circle but

vary with the polar angle ϕ . This results in an energy-dependent Fermi surface with a varying radius $k_0(\phi)$ and adds directionality to the transport properties.

The anisotropy is captured in the tight-binding energy model by including a β -dependent angular modulation term [57]:

$$E(k, \phi) = E_v - \alpha(k^2 - k_c^2)^2 + \beta k^4 \cos(4\phi), \quad (3.15)$$

In the above equation, β controls the degree of anisotropy, k_c represents the radius of the isotropic Fermi ring, and α influences the curvature. For $\beta = 0$, the dispersion remains isotropic. However, when $\beta \neq 0$, the energy becomes angle-dependent, leading to warping of the Fermi ring and energy splitting along different directions.

The Mexican-hat-like band structure's energy extrema no longer occur at a uniform energy level across all directions in momentum space. Instead, the energy reaches unique maximum and minimum values depending on crystallographic orientation.

The highest energy peak (E_+) and the lowest energy peak (E_-) are given by [55, 58]:

$$E_+ = E_v + \frac{\alpha\beta}{\alpha - \beta} k_c^4 \quad (3.16)$$

$$E_- = E_v - \frac{\alpha\beta}{\alpha + \beta} k_c^4 \quad (3.17)$$

The energy difference between these minimum and maximum values quantifies the degree of anisotropy:

$$\Delta E = E_+ - E_- = \frac{2\alpha^2\beta k_c^4}{\alpha^2 - \beta^2} \quad (3.18)$$

As β and ΔE approach zero, the system recovers the isotropic limit, and as β increases, the energy asymmetry becomes more apparent. This change could significantly affect the transport properties.

Similarly, the Fermi ring radius becomes angle-dependent in anisotropic systems. The general expression for the radius $k_0(\phi)$ as a function of angle ϕ in polar coordinates is:

$$k_0(\phi) = \sqrt{\frac{\alpha}{\alpha - \beta \cos(4\phi)}} k_c \quad (3.19)$$

At angles where $\cos(4\phi)$ reaches extrema, the radius reaches its maximum and minimum values:

$$k'_0 = \sqrt{\frac{\alpha}{\alpha - \beta}} k_c \quad (3.20)$$

$$k''_0 = \sqrt{\frac{\alpha}{\alpha + \beta}} k_c \quad (3.21)$$

As a result, these transformations alter the initially circular Fermi surface into a warped and angularly modulated structure, which affects electronic and thermoelectric responses.

The influence of β on the anisotropic Mexican-hat dispersion is visualized in Figure 3.3, where Figure 3.3(a) displays the 2D surface plot of the energy dispersion in k -space for $\beta > 0$, revealing the warping of the energy ring along different angular directions. Figure 3.3(b) shows 1D cross-sectional band structures for several β values along $\phi = 0^\circ$ and $\phi = 45^\circ$. As β increases, the radius of the Fermi ring becomes more dependent on direction, and the valence band edge flattens and splits, leading to $\Delta E \neq 0$.

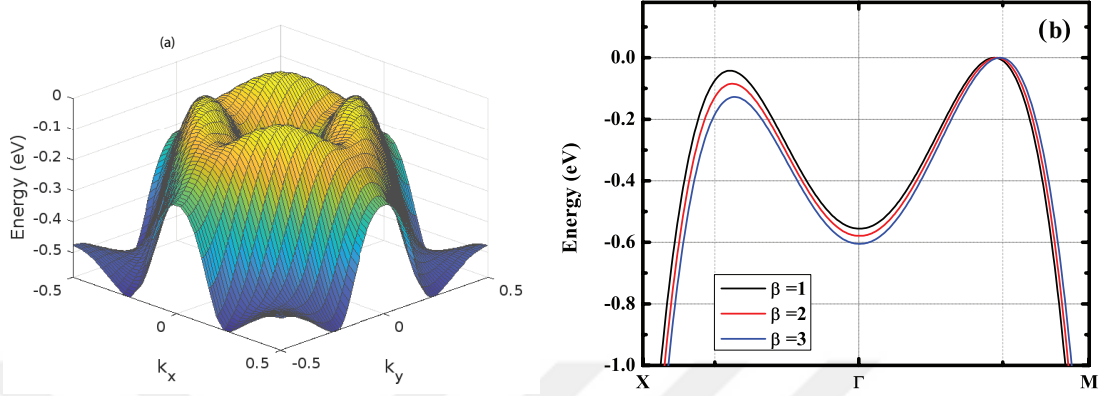


Figure 3.3: (a) Energy surface under anisotropy ($\beta \neq 0$) showing broken circular symmetry and angular warping of the Mexican-hat ring. (b) One-dimensional cuts reveal energy splitting and a directional variation of the ring radius $k_0(\phi)$ that grows with increasing β .

3.2.2.1 Modifications in Density of States and Transmission Spectrum

Anisotropy also affects the density of states (DOS), especially near the band edges [59]. For anisotropic band dispersion ($\beta \neq 0$), the DOS is obtained by integrating over the angular variable ϕ in momentum space:

$$g(E) = \frac{1}{16\pi^2} \int_0^{2\pi} d\phi \sqrt{\alpha^2(k_{1,2}^2 - k_c^2)^2 + \beta k_{1,2}^3 \cos^2(4\phi)} \quad (3.22)$$

where the roots $k_{1,2}$ correspond to the energy solutions along each angle and are defined as:

$$k_{1,2} = \left(\frac{\alpha k_c^2}{\alpha - \beta \cos(4\phi)} \right) \left[1 \pm \sqrt{1 - \frac{(\alpha - \beta \cos(4\phi))(E - E_v + \alpha k_c^4)}{\alpha^2 k_c^4}} \right]^{1/2} \quad (3.23)$$

In the isotropic limit ($\beta = 0$), this expression simplifies to:

$$g(E) = \frac{1}{8\pi\alpha} \sqrt{\frac{\alpha}{E_v - E}} \quad (3.24)$$

which shows a van Hove singularity at the band edge, a characteristic feature of the Mexican-hat dispersion. In the anisotropic case, the singularity becomes broadened, resulting in a smoother and wider density of states (DOS) peak. This change affects thermoelectric properties directly, including the Seebeck coefficient and the power factor.

Anisotropy also influences the transmission spectrum $T(\varepsilon)$, which no longer rises sharply at a single energy threshold [60]. Instead, the spread in energy extrema across different angular directions broadens the transmission onset.

The angle-resolved transmission can be written as [61]:

$$T(\varepsilon) = \theta(E_v - \varepsilon) \cdot \frac{a}{\pi} \int_0^{2\pi} [k_1(\phi) + k_2(\phi)] d\phi \quad (3.25)$$

where $k_1(\phi)$ and $k_2(\phi)$ are the two real momentum solutions of the quartic equation for a given direction ϕ .

For small deviations from the band edge ($\varepsilon \lesssim E_v$), a good approximation is obtained using:

$$T(\varepsilon) \approx \theta(E_v - \varepsilon) \cdot \frac{2a}{\pi} \int_0^{2\pi} k_0(\phi) d\phi \quad (3.26)$$

with the angle-dependent Fermi radius:

$$k_0(\phi) = \sqrt{\frac{\alpha}{\alpha - \beta \cos(4\phi)}} k_c \quad (3.27)$$

As shown in the plots below (Fig. 3.4), the DOS and transmission profiles

change systematically with β . For small β , the singularities are sharp and localized. As β increases, the singularities broaden and the sharp step-like increase in transmission becomes more gradual. This broadening causes a spread in the available conducting channels, which can reduce the asymmetry of carrier transport near the chemical potential and lower the Seebeck coefficient and power factor.

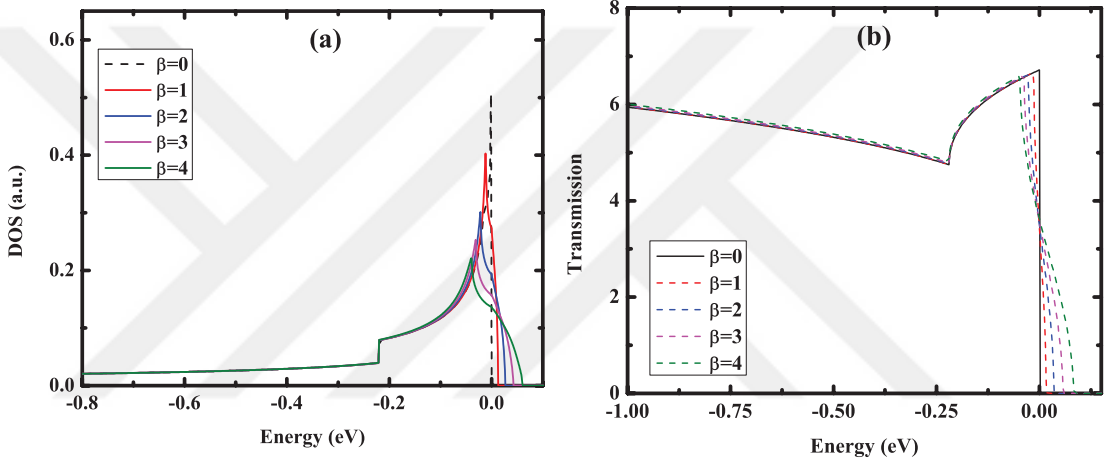


Figure 3.4: Effect of anisotropy β on (a) the density of states (DOS) and (b) the transmission spectrum $T(E)$ for the anisotropic Mexican-hat model. Increasing β broadens and lowers the van Hove singularity in the DOS and softens the step-like transmission onset, trends that diminish the near-edge thermopower.

3.3 Landauer Formalism and Transport Moments

To compute thermoelectric coefficients, we use the Landauer formalization in the linear response regime [62]. The energy-dependent transmission function $T(\varepsilon)$ shows the number of conducting channels; it is derived and used to evaluate the transport integrals analytically as:

$$L_n(\mu, T) = -\frac{2}{h} \int dE \frac{\partial f(E)}{\partial E} (E - \mu)^n T(E) \quad (3.28)$$

where μ is the chemical potential, $f(E)$ is the Fermi–Dirac distribution, and h is Planck’s constant.

Each transport moment, L_n , shows a unique physical aspect of charge and heat transport, described as [63]:

$$L_0 = -\frac{2}{h} \int dE \frac{\partial f(E)}{\partial E} T(E) \quad (3.29)$$

The transport moment, L_0 , is the electrical current carried by the system in response to an applied voltage. It shows the total number of available conducting channels, weighted by their occupation probability. A larger L_0 suggests that electrical conductivity is higher, as more states near the chemical potential will contribute to current flow. In the ballistic limit, L_0 is directly proportional to the quantum conductance of the system.

$$L_1 = -\frac{2}{h} \int dE \frac{\partial f(E)}{\partial E} (E - \mu) T(E) \quad (3.30)$$

The transport moment L_1 represents the net energy transported by charge carriers relative to the chemical potential. It determines the Seebeck coefficient and explains asymmetry in the transmission around the Fermi level. If the transmission function is symmetric, $L_1 = 0$ generates no thermoelectric voltage. A non-zero L_1 occurs when carriers above and below the chemical potential contribute unequally.

$$L_2 = -\frac{2}{h} \int dE \frac{\partial f(E)}{\partial E} (E - \mu)^2 T(E) \quad (3.31)$$

The transport moment L_2 quantifies the fluctuation or spread of the energy current. It captures how much energy electrons carry that deviates from the mean value μ . This moment enters the expression for the electronic part of the thermal conductivity and helps distinguish between reversible (electrical) and irreversible (thermal) energy transport. A higher L_2 indicates carriers carrying more heat

away from the Fermi level, which might reduce thermoelectric efficiency unless regulated.

In the Landauer framework, the moments L_n extracted from the transmission spectrum give a quantitative basis for evaluating electrical and thermoelectric transport coefficients:

Electrical conductance:

$$G = e^2 L_0 \quad (3.32)$$

where L_0 captures the availability of electronic states for conduction.

Seebeck coefficient:

$$S = \frac{1}{eT} \left(\frac{L_1}{L_0} \right), \quad (3.33)$$

which quantifies the voltage generated per unit temperature difference, determined by asymmetry in energy distribution.

Electronic thermal conductivity:

$$\kappa_{\text{el}} = \frac{1}{T} \left(L_2 - \frac{L_1^2}{L_0} \right) \quad (3.34)$$

describes heat flow carried by electrons under a temperature gradient.

Power factor and figure of merit:

$$\text{PF} = S^2 \sigma = S^2 G \cdot \frac{L}{A}, \quad ZT = \frac{S^2 \sigma T}{\kappa_{\text{el}} + \kappa_{\text{ph}}}, \quad (3.35)$$

where κ_{ph} is the lattice thermal conductivity.

This formalism allows us to systematically examine how tuning the band structure via ξ (in the isotropic case) and β (in the anisotropic case) influences thermoelectric performance. The transport integrals L_0 , L_1 , and L_2 explain the relation between electronic structure and energy transport; they are susceptible to features such as van Hove singularities and asymmetry near the Fermi level.

3.3.1 Thermoelectric Transport in the Isotropic Case

The thermoelectric response of materials with an isotropic Mexican-hat band structure is profoundly influenced by the unique dispersion profile characterized by a ring-like valence band maximum. As established in the analytical model, tuning the hopping ratio $\xi = t_2/t_1$ modulates both the depth of the energy minimum (valley height ε_0) and the radius of the Fermi ring k_c [16]. These features directly influence the density of states (DOS), transmission spectrum, and subsequently, the transport moments L_0 , L_1 , and L_2 .

The transmission spectrum exhibits a step-like behavior with respect to energy, and as ξ increases, the band becomes flatter and the Fermi ring expands, resulting in a larger number of available electronic states near the valence band edge. This increases transmission at energies just below ε_v , enhancing thermoelectric performance through improved energy filtering and carrier asymmetry.

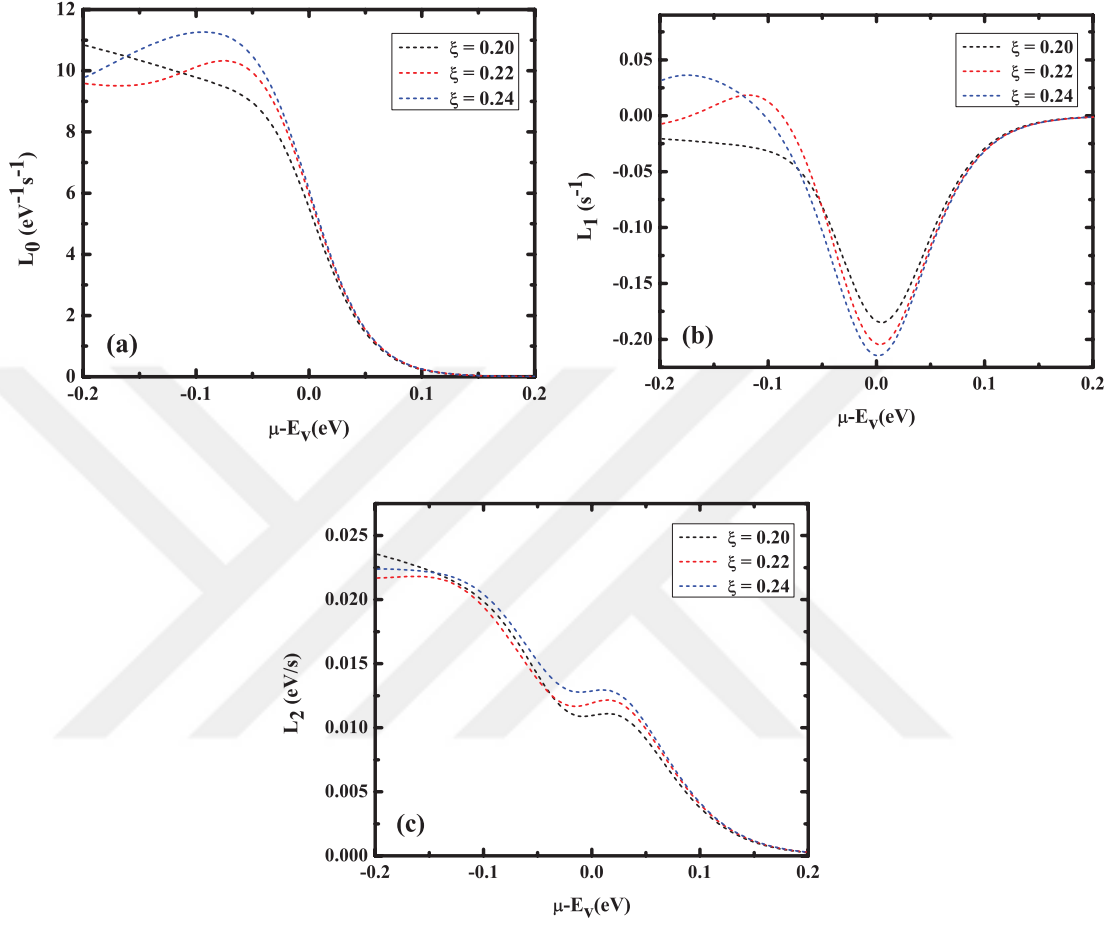


Figure 3.5: Energy-dependent transport integrals for different hopping ratios $\xi = t_2/t_1$ in the isotropic Mexican-hat model. (a) L_0 : particle (charge) transport kernel; (b) L_1 : energy-weighted transport kernel; (c) L_2 : energy-variance kernel. Increasing ξ accentuates the Mexican-hat character, enhancing the near-edge L_0 , the thermopower asymmetry in L_1 , and the energy spread captured by L_2 .

Figure 3.5 shows the calculated transport integrals L_0 , L_1 , and L_2 as functions of chemical potential μ for different values of ξ . L_0 represents the electrical current response, and it increases with ξ , particularly around the energy corresponding to the band edge. This is because a larger Fermi ring introduces more conducting channels, resulting in higher transmission. L_1 , which governs the Seebeck coefficient, shows a sharp sign change near $\mu = \varepsilon_v$, reflecting the shift in the balance between electron-like and hole-like carriers. L_2 , related to energy fluctuations and thermal conductivity, also increases with ξ and becomes more

asymmetric, indicating a broader energy range for efficient carrier transport.

Figure 3.6 further illustrates the influence of ξ on the derived thermoelectric coefficients. As ξ increases, the electrical conductivity σ improves due to the larger L_0 , while the electronic thermal conductivity κ_{el} also increases due to a broader energy distribution in L_2 .

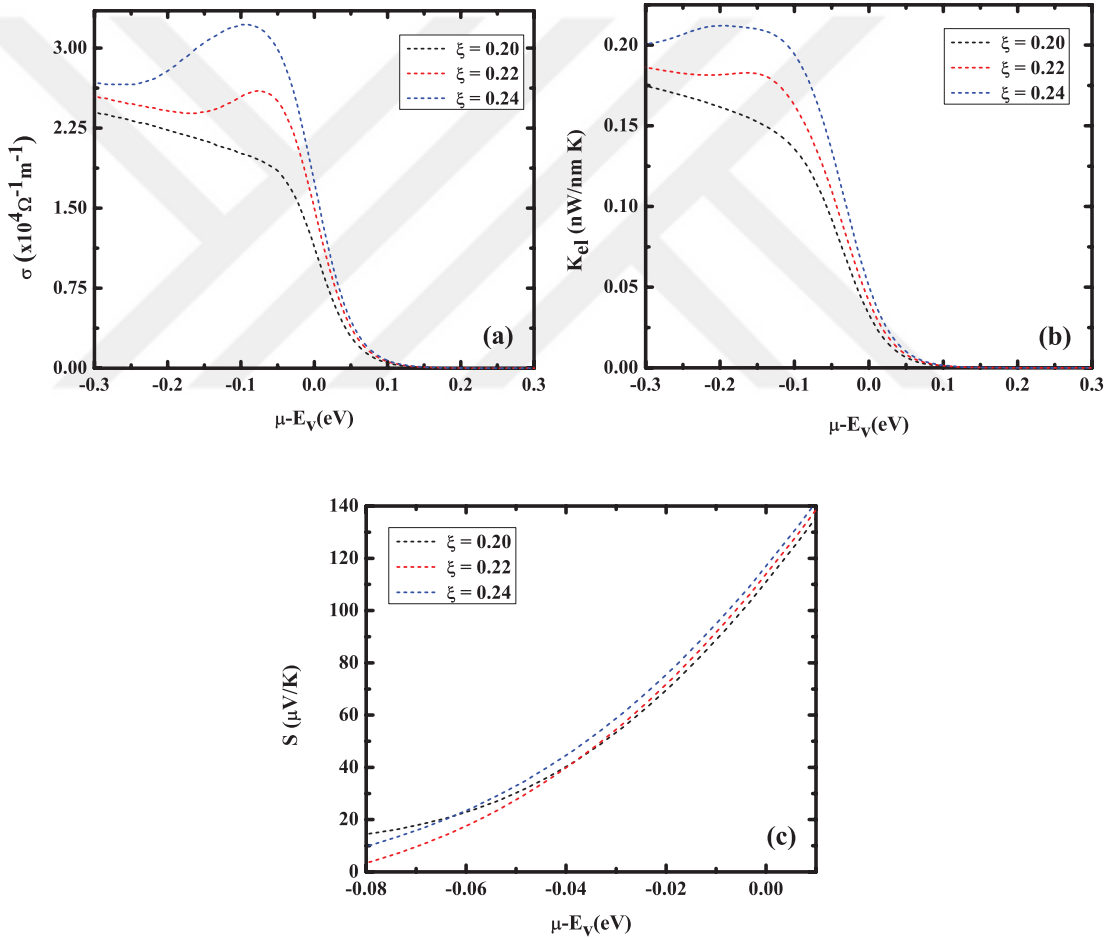


Figure 3.6: Thermoelectric transport coefficients from transport integrals for the *isotropic* Mexican-hat model. (a) Electrical conductivity σ vs chemical potential μ for various hopping ratios $\xi = t_2/t_1$; (b) electronic thermal conductivity κ_{el} vs μ ; (c) Seebeck coefficient S vs μ . Increasing ξ flattens the band edge and sharpens the DOS onset, which boosts near-edge σ and enhances the asymmetry that drives S , while κ_{el} follows the conductivity trend through the same transport kernels.

The Seebeck coefficient S seems to show a peak that shifts and grows with ξ , reflecting enhanced energy filtering as the density of states becomes steeper near the Fermi level. This trend highlights the importance of tailoring band curvature and Fermi surface topology for optimized thermoelectric performance.

Finally, figure 3.7 shows the behavior of the power factor ($PF = S^2\sigma$) and the dimensionless figure of merit (ZT). A clear enhancement in PF is observed with increasing ξ , resulting from the simultaneous increase in Seebeck coefficient and electrical conductivity. Broadening the PF peak over a wider chemical potential window implies improved tolerance to doping fluctuations.

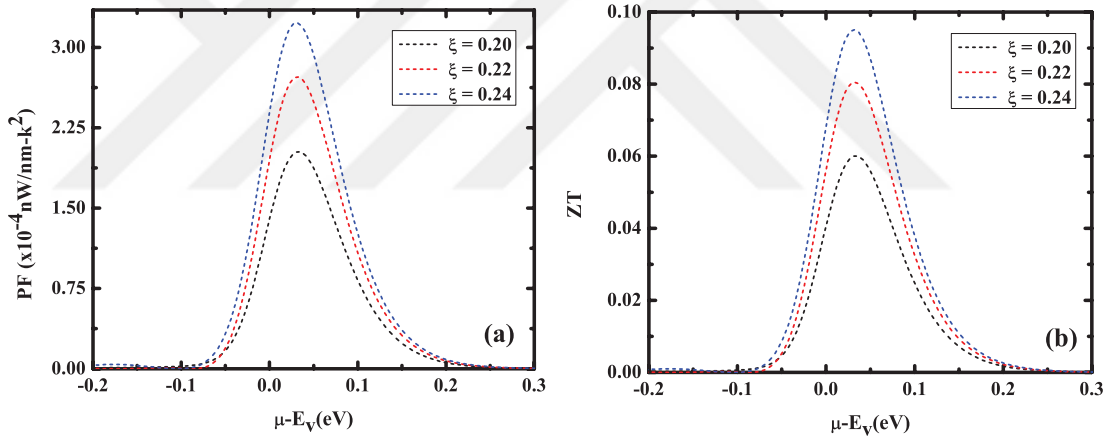


Figure 3.7: (a) Power factor $PF = S^2\sigma$ and (b) figure of merit ZT for the *isotropic* Mexican-hat dispersion as functions of reduced chemical potential μ at various hopping ratios $\xi = t_2/t_1$. Increasing ξ sharpens the near-edge DOS and widens the energy window of optimal performance, yielding higher peak PF and ZT .

Similarly, the figure of merit ZT also improves significantly with ξ , particularly near the band edge. This improvement arises from high S , increased σ , and moderate growth in κ_{el} . These results confirm that tailoring the hopping ratio ξ —and hence the Mexican-hat features—offers an effective strategy for enhancing thermoelectric performance in isotropic 2D materials.

3.3.2 Thermoelectric Transport in the Anisotropic Case

Angular distortions in the valence band extremum control the thermoelectric behavior of materials with an anisotropic Mexican-hat band structure. These distortions result in a non-uniform Fermi ring and direction-dependent transport characteristics. In realistic two-dimensional materials, perfect circular symmetry is often disrupted by structural anisotropy, spin-orbit coupling, strain, or orbital orientation effects [45, 64]. As introduced in the analytical model, the anisotropy is parameterized by β , which modulates the angular warping of the Fermi surface and introduces energy splitting between extremal directions. This results in an energy-dependent Fermi ring radius $k_0(\phi)$ and an angular spread in the band edge energy, denoted by ΔE .

As established in the analytical model, increasing β introduces asymmetry and angular warping to the band edge, transforming the Fermi ring into a distorted structure and splitting the energy maximum into directional peaks. This reduces the degeneracy of states at the valence band maximum and smooths sharp features, which allows optimal thermoelectric filtering in isotropic systems. The broadened energy distribution softens the divergence of DOS and the step-like transmission, which changes the transport response on moments L_0 , L_1 , and L_2 .

Figure 3.8 illustrates the calculated transport moments for varying values of β . As β increases, L_0 , which governs electrical conductivity, displays a wider energy window and a slightly reduced peak. This change indicates a more distributed set of conducting channels. The moment L_1 , responsible for the Seebeck coefficient, becomes more shallow and less sharp-peaked with β , suggesting a reduced asymmetry in energy transport. Similarly, L_2 , which relates to the variance in energy distribution and contributes to the electronic thermal conductivity, broadens and flattens, reflecting a more delocalized energy spread.

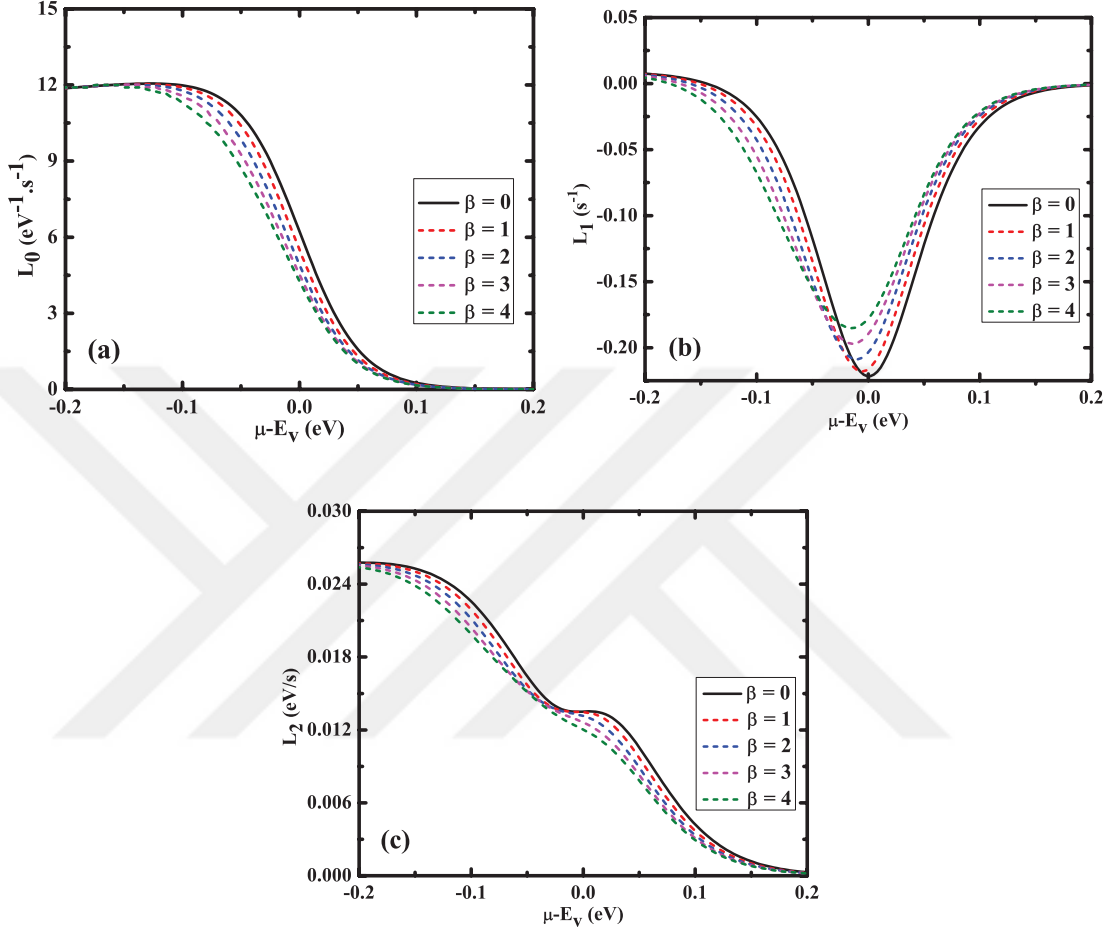


Figure 3.8: Energy-resolved transport moments for the *anisotropic* Mexican-hat model as a function of reduced chemical potential μ : (a) L_0 (charge-transport kernel), (b) L_1 (energy-weighted, odd moment driving thermopower), (c) L_2 (energy-variance kernel linked to κ_{el}). Increasing anisotropy β broadens the near-edge features, reduces sharp asymmetries in L_1 , and modifies L_0 and L_2 in ways that tend to lower S and reshape σ and κ_{el} .

The effect of anisotropy on derived thermoelectric coefficients is shown in Figure 3.9. As β increases, the electrical conductivity σ decreases slightly and spreads over a wider chemical potential range due to the smoothed L_0 . The Seebeck coefficient S displays a damped peak and reduced magnitude with increasing β , mainly due to the loss of strong energy filtering and transport asymmetry. In contrast, the electronic thermal conductivity κ_{el} becomes slightly enhanced due to the broadened L_2 , indicating electrons can carry heat across a broader range

of energies.

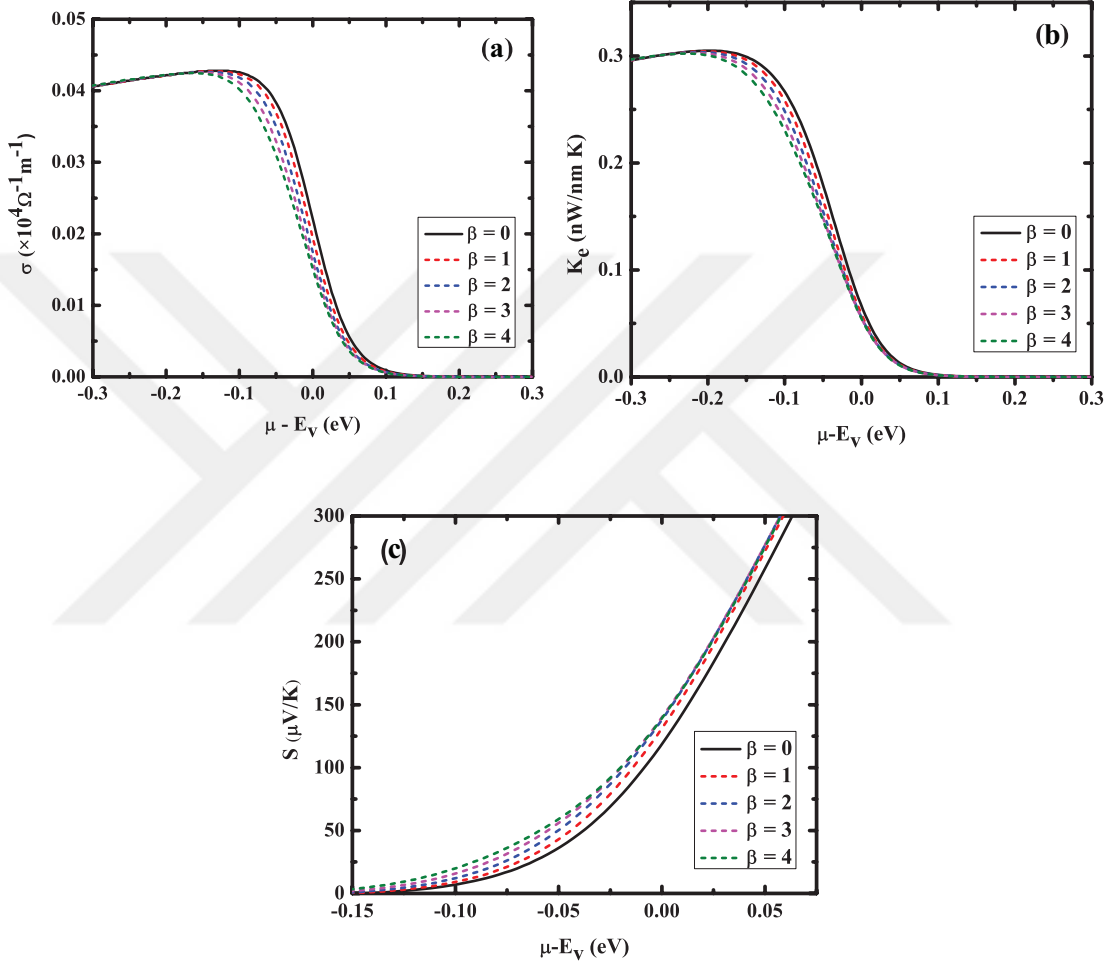


Figure 3.9: Thermoelectric transport coefficients for the *anisotropic* Mexican-hat model as functions of reduced chemical potential μ : (a) electrical conductivity σ , (b) electronic thermal conductivity κ_{el} , (c) Seebeck coefficient S , each shown for various anisotropy parameters β . Increasing β broadens/softens the band-edge features, which reduces the near-edge asymmetry that drives S and modifies σ and κ_{el} through the same transport kernels.

Finally, Figure 3.10 summarizes the performance metrics which includes the power factor $PF = S^2\sigma$ and figure of merit ZT across different anisotropy levels. The effect of increasing β is visible. The power factor peak is lowered and broadened, indicating reduced thermoelectric performance due to diminished Seebeck

contribution.

The ZT value, while still showing a peak, is significantly suppressed with higher β values. The broadening of conduction pathways and loss of energy filtering reduce both S and the benefit from increased σ . These results emphasize that while moderate anisotropy can maintain balanced performance and directional control, strong anisotropy generally degrades thermoelectric efficiency due to the smearing of electronic structure features.

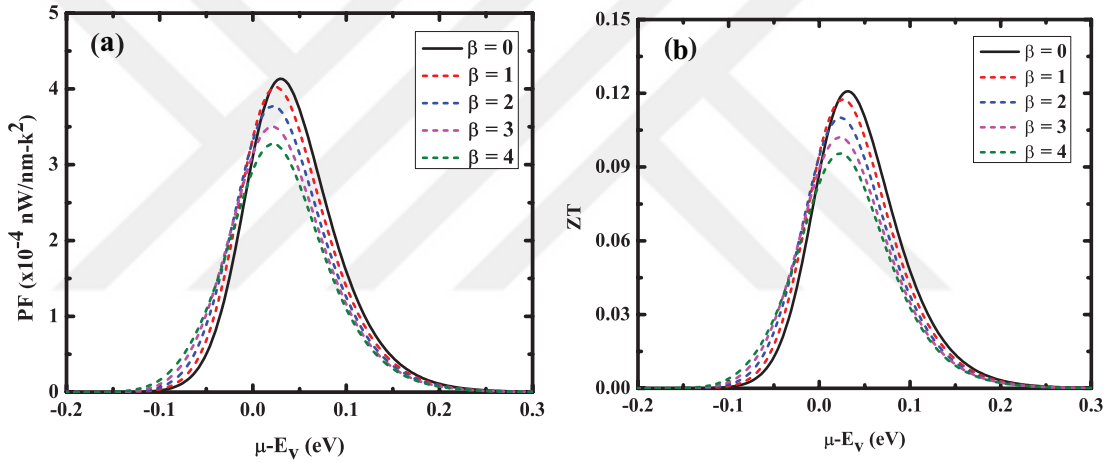


Figure 3.10: (a) Power factor $PF = S^2\sigma$ and (b) figure of merit ZT for the *anisotropic* Mexican-hat model as functions of chemical potential μ at various anisotropy parameters β . Increasing β broadens/softens the near-edge energy filtering, which lowers the peak PF and ZT and can shift the optimal μ -window.

Together, these observations confirm that anisotropy encoded via the parameter β softens the sharp electronic features that benefit thermoelectric transport in isotropic systems. The broader energy distribution reduces the strength of energy filtering and sharp conductance onset, often leading to lower Seebeck coefficients and reduced thermoelectric efficiency. However, moderate anisotropy can balance broadened conduction and directional control, which may benefit certain device geometries or applications.

Chapter 4

First-Principles Study of Thermoelectric Performance

First-principles methods, based on Density Functional Theory (DFT), provide a robust and predictable framework for exploring the electronic, structural, and thermoelectric properties of materials. Without relying on empirical parameters, DFT enables the accurate modeling of complex low-dimensional materials, including nontrivial band topologies such as Mexican-hat-like dispersions.

In this chapter, we employ DFT along with the semi-classical Boltzmann Transport Equation (BTE) to study a set of two-dimensional (2D) compounds. We obtain electronic transport coefficients, including the Seebeck coefficient, electrical conductivity, and electronic thermal conductivity, from the DFT-based band structures and investigate the correlation between the electronic transport coefficients and energy-resolved features of electronic band structure. The Lattice thermal conductivity is computed by explicitly solving the phonon BTE, enabling a comprehensive assessment of thermoelectric performance.

4.1 Computational Details

The thermoelectric properties of the 2D materials, including PbBrF, PbClF, PbIF, BaHI, BiOCl, and CaHBr, were systematically analyzed using a first-principles computational approach. The electronic structure of these two-dimensional materials was studied using density functional theory, and lattice transport analysis was performed using the semi-classical Boltzmann transport equation.

All first-principles calculations were performed using the Vienna *Ab initio* Simulation Package (VASP), based on the projector augmented wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange–correlation functional [65, 66, 67]. A plane-wave energy cutoff of 520 eV was used throughout the calculations. Structural optimizations were performed using a Monkhorst–Pack k -point mesh of $11 \times 11 \times 1$, with energy and force convergence thresholds of 10^{-7} eV and 10^{-7} eV/Å, respectively. A vacuum spacing of 25 Å was added along the out-of-plane (z) direction to eliminate interlayer interactions due to periodic boundary conditions.

Once the structure was fully relaxed, NSCF calculations were performed to obtain the electronic band structure and density of states (DOS). A denser mesh of $21 \times 21 \times 1$ k -points was employed for the DOS calculations to ensure accurate sampling near the Fermi level. Band structures were computed along high-symmetry paths within the 2D Brillouin zone. Spin–orbit coupling (SOC) effects were included for Pb-based compounds (PbBrF, PbClF, PbIF), where relativistic interactions significantly influence the band gap and curvature.

To evaluate electronic transport properties, the semi-classical Boltzmann transport equation (BTE) was solved using the **BoltzTraP** code under the constant relaxation time approximation (CRTA) [68]. The Seebeck coefficient (S), electrical conductivity (σ), and electronic thermal conductivity (κ_{el}) were calculated as functions of temperature and chemical potential. Doping effects were simulated using the rigid band approximation.

For lattice dynamics, harmonic (second-order) and anharmonic (third-order) interatomic force constants (IFCs) were obtained prior to thermal conductivity calculations. The second-order IFCs were computed using density functional perturbation theory (DFPT) as implemented in the Phonopy package. A $5 \times 5 \times 1$ supercell was employed for PbXF and BiOCl compounds, while a $3 \times 3 \times 1$ supercell was sufficient for BaHI and CaHBr. The corresponding $5 \times 5 \times 1$ k -mesh was used for force calculations. The third-order IFCs were generated using the density functional perturbation theory (DFPT) via `thirdorder.py`, with VASP providing forces for all symmetry-inequivalent displaced configurations [66, 69, 70].

The lattice thermal conductivity (κ_{ph}) was determined using 2nd order (harmonic) and 3rd order (anharmonic) interatomic force constants (IFCs) by solving the phonon Boltzmann transport equation as implemented in the ShengBTE code [71]. Calculations employed a $16 \times 16 \times 1$ q -mesh to sample the Brillouin zone. This methodology incorporates both harmonic phonon dispersion and anharmonic phonon-phonon scattering, providing a robust description of lattice heat transport. Subsequently, the power factor ($S^2\sigma$) and thermoelectric figure of merit (ZT) were evaluated.

This computational protocol provides a comprehensive and accurate assessment of both electronic and phononic contributions to thermoelectric performance in the studied materials. The following sections present results from each methodological step.

2D Structure

All the two-dimensional (2D) compounds investigated in this work crystallize in a tetragonal lattice belonging to the $P4/nmm$ space group. The primitive unit cell of each material contains six atoms arranged in five alternating atomic layers. The crystal structure adopts a layered matlockite-type motif with the general stacking sequence (A–B–C–B–A), where A denotes a heavy cation such as Pb, Ba, Bi, or Ca; B corresponds to a halogen or hydrogen species (Br, Cl, I, or H);

and C represents a light terminal anion such as F or O.

This stacking sequence produces a mirror-symmetric configuration about the central atomic plane. It gives rise to a puckered surface topology, where atoms exhibit alternating displacements perpendicular to the basal plane. As illustrated in Figure 4.1, both the top and side views of the optimized structure reveal a quasi-bilayer arrangement with weak van der Waals interactions along the out-of-plane direction. The presence of this van der Waals gap ensures that the layers can exist as stable monolayers without strong inter-layer bonding.

The puckered geometry and layered architecture have essential implications for transport. The structural asymmetry enhances phonon scattering, while the mass contrast between the constituent atoms further suppresses lattice thermal conductivity. Such features are advantageous for achieving improved thermoelectric performance in these 2D compounds.

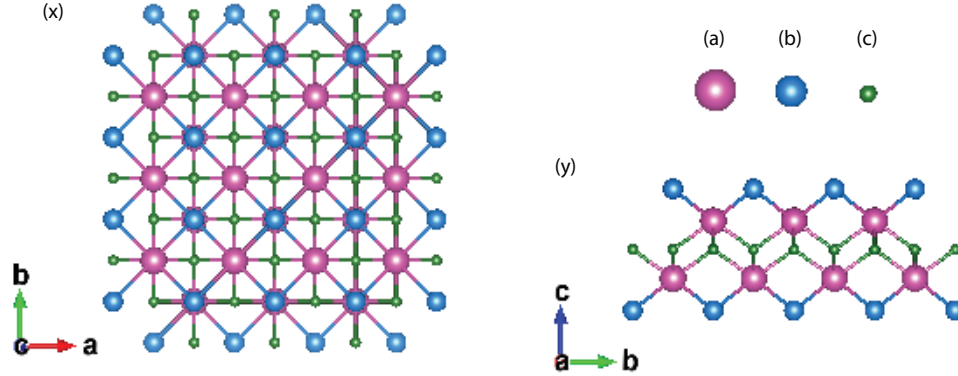


Figure 4.1: Optimized unit cell of the studied matlockite-type 2D materials, showing both top and side views.

All structural relaxations were carried out using the conjugate gradient algorithm, with no symmetry constraints imposed. To eliminate spurious interlayer interactions arising from periodic boundary conditions, a vacuum spacing of 25 Å was introduced along the out-of-plane (z) direction. The relaxed structures exhibit a puckered (or folded) configuration, which plays a crucial role in enhancing phonon scattering and thereby reducing lattice thermal conductivity. The optimized in-plane lattice constants ($a = b$) and monolayer thicknesses (d), obtained from the fully relaxed geometries, are summarized in Table 4.1.

Electronic Band Structure and Density of States (DOS)

The electronic band structures and corresponding densities of states (DOS) for the studied two-dimensional materials were computed using the PBE functional under the framework of density functional theory. The results, found in Figure 4.2, reveal several critical features relevant to their thermoelectric properties. All six compounds exhibit a Mexican-hat-like dispersion near the valence band maximum (VBM), a unique characteristic where the band shows a flat or slightly inverted curvature around the Γ point. This dispersion results in a ring-shaped Fermi surface in k -space, which gives rise to a high density of states due to a Van Hove singularity just below the Fermi level. Such a sharp DOS peak is highly desirable for thermoelectric performance, as it can enhance the Seebeck coefficient (S) through energy filtering.

The influence of spin-orbit coupling (SOC) is particularly notable in the Pb-based compounds (PbBrF, PbClF, and PbIF) due to the heavy atomic number of lead. The inclusion of SOC in the calculations, represented by the dashed blue lines, results in a distinct splitting of the valence and conduction bands. This leads to a systematic reduction of the electronic band gap, a crucial consideration for practical applications. For instance, the band gap of PbIF decreases from 2.30 eV (without SOC) to 1.98 eV (with SOC), while PbClF's gap narrows from 3.50 eV to 3.28 eV. The SOC-induced modifications are not limited to band gap narrowing; they also subtly change the curvature of the Mexican-hat dispersion, directly impacting the position and sharpness of the Van Hove singularity and, consequently, the thermoelectric properties. Furthermore, the electronic band extrema for these compounds have different energies at the X' and M' high-symmetry points, leading to anisotropy in the Fermi surface, which modulates the shape of the Van Hove singularity.

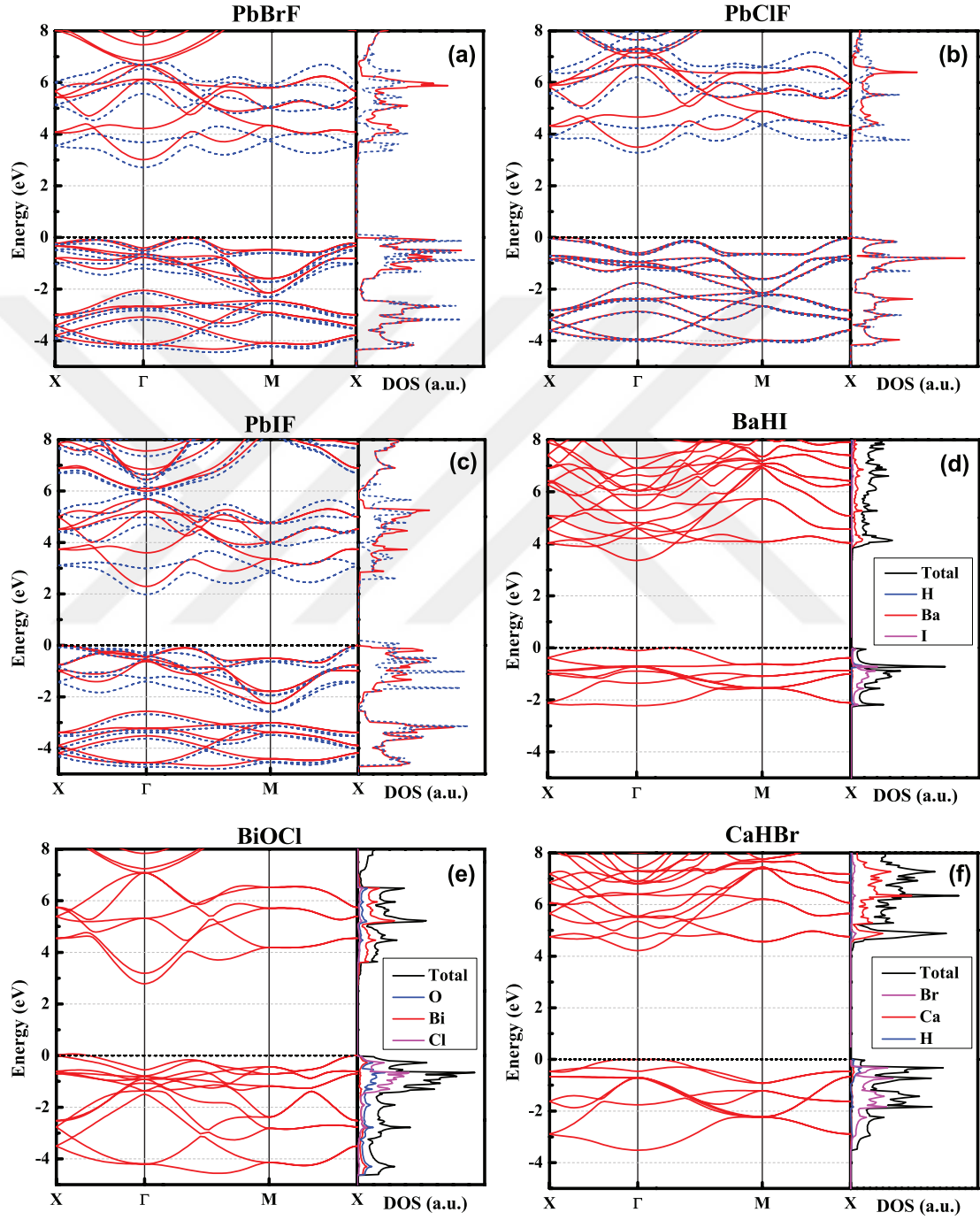


Figure 4.2: Electronic band structures and total density of states (DOS) for the studied 2D compounds. Solid lines represent calculations without SOC, dashed blue lines include SOC effects for Pb-based compounds. All compounds display valence band maxima with Mexican-hat-like features, and high DOS near the Fermi level.

Beyond the PbXF compounds, the other compounds also exhibit promising electronic features. BaHI and BiOCl show clear Mexican-hat features with sharp DOS peaks, indicating their potential for high thermoelectric performance. In contrast, CaHBr presents a flatter dispersion at the VBM, leading to a less pronounced DOS peak. This suggests that its thermoelectric potential may not be as high as that of the other materials. The distinct contributions from different atomic species are also evident in the partial DOS (PDOS) plots. For example, in the Pb-based compounds, the valence band is dominated by the hybridization of Pb-p and halogen-p orbitals. In contrast, in the other compounds, contributions from the respective heavy cations and anions define the states near the Fermi level. This detailed analysis of the band structure and DOS, including the unique parameters of the Mexican-hat dispersion, provides a fundamental understanding of the electronic factors that govern the thermoelectric performance of these materials.

The optimized lattice parameters and electronic band gaps for the studied 2D monolayers are summarized in Table 4.1. For 2D-PbXF compounds, the band gap values with and without SOC are provided. As expected, the heavy Pb atom in PbBrF, PbClF, and PbIF leads to a significant influence from SOC, systematically reducing the band gap compared to calculations without it. For instance, PbIF's band gap decreases from 2.30 eV to 1.98 eV, while PbClF shows a reduction from 3.50 eV to 3.28 eV. These relativistic effects are crucial for an accurate description of the electronic properties near the band edges, which are critical for transport.

Table 4.1: Optimized lattice constants ($a = b$), 2D layer thickness d , and PBE band gaps with and without SOC for the studied monolayers.

Compound	$a = b$ (Å)	d (Å)	E_g (eV)	$E_g(\text{SOC})$ (eV)
PbBrF	4.08	6.71	3.01	2.71
PbClF	4.01	6.23	3.50	3.28
PbIF	4.19	7.31	2.30	1.98
BaHI	4.61	6.92	3.35	—
BiOCl	3.89	6.18	2.72	—
CaHBr	3.83	6.28	4.20	—

The unique electronic features of these compounds extend to the characteristics of their Mexican-hat dispersions. The key parameters defining these features, the energy height of the peak at $k = 0$ (ϵ_0), the ring radius in k-space (k_c), and the directional anisotropy, are summarized in Table 4.2. Spin-orbit coupling tends to modify these parameters slightly; for example, it can reduce the ring height ϵ_0 and the radius k_c . Notably, PbClF and BiOCl exhibit large ϵ_0 and sharp k_c values, which are key indicators of a strong Van Hove singularity at the valence band edge. This feature is particularly beneficial for thermoelectric performance by enhancing the Seebeck coefficient through energy filtering. However, the strong anisotropy, especially pronounced in BiOCl, also indicates a directional dependence of transport properties, which must be considered for device design.

Table 4.2: Mexican-hat parameters for the studied compounds. Values in parentheses include spin-orbit coupling.

Compound	ϵ_0 (meV), (SOC)	k_c ($\text{\AA}^{-1}$), (SOC)	Anisotropy (meV), (SOC)
PbBrF	409, (478)	0.067, (0.059)	77.9, (90.3)
PbClF	603, (603)	0.088, (0.103)	121, (113.8)
PbIF	336, (277)	0.046, (0.046)	135, (134)
BaHI	112	0.041	6.8
BiOCl	616	0.084	223
CaHBr	8.2	0.021	2.8

The band structure analysis confirmed that all these monolayers exhibit Mexican-hat dispersions in their valence bands with varying degrees of ring depth, radius, and anisotropy. These intrinsic electronic features have a significant impact on their thermoelectric response, which will be analyzed in detail in the following sections.

Electronic Transport Properties (BTE)

The electronic transport coefficients of the studied 2D compounds were computed by combining first-principles band structures with semiclassical Boltzmann transport in the constant-relaxation-time approximation (CRTA). Calculations were performed with BoltzTraP and BoltzTraP2, which reconstruct the band energies

$E(\mathbf{k})$ and group velocities on dense $\mathbf{k}$ -meshes via Fourier interpolation of the DFT band structures [72, 73]. This approach enables dense Brillouin-zone sampling at modest cost, facilitating the convergence of transport integrals.

Within this framework, the electrical conductivity (σ), Seebeck coefficient (S), and electronic thermal conductivity (κ_{el}) were evaluated as functions of temperature for a range of carrier concentrations. Since a first-principles determination of the relaxation time τ is system-dependent and beyond the scope of this work, we report σ and κ_{el} considering a constant relaxation time of (10^{-14}s), while the seebeck coefficient S is τ -independent in CRTA, can be compared directly across materials and computational settings.

For heavy-element systems, notably the Pb-containing compounds, relativistic spin-orbit coupling (SOC) noticeably modifies band curvature and near-degeneracies around the Fermi level, thereby affecting transport. We therefore analyzed all Pb-based compounds both with and without SOC. SOC was included self-consistently in VASP, and the resulting band structures were used as inputs to BoltzTraP/BoltzTraP2.

The calculated trends mirror the underlying electronic structure: an enhanced density of states near E_F and sharp band-edge features generally promote larger S , whereas more dispersive bands favor higher σ . By examining σ , S , and κ_{el} versus temperature and chemical potential, we directly relate the Mexican-hat-like valence-band maxima identified above to their impact on the thermoelectric response.

Figures 4.3 show the calculated Seebeck coefficient $S(T)$ for the PbXF compounds ($X = \text{Br}, \text{Cl}, \text{I}$) both with and without spin-orbit coupling (SOC), also for the complete set of monolayers we studied at two representative carrier concentrations ($n, p = 10^{18}$ and 10^{19}cm^{-3}).

For the Pb-based materials, the p -type Seebeck coefficient at 10^{18}cm^{-3} mainly in PbBrF and PbClF is noteworthy, due to a sharp density of states (DOS) increase near the Mexican-hat-like valence band maximum. Inclusion of SOC

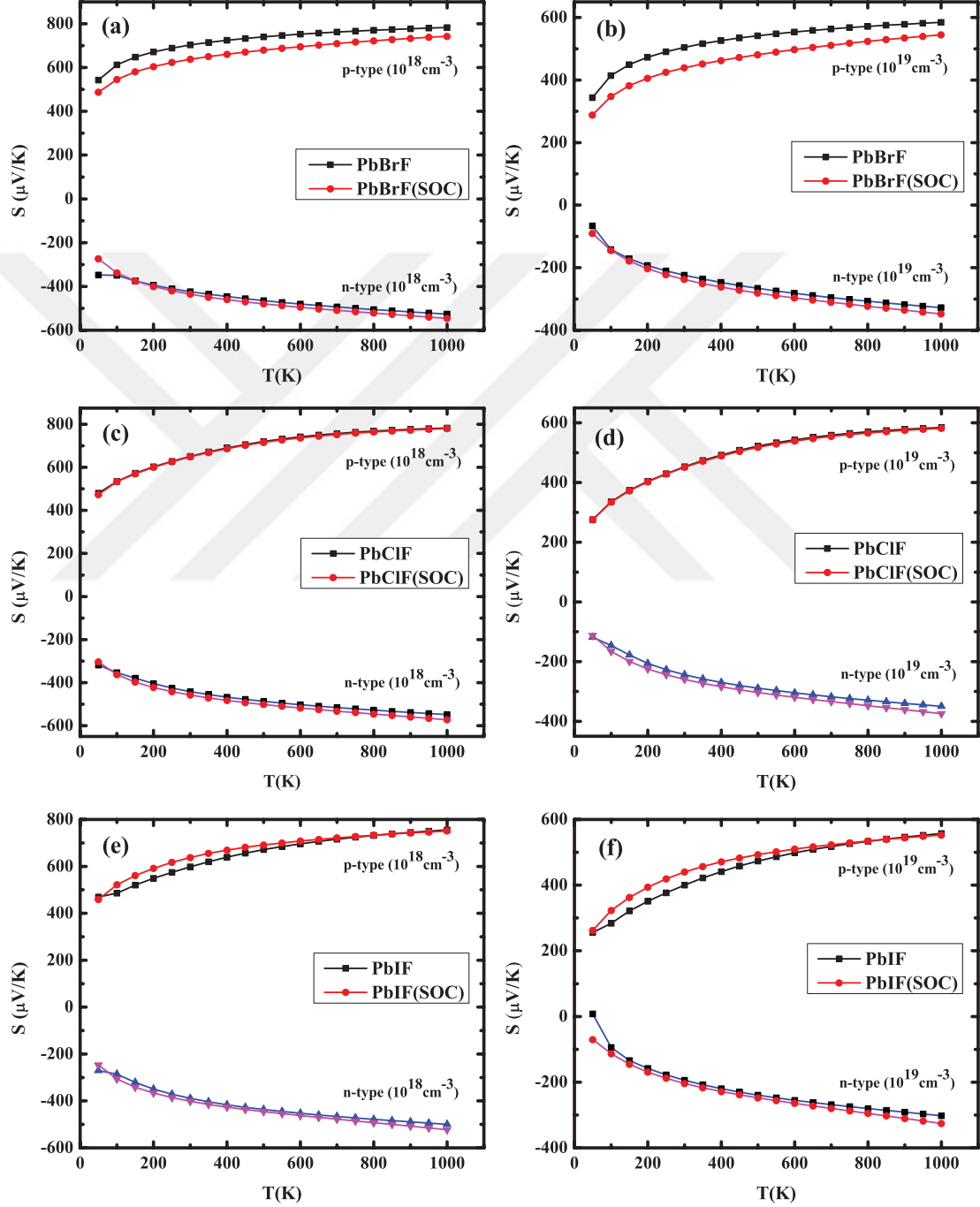


Figure 4.3: Seebeck coefficient $S(T)$ vs temperature for 2D-PbXF (X = Br, Cl, I), comparing calculations without and with SOC at carrier concentrations of 10^{18} cm^{-3} and 10^{19} cm^{-3} .

leads to a noticeable decrease in the band gap and a modification of the valence-band curvature, shifting the $S(T)$ peak and slightly reducing its magnitude. The effect is most pronounced in PbIF, where relativistic band reshaping is strongest.

Increasing the carrier concentration to 10^{19}cm^{-3} results in a systematic reduction of $|S|$ for both n -type and p -type doping, consistent with the Mott relation, which predicts that S decreases as the Fermi level moves further into the band. SOC effects remain visible at high doping, but the relative changes in S become smaller compared to the low-doping case.

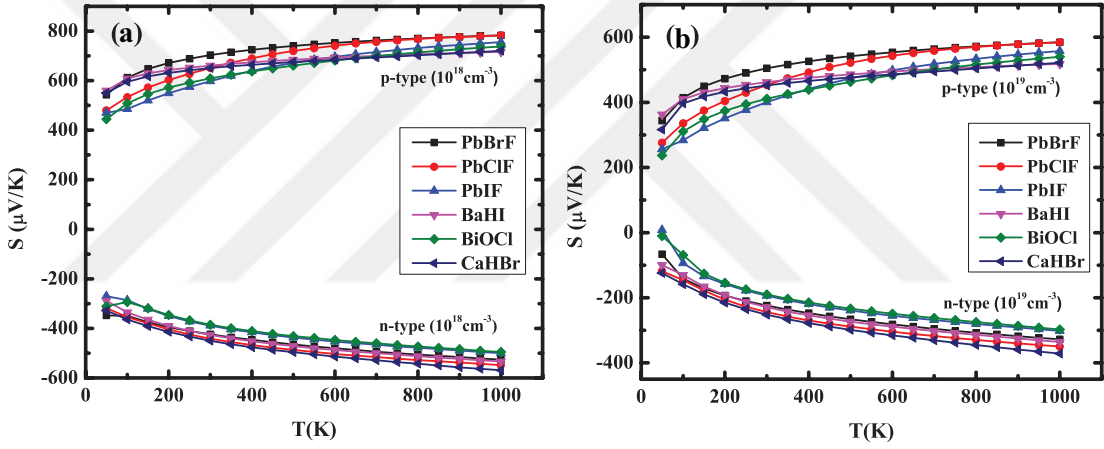


Figure 4.4: Comparison of $S(T)$ for 2D-PbXF, BaHI, BiOCl, and CaHBr at carrier concentrations of 10^{18}cm^{-3} (a) and 10^{19}cm^{-3} (b).

The comparison across all studied materials as presented in figure 4.4 highlights that, at low doping, PbBrF and PbClF exhibit the highest p -type S values, while BaHI and BiOCl achieve competitive n -type S due to their flatter conduction bands. CaHBr displays the lowest $|S|$ consistently, showing its more dispersive band edges. These results demonstrate that combining a flat valence band and a sharp DOS feature is essential to achieve high p -type thermopower.

The electrical conductivity σ of a thermoelectric material is determined by the density and mobility of charge carriers, which are both heavily influenced by the details of the electronic band structure. Within the constant relaxation time approximation (CRTA) used in our Boltzmann transport calculations, σ is evaluated as σ/τ , where $\tau = 10^{-14}\text{s}$ is the carrier relaxation time. The σ trends provide a reliable basis for comparing different compounds and identifying

promising candidates for high thermoelectric performance.

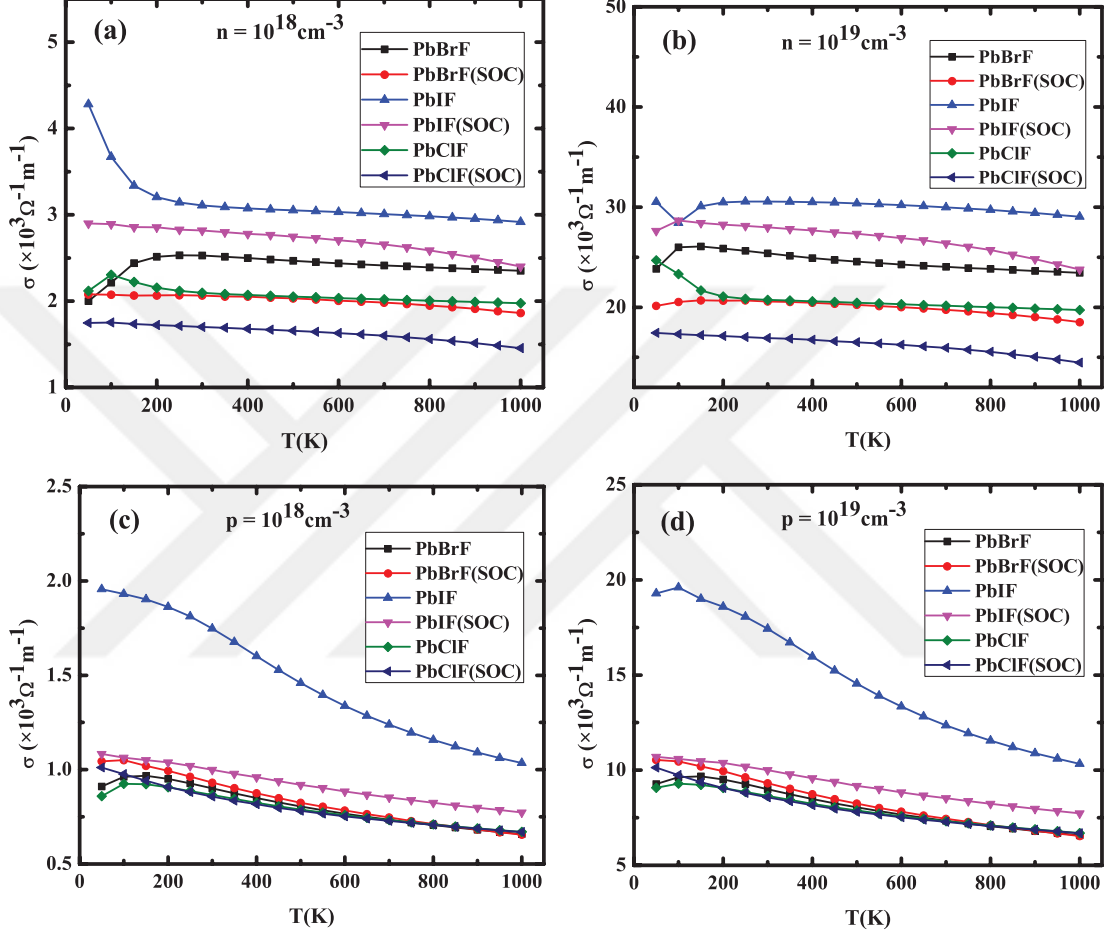


Figure 4.5: Electrical conductivity $\sigma(T)$ vs temperature for 2D-PbXF with and without SOC. (a) and (b) n -type at 10^{18} and 10^{19} cm^{-3} . (c) and (d) p -type at 10^{18} and 10^{19} cm^{-3} , respectively. SOC typically reduces σ for p -type conduction due to band flattening, while n -type shows smaller SOC-induced changes.

For the Pb-containing compounds, spin-orbit coupling (SOC) mainly changes the near-edge band dispersion. This reduces the band gap and modifies the effective mass of carriers [74]. These effects influence σ differently for n - and p -type doping: SOC may enhance or suppress σ , depending on the curvature of the conduction or valence bands.

Carrier concentration plays a powerful role as well. At lower concentrations ($n, p = 10^{18} \text{ cm}^{-3}$), the Fermi level is close to the band edges, where carrier velocities are lower, resulting in reduced σ . Increasing the carrier density

to $n, p = 10^{19} \text{cm}^{-3}$ shifts the Fermi level deeper into the bands, activating higher-velocity states and significantly increasing σ . This enhancement is more pronounced in materials with dispersive bands near the Fermi level.

By comparing n -type and p -type conductivities on the studied compounds, it can be seen that those with flatter conduction or valence bands exhibit lower conductivity, despite sometimes showing higher Seebeck coefficients. Thus, optimal thermoelectric performance requires balancing high σ with a sufficiently large Seebeck coefficient.

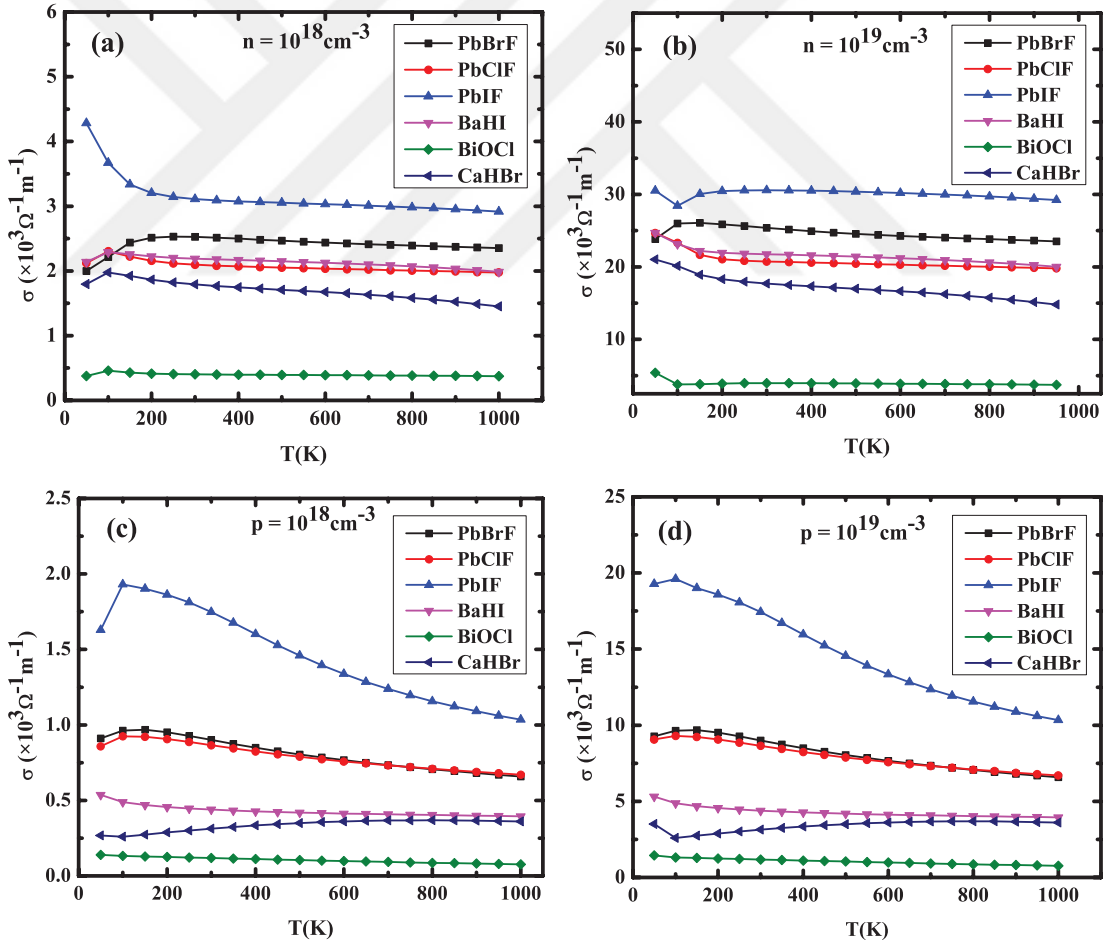


Figure 4.6: comparison of electrical conductivity ($\sigma(T)$) for all the studied compounds at p -type and n -type carrier concentration of 10^{18} and 10^{19}cm^{-3} .

The electrical conductivity, σ , reflects the ability of charge carriers to move through the crystal under an applied electric field and is directly linked to the

group velocity and carrier concentration. Figures 4.5 and 4.6 summarize the temperature dependence of σ for both carrier types at two representative doping levels.

For the Pb-based compounds, inclusion of SOC (Fig. 4.5) modifies the near-edge band curvature, generally reducing σ in *p*-type conduction, especially at lower doping levels where transport is dominated by states at the top of the valence band. In *n*-type conduction, the effect of SOC is less pronounced, suggesting that the conduction band dispersions are less sensitive to relativistic splitting.

The comparison across all studied materials without SOC (Fig. 4.6) shows that PbBrF and PbClF achieve the highest *p*-type σ values, consistent with their dispersive valence bands and high density of available states near the Fermi level. For *n*-type conduction, BaHI and BiOCl display competitive conductivity, attributable to flat yet sufficiently dispersive conduction bands that balance high DOS with decent mobility. In all systems, raising the carrier concentration from 10^{18} to 10^{19}cm^{-3} leads to a substantial increase in σ , as more carriers participate in conduction and the Fermi level moves deeper into the band, accessing higher-velocity states.

The patterns in κ_{el} follow the energy moments of the transmission that define the Landauer/BTE integrals. For the PbXF series, SOC modifies the band curvature and lifts/splits degeneracies near the valence/conduction edges. This widens the energy distribution of active carriers and shifts the temperature where κ_{el} peaks.

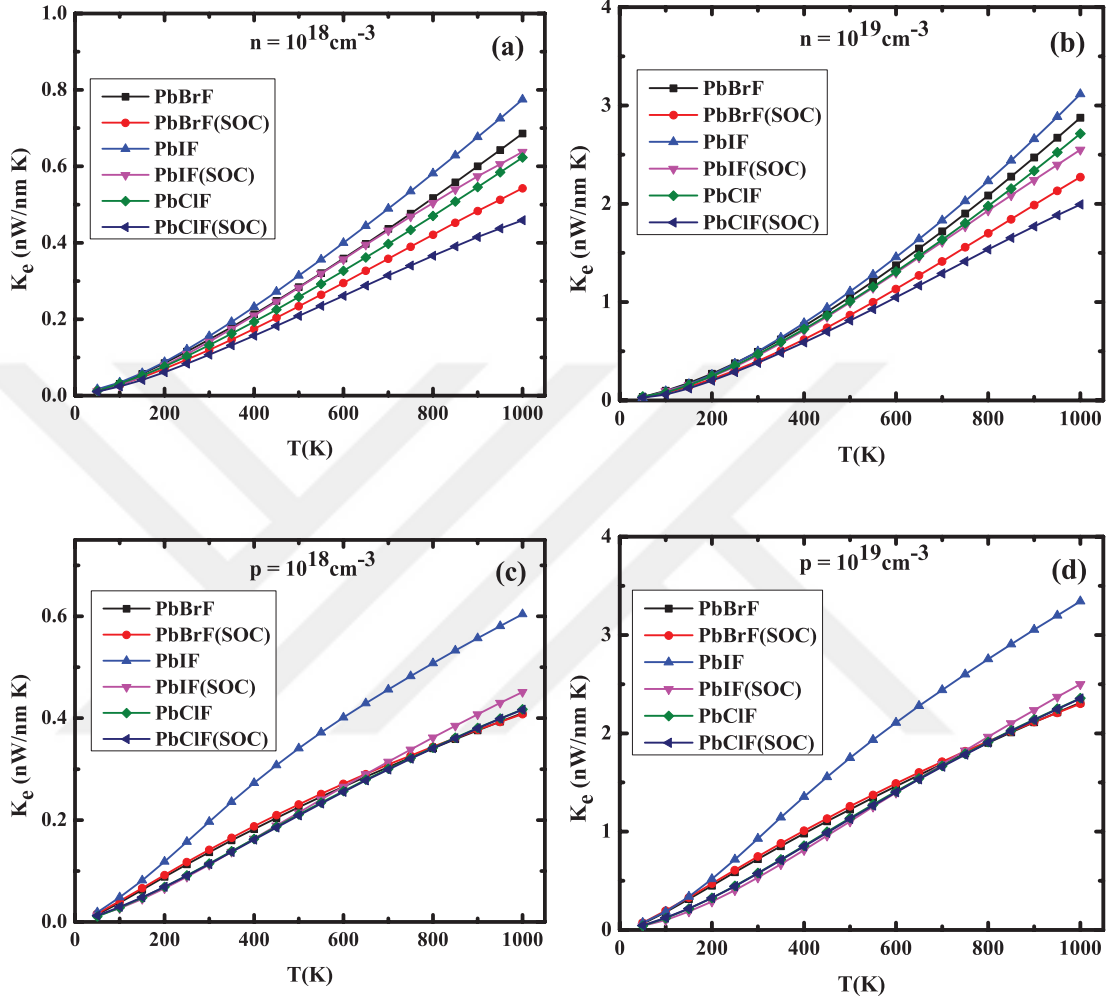


Figure 4.7: Electronic thermal conductivity κ_{el} for 2D-PbXF compounds with and without SOC against temperature for p-type and n-type carrier concentrations of 10^{18} and 10^{19} cm^{-3} . SOC reshapes near-edge dispersion (gap narrowing and curvature changes), shifting the magnitude and peak position of κ_{el} ; increasing carrier concentration generally increases κ_{el} .

Across all compounds, raising the carrier concentration from 10^{18} to 10^{19} cm^{-3} increases κ_{el} , consistent with the larger number of heat-carrying carriers and the higher-energy tails sampled at finite temperature. Materials with more dispersive transport edges (higher group velocity and wider energy window) tend to show larger κ_{el} . In contrast, flatter, Mexican-hat-like edges suppress it and maintain the balance between $S^2\sigma$ and ZT once κ_{ph} is included.

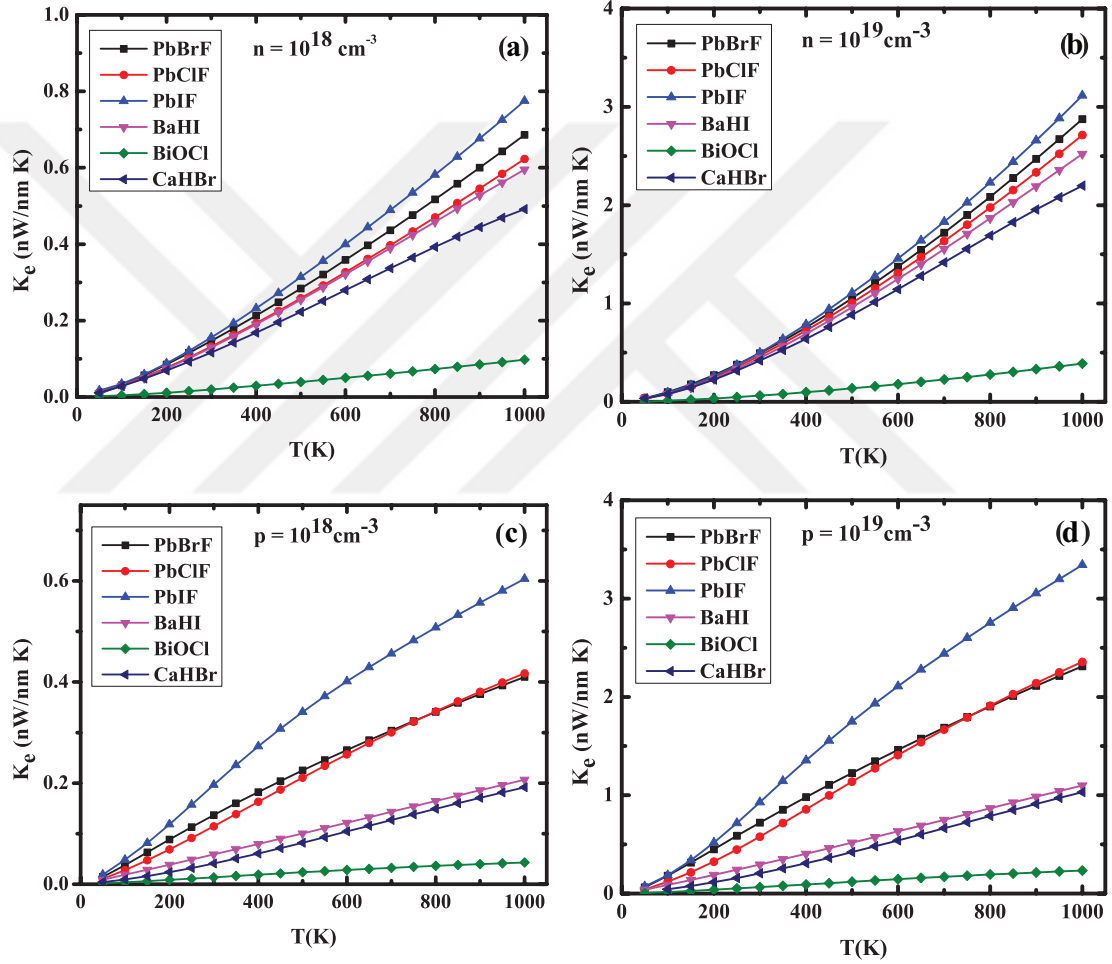


Figure 4.8: Comparison of electronic thermal conductivity κ_{el} across all monolayers plotted against temperature at p-type and n-type carrier concentrations of 10^{18} and 10^{19} cm^{-3} . More dispersive bands near the transport-relevant edges yield larger κ_{el} , whereas flatter edges give comparatively lower values. Increasing carrier concentration generally elevates κ_{el} due to enhanced carrier populations.

4.1.1 Lattice Transport Properties

The material’s lattice transport behavior is governed by its phonons’ intrinsic properties, such as dispersion relations, group velocities, scattering rates, and specific heat [75]. To quantify these properties for the studied monolayer systems, PbXF ($X = \text{Br, Cl, I}$), BaHI, BiOCl, and CaHBr, we employed a first-principles framework combining Density Functional Perturbation Theory (DFPT) for 2nd order (harmonic) force constants and 3rd order (anharmonic) force constants, and solution of the phonon Boltzmann Transport Equation (BTE) using the **ShengBTE** package.

4.1.1.1 Phonon dispersion.

The phonon dispersion relations, shown in figure 4.9, were computed using harmonic (second-order) interatomic force constants obtained from DFPT calculations in VASP, processed with the **Phonopy** code. The absence of imaginary (negative) frequencies in branches across the Brillouin zone proves that all optimized structures are stable dynamically.

In each case, the acoustic modes consist of a longitudinal acoustic (LA) branch, a transverse acoustic (TA) branch, and an out-of-plane flexural acoustic (ZA) branch coming from the Γ point. The optical branches at higher frequencies follow; their separation and curvature change depending on each system’s atomic mass and bonding stiffness.

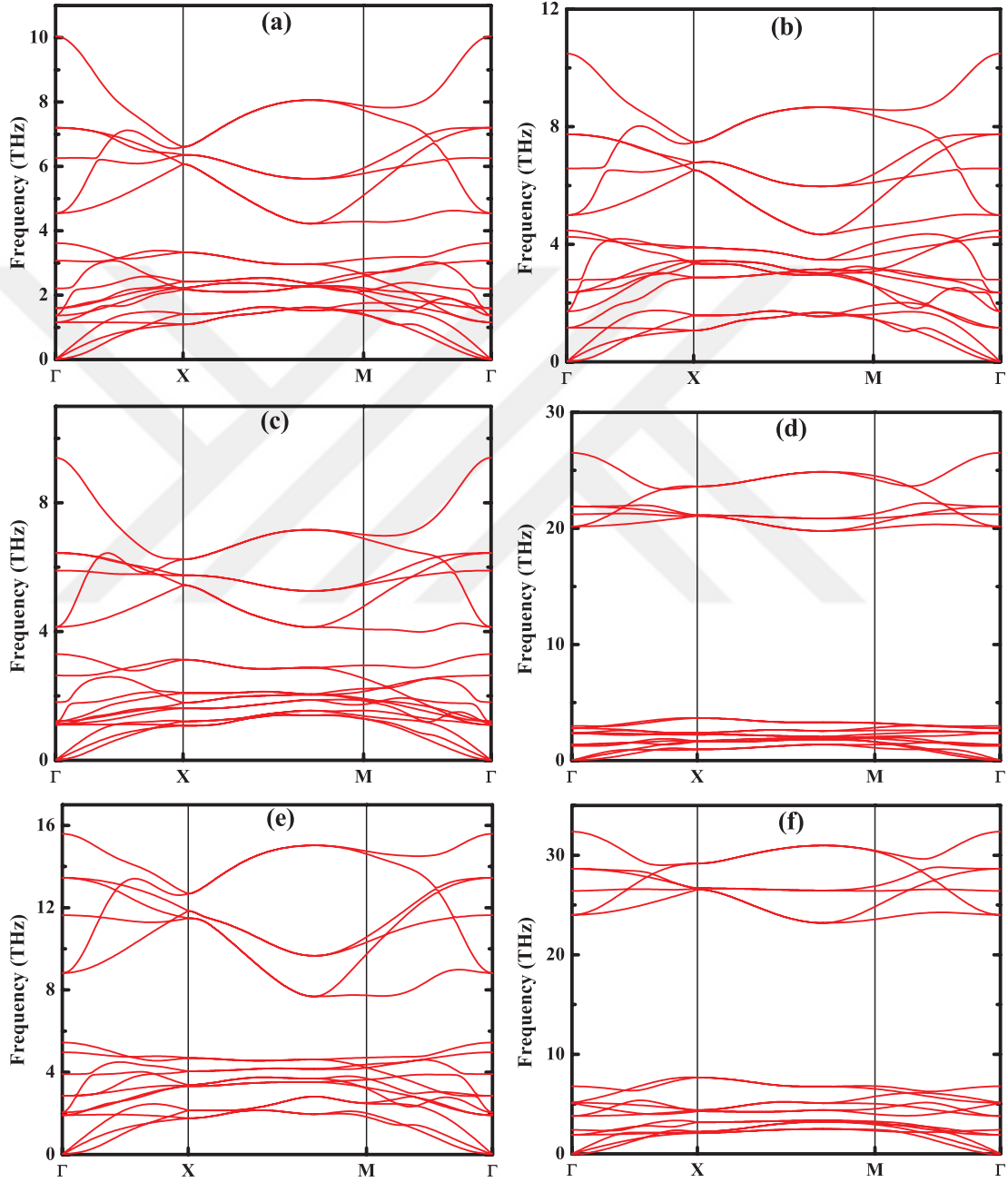


Figure 4.9: Phonon dispersion relations for PbXF ($X = \text{Br}, \text{Cl}, \text{I}$), BaHI , BiOCl , and CaHBr monolayers. The absence of imaginary frequencies indicates dynamical stability. Acoustic branches occupy the low-frequency region and optical branches appear at higher energies, with mode separation governed by mass contrast and bonding strength.

4.1.1.2 Phonon density of states.

To identify the atomic origin of various vibrational modes, we computed total and partial phonon density of states (PDOS) for each monolayer, as shown in Figure 4.10. The phonon band structures of all monolayers comprise the three acoustic modes longitudinal (LA), transverse (TA), and the out-of-plane flexural (ZA) emanating from the Γ point, followed by groups of optical branches at higher frequencies. The element-resolved PDOS clarifies the character and separation of these branches. In the PbXF series, the low-frequency manifold is dominated by Pb vibrations, while the optical branches are carried mainly by the halogen X . As X varies from F to Cl to Br (increasing mass), the X -dominated optical band shifts to lower frequencies and becomes narrower, reducing the acoustic–optical separation and indicating progressively softer Pb– X force constants. This trend is consistent with flatter optical dispersions and increased overlap between the acoustic and optical manifolds for heavier halogens.

Hydride-containing BaHI and CaHBr exhibit a pronounced mass-contrast signature: Ba/Ca and halogen vibrations populate the low-frequency acoustic region, whereas H contributes sharp, high-frequency optical modes that are well separated from the acoustic manifold. The resulting optical cluster produces a large phonon gap and relatively weak hybridization between H-modes and acoustic branches, a feature that limits scattering channels between the two manifolds and is consistent with their comparatively higher κ_1 .

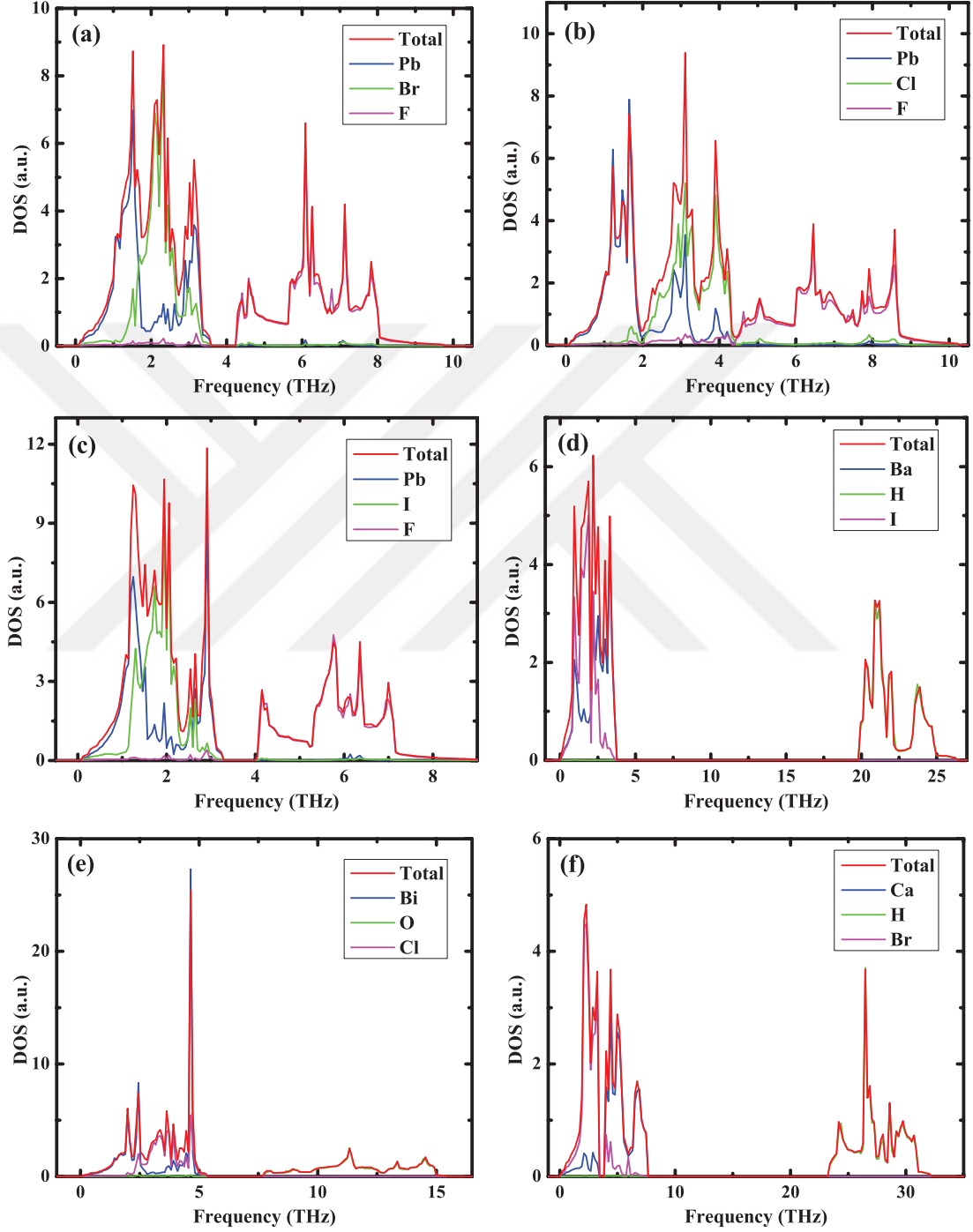


Figure 4.10: Total and partial phonon density of states (PDOS) for PbXF ($X = \text{Br}, \text{Cl}, \text{I}$), BaHI , BiOCl , and CaHBr monolayers. Low-frequency acoustic modes are dominated by heavier atoms (Pb, Ba, Bi, Ca, and halogens), while high-frequency optical modes are primarily due to lighter atoms such as F, O, and H.

For BiOCl, Bi dominates the acoustic region while O supplies narrow, high-frequency optical modes and Cl occupies the mid-frequency range, yielding a moderate acoustic–optical separation. Overall, the PDOS patterns corroborate the expected mass- and bonding-driven hierarchy: heavy cations (Pb, Ba, Bi, Ca) set the acoustic bandwidth, while light anions (F, O, H) harden the optical modes. Materials with larger acoustic–optical separation (e.g., hydrides) show reduced phase space for three-phonon processes mixing the two manifolds, whereas more minor separations in the heavier-halogen PbXF compounds increase acoustic–optical interactions and promote stronger Umklapp scattering.

4.1.1.3 Lattice thermal conductivity.

The lattice thermal conductivity κ_l was calculated by solving the phonon BTE:

$$\kappa_l = \frac{1}{N} \sum_{\lambda, \mathbf{q}} C_{\text{ph}}(\lambda, \mathbf{q}) v_{g,i}^2(\lambda, \mathbf{q}) \tau(\lambda, \mathbf{q}), \quad (4.1)$$

where C_{ph} is the mode-dependent specific heat, $v_{g,i}$ is the group velocity along the direction i , τ is the phonon lifetime, λ iterates phonon branches, and $\mathbf{q}$ iterates over phonon wavevectors in the Brillouin zone. The second and third-order force constants required for τ were computed using DFPT (harmonic) and finite-displacement (anharmonic) methods, respectively, and processed using **ShengBTE**.

Figure 4.11 presents the temperature dependence of κ_l for all studied compounds. In all cases, κ_l decreases significantly with temperature due to enhanced Umklapp phonon–phonon scattering at elevated temperatures. PbXF compounds exhibit particularly low κ_l values across the entire temperature range, primarily due to strong acoustic–optical scattering driven by a large mass contrast between heavy Pb/X atoms and light F atoms.

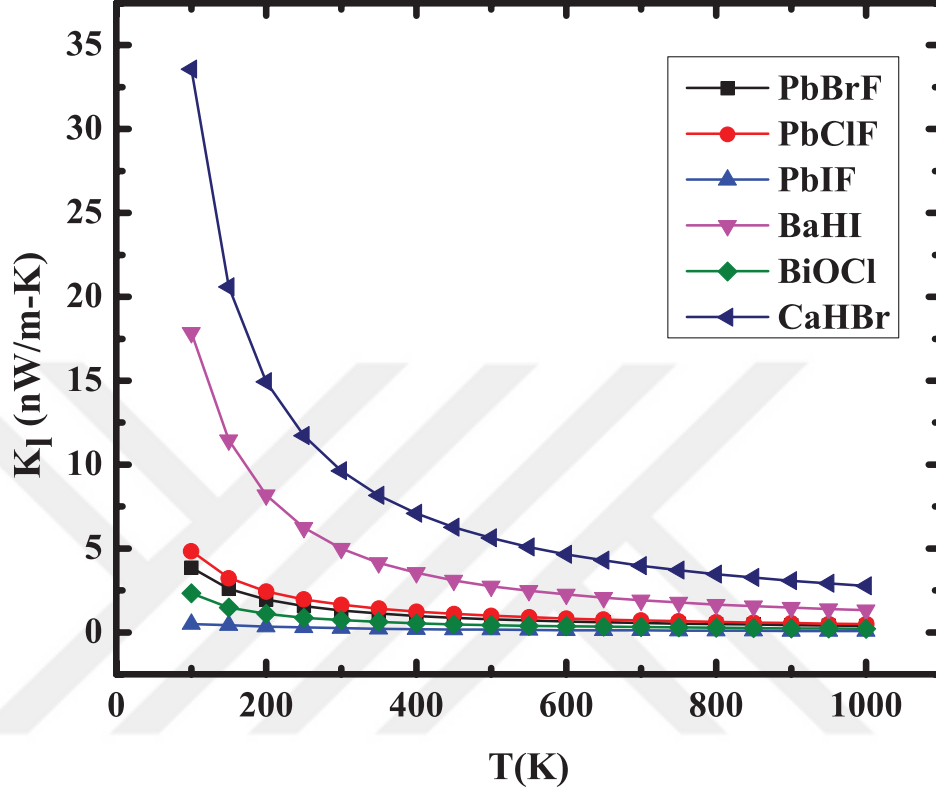


Figure 4.11: Temperature dependence of lattice thermal conductivity $\kappa_l(T)$ for PbXF ($X = \text{Br}, \text{Cl}, \text{I}$), BaHI , BiOCl , and CaHBr monolayers. With increasing temperature, all compounds show a decrease in κ_l due to stronger phonon–phonon Umklapp scattering. PbXF materials exhibit the lowest κ_l , consistent with strong mass contrast between constituent atoms and enhanced acoustic–optical scattering.

BaHI and BiOCl display moderately higher κ_l values, reflecting somewhat stiffer bonds and higher phonon group velocities. CaHBr shows intermediate behavior, with κ_l values lying between PbXF and BaHI . The overall low κ_l values in all materials benefit thermoelectric applications, as they help maintain a high figure of merit ZT when combined with promising electronic transport coefficients.

The phonon dispersion, PDOS, and κ_l results consistently demonstrate that these layered 2D compounds possess low lattice thermal conductivities, especially in the PbXF series. The combination of low κ_l , tunable electronic structure,

and good Seebeck coefficients makes them suitable candidates for thermoelectric applications.

4.2 Figure of Merit (ZT)

The thermoelectric figure of merit, ZT , is a dimensionless quantity that comprehensively indicates thermoelectric performance [2]. It is defined as:

$$ZT = \frac{S^2 \sigma T}{\kappa_{\text{el}} + \kappa_l}, \quad (4.2)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_{el} is the electronic thermal conductivity, and κ_l is the lattice thermal conductivity. A high ZT value requires simultaneously large S and σ while keeping κ_{el} and κ_l low, which presents a well-known materials design challenge due to the often-competing nature of these parameters.

In this work, ZT is calculated at room temperature using the electronic transport parameters obtained from **BoltzTraP** combined with lattice thermal conductivity values derived from **ShengBTE** calculations [72, 71]. For comparison, two scenarios are considered: (a) an idealized case where lattice thermal conductivity is fixed to $\kappa_l = 1$ (nW – nm⁻¹K⁻¹) for all compounds, representing a hypothetical low- κ_l material, (b) a realistic case where κ_l is from our first-principles phonon transport calculations.

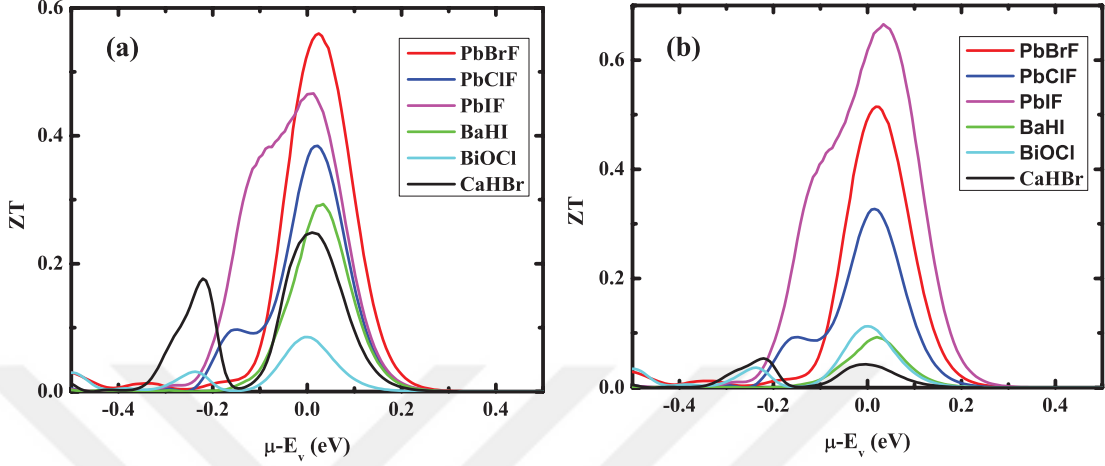


Figure 4.12: Figure of merit ZT vs. chemical potential $\mu - E_v$ at $T = 300$ K for 2D-PbXF ($X = \text{Br}, \text{Cl}, \text{I}$), BaHI, BiOCl, and CaHBr. Left (a): idealized case with $\kappa_l = 1$ (nW nm $^{-1}$ K $^{-1}$). Right (b): realistic case using κ_l from ShengBTE phonon calculations.

Figure 4.12 compares the calculated ZT values across all investigated materials under the two κ_l scenarios. In the idealized case figure 4.12 (a), the ZT profiles are dominated purely by the electronic transport properties. PbBrF and PbClF display the highest peak ZT values for p -type doping, mainly due to their steep density of states near the valence band maximum and favorable electrical conductivity. PbIF shows a slightly reduced peak compared to PbBrF and PbClF, which is consistent with its smaller band gap and altered band curvature. Among the non-Pb systems, BaHI and BiOCl show competitive n -type ZT values, while CaHBr remains the lowest performer in both doping types.

When realistic κ_l values from ShengBTE are included figure 4.12 (b), the absolute ZT values decrease for all compounds, as expected due to finite lattice heat conduction. In materials such as BiOCl and CaHBr, a decrease in ZT can be seen more clearly, as their thermal conductivity κ_l is higher. For materials like PbBrF and PbClF, most of their high- ZT potential is kept, since their lattice thermal conductivity is naturally lower. This indicates that the combination of low κ_l and favorable electronic structure features, such as Mexican-hat-like dispersions, makes PbBrF and PbClF promising candidates for high-efficiency thermoelectric

applications.

Notably, the position of the ZT maxima remains unchanged mainly between the two cases, implying that the optimal doping level is mainly determined by the electronic band structure rather than the phonon thermal transport. However, the magnitude of the peaks is strongly affected by κ_l , reinforcing the importance of phonon engineering strategies such as alloying, defect introduction, or nanostructuring to suppress lattice thermal conductivity and enhance overall thermoelectric performance.

Figures 4.13(a–d) compare ZT for p - and n -type doping at $n = 10^{18}$ and 10^{19} cm^{-3} for PbBrF, PbClF, and PbIF, with and without SOC. It is evident that ZT grows nearly monotonically with temperature and tends to level off above $\sim 600 - 800 \text{ K}$ and as the carrier concentration increases from 10^{18} to 10^{19} cm^{-3} the overall ZT increases.

At $p = 10^{18} \text{ cm}^{-3}$, PbIF with SOC is the best performer across the entire range, whereas SOC depresses ZT for PbBrF and PbClF over most temperatures. At $p = 10^{19} \text{ cm}^{-3}$ all three materials gain in ZT and PbIF (with and without SOC) approaches ZT value close to 1 around 600-800 K, whereas PbClF remains lowest. The sign of the SOC effect is unchanged: it slightly reduces p -type ZT in PbBrF/PbClF but gives a modest increase in PbIF.

For n -type doping, SOC increases ZT for all three compounds at both concentrations. At $n = 10^{18} \text{ cm}^{-3}$, PbIF achieves the highest ZT with the inclusion of SOC, while PbClF shows a moderate gain. At $n = 10^{19} \text{ cm}^{-3}$ the SOC-enhanced ordering persists with PbIF(SOC) at highest followed by PbBrF and then PbClF with lowest ZT .

These behaviors are consistent with the SOC-induced reshaping of band edges inferred from our $S(T)$ and σ analyses. In PbBrF and PbClF, SOC smooths/lowers the effective valence-band DOS peak and slightly flattens the valence curvature, reducing the p -type power factor and thus ZT with the most significant gain observed for PbIF and a moderate improvement for PbIF.

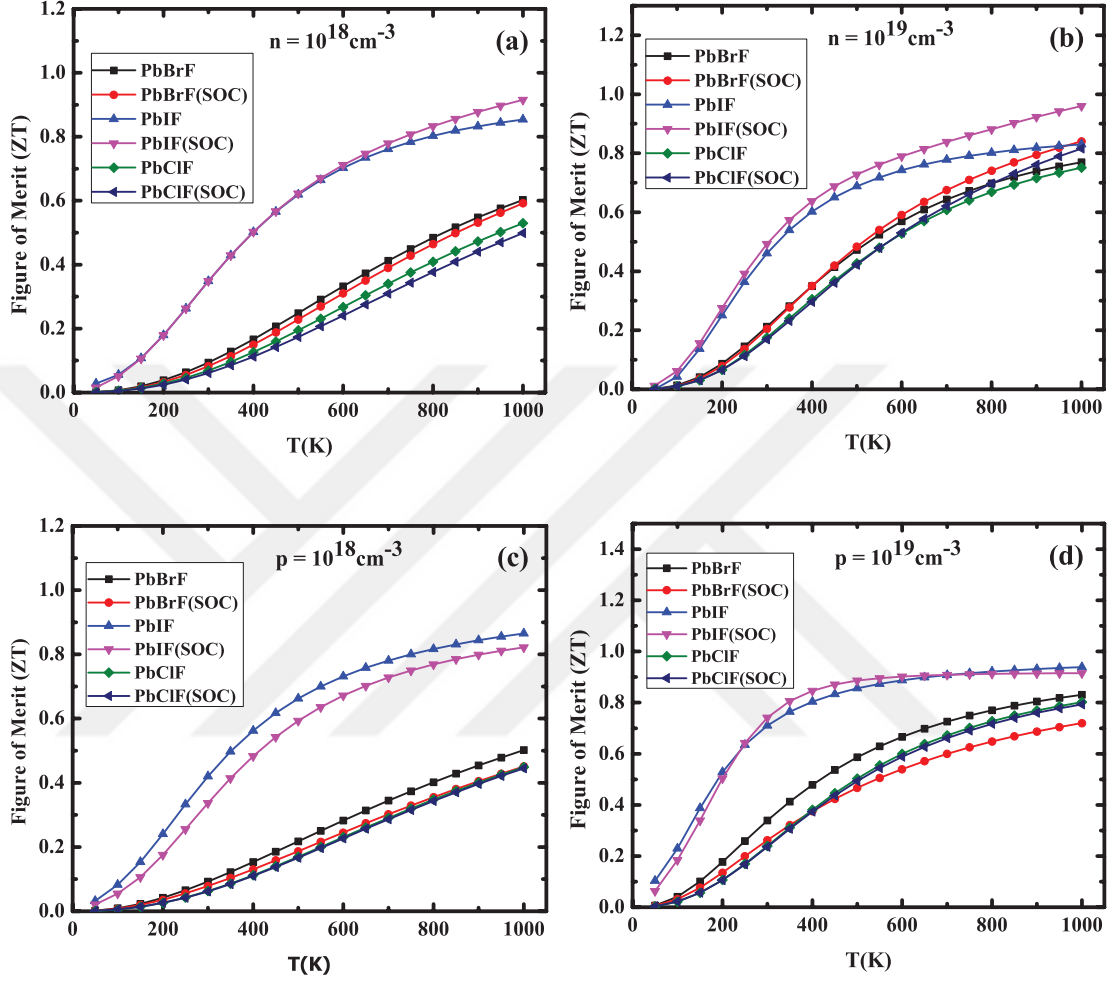


Figure 4.13: Temperature dependence of the thermoelectric figure of merit ZT for PbBrF, PbClF, and PbIF with and without SOC. Top row: p -type at 10^{18} and 10^{19} cm^{-3} . Bottom row: n -type at 10^{18} and 10^{19} cm^{-3} . SOC tends to reduce ZT for p -type PbBrF and PbClF by lowering the effective DOS peak near the valence-band edge, whereas in n -type doping SOC can enhance ZT by sharpening conduction-edge features.

Figure 4.14 compares $ZT(T)$ for all monolayers at p - and n -type carrier concentrations of 10^{18} and 10^{19} cm^{-3} . At all carrier concentrations, ZT increases with T and tends to saturate at high temperature. Across both carrier types and both concentrations, PbIF has the largest ZT followed by PbBrF, PbClF, BiOCl, BaHI, and CaHBr with the lowest ZT .

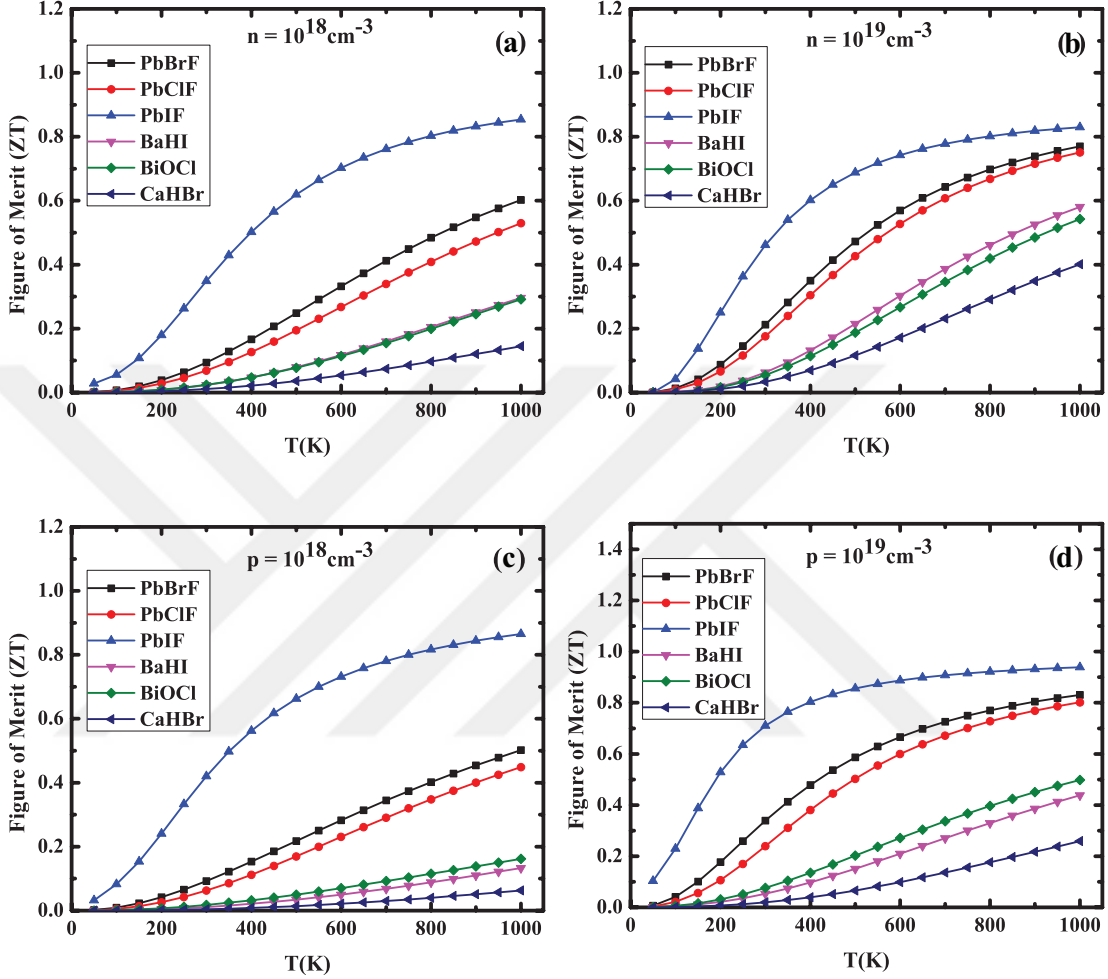


Figure 4.14: Temperature dependence of $ZT(T)$ for all studied compounds without SOC. Top row: p -type at 10^{18} and 10^{19} cm^{-3} ; bottom row: n -type at 10^{18} and 10^{19} cm^{-3} . For p -type doping, PbIF attains the highest ZT , followed by PbBrF and PbClF. For n -type doping, BaHI surpasses BiOCl at higher carrier concentrations, while PbIF remains competitive.

This ordering reflects how band-edge features and lattice heat transport combine in $ZT = S^2\sigma T/(\kappa_{\text{el}} + \kappa_{\text{l}})$. Within the PbXF family, the “Mexican-hat” valence topology explains much of the p -type behavior, larger hat height/radius and favorable (less anisotropic) curvature support larger $|S|$ and thus larger ZT . PbIF is an important exception: despite having smaller hat parameters than PbClF (Table 4.2), a band crossing very close to the valence edge boosts the

near-edge DOS and power factor, and its exceptionally low lattice thermal conductivity further elevates ZT . In contrast, CaHBr's very small hat parameters and relatively large κ_l suppress $S^2\sigma$ and keep ZT minimal. BiOCl and BaHI fall in the middle due to modest power factors and/or higher κ_l compared with the PbXF compounds.

For p -type doping at $n = 10^{19} \text{ cm}^{-3}$, Table 4.3 summarizes the calculated S , σ , κ_{el} , κ_l , and ZT . Among the PbXF compounds, SOC reduces ZT in PbBrF and PbClF, whereas it increases ZT in PbIF.

Compound	S ($\mu\text{V/K}$)	σ ($10^3 \Omega^{-1} \text{ cm}^{-1}$)	κ_{el} ($\text{W m}^{-1} \text{ K}^{-1}$)	κ_l ($\text{W m}^{-1} \text{ K}^{-1}$)	ZT
PbBrF	505 (439)	8.95 (9.30)	0.717 (0.747)	1.31	0.34 (0.26)
PbClF	451 (451)	8.75 (8.57)	0.585 (0.573)	1.64	0.24 (0.23)
PbIF	400 (439)	17.3 (10.0)	0.924 (0.533)	0.249	0.71 (0.74)
BaHI	462	4.34	0.295	4.988	0.053
BiOCl	411	1.18	0.064	0.722	0.076
CaHBr	452	3.14	0.200	9.63	0.019

Table 4.3: Thermoelectric parameters for p -type doping at $n = 10^{19} \text{ cm}^{-3}$. Values in parentheses for PbXF include SOC.

At p -type 10^{19} cm^{-3} , PbIF benefits from SOC (higher ZT) due to favorable changes near the valence edge, while PbBrF and PbClF show reduced ZT consistent with SOC-induced band flattening. Non-Pb systems are limited primarily by larger κ_l (e.g., BaHI, CaHBr) or modest σ (BiOCl).

For n -type doping at $n = 10^{19} \text{ cm}^{-3}$, Table 4.4 shows SOC increasing ZT across all PbXF compounds, attributable to enhanced conduction-band transport.

Compound	S ($\mu\text{V/K}$)	σ ($10^3 \Omega^{-1} \text{cm}^{-1}$)	κ_{el} ($\text{W m}^{-1}\text{K}^{-1}$)	κ_{l} ($\text{W m}^{-1}\text{K}^{-1}$)	ZT
PbBrF	224 (237)	24.5 (20.6)	0.480 (0.400)	1.31	0.212 (0.20)
PbClF	245 (259)	20.7 (16.9)	0.469 (0.380)	1.64	0.176 (0.16)
PbIF	194 (203)	31.3 (28.0)	0.510 (0.456)	0.249	0.461 (0.49)
BaHI	229	21.7	0.446	4.988	0.062
BiOCl	190	3.96	0.062	0.722	0.054
CaHBr	252	17.7	0.418	9.63	0.0335

Table 4.4: Thermoelectric parameters for n -type doping at $n = 10^{19} \text{cm}^{-3}$. Values in parentheses for PbXF include SOC.

In n -type at 10^{19}cm^{-3} , SOC consistently benefits PbXF by sharpening conduction-edge transport, raising ZT . PbIF remains the strongest within the series, while BaHI achieves competitive n -type values despite a relatively high κ_{l} .

The trends in Tables 4.3 and 4.4 clarify how the ingredients of $ZT = S^2\sigma T/(\kappa_{\text{el}} + \kappa_{\text{l}})$ combine at high carrier density ($n = 10^{19} \text{cm}^{-3}$). For p -type PbXF, SOC lowers ZT in PbBrF and PbClF but raises it in PbIF. The reduction stems from SOC smoothing the valence-band edge, which diminishes the Seebeck-driving DOS slope and slightly reduces the p -type power factor $S^2\sigma$; the accompanying increase in $\kappa_{\text{el}} \propto \sigma$ (Wiedemann–Franz) further weighs against ZT . PbIF is the outlier: a near-edge band crossing enhances the valence DOS and preserves a large $S^2\sigma$ despite SOC, and its very small κ_{l} (from ShengBTE) keeps the denominator low, yielding the highest p -type ZT .

For n -type at the same carrier density, SOC benefits all three PbXF compounds. Here, SOC sharpens conduction-band features and can increase valley multiplicity or reduce the transport effective mass, which raises S without an excessive penalty from κ_{el} , so $S^2\sigma$ grows net-positive. PbIF again leads within the series, followed by PbBrF and PbClF. Among the non-Pb systems, BaHI reaches respectable n -type σ but is held back by a comparatively large κ_{l} ; BiOCl is limited mainly by a modest σ . CaHBr is consistently lowest in ZT across polarities because its power factor collapses at high n (strong $|S|$ reduction) while κ_{el} and

κ_1 remain relatively high.

Linking back to the electronic structure analysis, the p -type ordering inside PbXF is broadly consistent with the Mexican-hat descriptors (height, ring radius, and anisotropy): larger hat height/radius and weaker in-plane anisotropy support larger $|S|$. PbIF exceeds that expectation because the band crossing near the valence edge boosts the DOS beyond what the hat parameters alone predict, while its ultralow κ_1 supplies an additional advantage.

Chapter 5

Strain engineering of SrHI

This chapter explores biaxial strain as a route to tune the Mexican-hat-like valence band in monolayer SrHI and, in turn, its thermoelectric (TE) response. In the previous chapters, we observed that when the ring of degenerate valence band maxima in momentum space is highly anisotropic (warped), the angular degeneracy is partially lifted and the near-edge density of states (DOS) is broadened. The corresponding transmission spectrum has a smoother and broader onset. As a result, the transport coefficients are significantly reduced, leading to a low thermoelectric figure of merit. Reducing anisotropy sharpens the DOS and corresponding transmission onset. It can enhance the Seebeck coefficient via a steeper energy derivative of the transport function, provided the proper radial curvature and band gap are maintained.

We therefore apply controlled biaxial strain to SrHI and track (i) the energy profile and geometry of the valence-band ring, (ii) the position and sharpness of the DOS and transmission function feature at the valence edge, and (iii) the implications for the TE coefficients S , σ , and κ_{el} within the constant-relaxation-time approximation.

5.1 Computational methods Under Biaxial Strain

Biaxial strain is defined as $\Delta = (a - a_0)/a_0$, with a_0 the fully relaxed in-plane lattice constant at zero strain [76]. We consider $\Delta = 0, 2, 4$, and 6% (tensile) by uniformly scaling the two in-plane lattice vectors; the out-of-plane lattice parameter is fixed at a vacuum of 25. For each Δ , all the atomic coordinates are fully relaxed until convergence of the electronic energy to 10^{-7} eV and forces reduced to 10^{-7} eV, keeping the in-plane cell shape fixed.

Electronic structures are then computed with VASP using the PBE generalized-gradient approximation and PAW datasets [66, 67]. A plane-wave cutoff of 520 eV is employed for all strains. Self-consistent calculations and band/DOS post-processing use dense Brillouin-zone sampling; for DOS, we employed a $21 \times 21 \times 1$ Monkhorst–Pack mesh. All bands at different Δ are plotted along the same high-symmetry path to ensure comparability. For visual comparison of near-edge features, energies are aligned so that the valence-band maximum (VBM) at each strain is set to $E = 0$.

For thermodynamic stability, we evaluate both the formation energy E_{form} and the cohesive energy E_{coh} at each Δ :

$$E_{\text{form}}(\Delta) = E_{\text{tot}}(\text{SrHI}; \Delta) - \mu_{\text{Sr}}^{\text{bulk}} - \frac{1}{2}E(\text{H}_2) - \frac{1}{2}E(\text{I}_2). \quad (5.1)$$

and

$$E_{\text{coh}}(\Delta) = \frac{E_{\text{tot}}^{(\text{cell})}(\text{SrHI}; \Delta) - [n_{\text{Sr}}E_{\text{Sr}}^{\text{atom}} + n_{\text{H}}E_{\text{H}}^{\text{atom}} + n_{\text{I}}E_{\text{I}}^{\text{atom}}]}{N_{\text{atoms}}}. \quad (5.2)$$

These quantities are used to confirm that strained SrHI remains thermodynamically reasonable against elemental references and monitor whether strain pushes the system toward unfavorable bonding (significant loss of cohesion).

For each Δ , the converged band structure is interpolated on a denser $40 \times 40 \times 1$ $\mathbf{k}$ grid using BoltzTraP2 to obtain S , σ , and κ_{el} [73]. Results are presented at

fixed nominal carrier concentrations (sign indicates p or n type) and as functions of temperature. A constant relaxation time $\tau = 10^{-14}$ s is used throughout to isolate the effect of band-structure changes; where appropriate we also report $\text{PF}/= S^2(\sigma)$. Second-order (harmonic) force constants are obtained for each Δ using phonopy with DFPT/VASP in a $3 \times 3 \times 1$ supercell and a $7 \times 7 \times 1$ $\mathbf{k}$ mesh; phonon band structures are plotted to check for imaginary frequencies and thus dynamical stability [70, 66, 77]. Third-order (anharmonic) force constants are computed with `thirdorder.py` and VASP with $3 \times 3 \times 1$ supercell and $7 \times 7 \times 1$ $\mathbf{k}$ mesh. The second and third-order force constants are then used as inputs in ShengBTE with a $16 \times 16 \times 1$ $\mathbf{q}$ grid to obtain the lattice thermal conductivity $\kappa_l(T)$ for each Δ .

5.2 Structure

Table 5.1 summarizes the structural and energetic response of monolayer SrHI under biaxial strain. As expected, the in-plane lattice constants expand nearly linearly with strain ($a = b$: $4.27 \rightarrow 4.53$ Å from 0% to 6%). Concomitantly, the out-of-plane metric d contracts ($5.84 \rightarrow 5.35$ Å), consistent with a Poisson-like relaxation that thins the layer as it is stretched in plane.

Strain (%)	$a = b$ (Å)	d (Å)	E_{form} (eV/f.u.)	E_{coh} (eV/atom)
0	4.27	5.84	-8.83	-2.917
2	4.36	5.68	-8.82	-2.913
4	4.44	5.51	-8.79	-2.904
6	4.53	5.35	-8.75	-2.88

Table 5.1: Structural and energetic properties of monolayer SrHI under biaxial strain Δ .

The formation energy E_{form} becomes slightly less negative with increasing strain ($-8.83 \rightarrow -8.75$ eV/f.u.), indicating a modest thermodynamic penalty to stretching. The cohesive energy per atom $|E_{\text{coh}}|$ also decreases in magnitude

($\sim 2.92 \rightarrow 2.88$ eV/atom), i.e., bonds weaken slightly under tension—again in line with expectations. Taken together, the trends point to a mechanically and dynamically robust monolayer within the 0–6% strain window, with only small energetic costs that are typical for biaxial deformation of ionic/ionic-covalent 2D materials.

5.3 Electronic Structure vs Strain: Bands and DOS

The electronic band structure and density of states (DOS) were computed using PBE-GGA for 2D-SrHI at each strain Δ to investigate the effect of biaxial strain [24, 78, 79]. Fig. 5.1 represents the electronic band dispersion and DOS at $\Delta = 0, 2, 4, 6\%$, with the valence-band maximum (VBM) set to $E = 0$. At zero strain, the valence maximum has the highest degree of anisotropy. The near-edge states are spread in energy. The warping of the Fermi ring near the band edge is reflected in the DOS, which shows a smoother rise and a broader peak rather than a sharp, step-like onset.

As the applied biaxial strain increases from 0% to 6%, the azimuthal warping of the valence-band ring decreases monotonically: the spread in ring radius between symmetry-inequivalent directions shrinks, i.e., the anisotropy parameter β decreases, with the smallest β at 6% strain. Correspondingly, the DOS onset becomes noticeably steeper and its near-edge ridge narrows, indicating that the van-Hove-like contribution is no longer smeared over angle. A mild reduction of both the Mexican-hat height ε_0 and the ring radius k_0 is also observed, consistent with a modest flattening of the azimuthal modulation. In short, strain alters both the angular energy profile and the radial position of the Mexican-hat band.

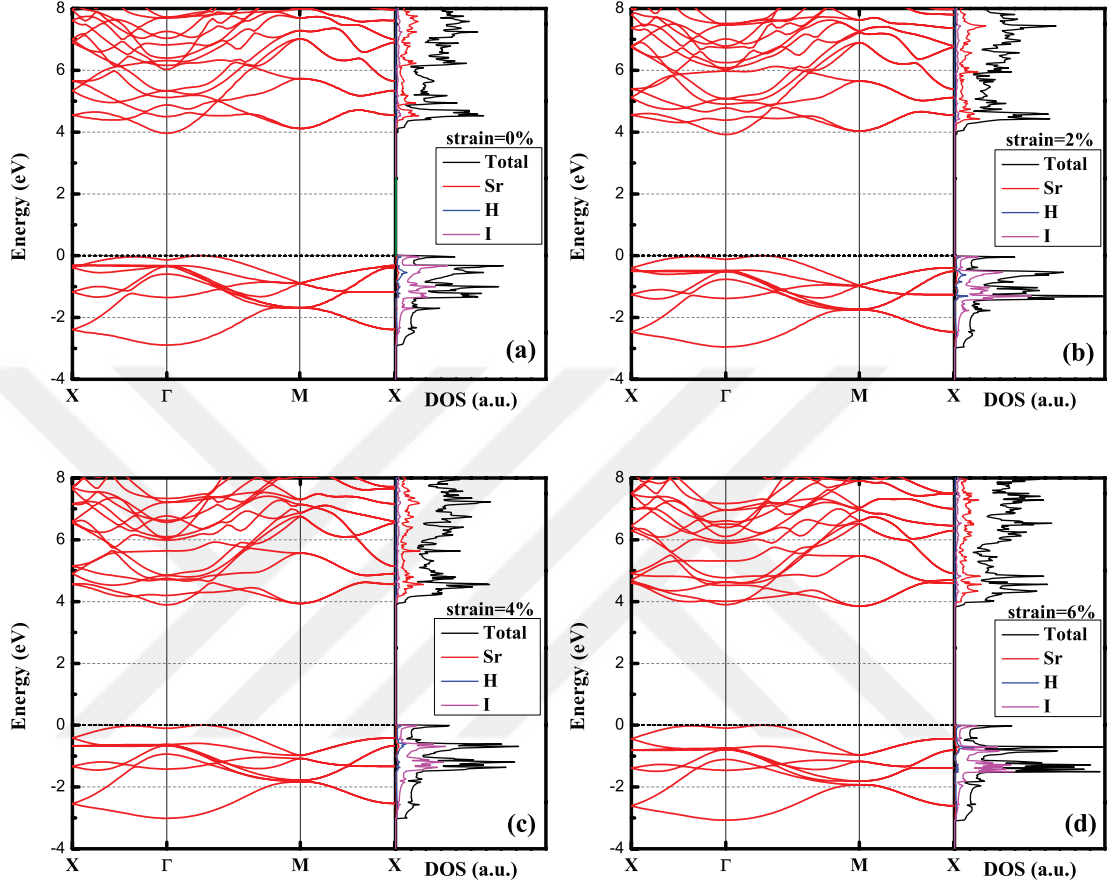


Figure 5.1: Electronic band structures and DOS of monolayer SrHI at biaxial strain $\Delta = 0, 2, 4, 6\%$ ($\Delta \equiv (a - a_0)/a_0$). Energies are aligned so that the VBM at each strain is at $E = 0$. Tensile strain suppresses the azimuthal anisotropy of the Mexican-hat valence manifold and sharpens the DOS onset.

Increasing strain also reduces the fundamental band gap. Overall, from 0% to 6% tensile strain, we observe a monotonic suppression of Mexican-hat anisotropy and a progressive sharpening of the DOS onset. From a transport perspective this increases $\partial \ln \sigma(E) / \partial E$ at the VBM and is therefore expected to enhance the hole-type Seebeck coefficient; provided that the radial curvature on the ring and the band gap are not overly degraded, the power factor $S^2 \sigma$ should improve as well.

Figure 5.2 represents a close-up of the valence-band maximum (VBM) clarifies

how biaxial strain tunes the Mexican-hat dispersion. At zero strain the Fermi-ring is anisotropic: the band-edge energy differs along in-plane directions (e.g., Γ - X vs. Γ - M), producing a finite angular splitting ΔE and a noncircular ring. With applied strain, the Fermi-ring becomes progressively more isotropic and ΔE reduces, indicating suppressed in-plane anisotropy. At the same time, the sombrero height ε_0 (the energy offset between the VBM on the ring and the local extremum at Γ) and the ring radius k_0 (the distance of the VBM from Γ) both shift, evident as a systematic movement of the band-edge ring relative to Γ . These coupled changes explain the strain-driven evolution of the near-edge DOS: reduced anisotropy ($\Delta E \rightarrow 0$) together with adjustments of ε_0 and k_0 modifies the magnitude and position of the van-Hove-like peak and favors more isotropic in-plane transport.

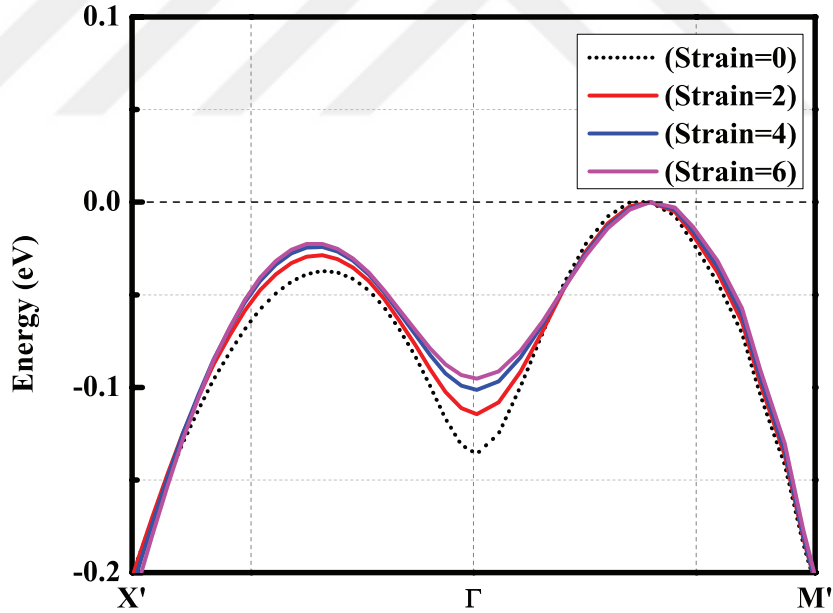


Figure 5.2: Close-up of the VBM under biaxial strain showing strain-induced suppression of anisotropy in the Mexican-hat dispersion. Strain reduces the angular energy splitting ΔE while simultaneously tuning the sombrero height ε_0 and ring radius k_0 , yielding a more circular, isotropic band edge.

Table 5.2 shows a clear strain response of the Mexican-hat descriptors in SrHI. From $\Delta = 0\%$ to 6% , the hat height decreases from $136.2 \rightarrow 95.3$ meV), the ring radius contracts slightly ($k_0 : 0.286 \rightarrow 0.270 \text{ \AA}^{-1}$), and the azimuthal anisotropy energy drops ($37.2 \rightarrow 22.5$ meV). The energy gap also reduces modestly by

(3.98 $\rightarrow$ 3.85 eV).

Strain (%)	ε_0 (meV)	k_0 ($^{-1}$)	Anisotropy (meV) [§]	E_g (eV)
0	136.2	0.286	37.2	3.98
2	114.4	0.281	28.7	3.92
4	101.4	0.275	24.2	3.89
6	95.3	0.270	22.5	3.85

Table 5.2: Mexican-hat descriptors for SrHI under biaxial strain Δ . ε_0 : hat height in (meV). k_0 : ring radius at the valence maximum (in reciprocal units). Anisotropy (ΔE) in meV. E_g : band gap.

Physically, tensile strain is suppressing the anisotropy in the VBM ring, which sharpens the DOS onset at the valence edge, and slightly lowers both the hat height ε_0 and ring radius k_0 . The first effect tends to increase the hole-type Seebeck coefficient via a steeper energy derivative of the transport function at the VBM; the second can modestly reduce the available near-edge phase space and alter velocities. The small band-gap reduction is consistent with tensile strain. Overall, the dominant trend is the substantial reduction of anisotropy, which, with the sharpened DOS onset, favors enhanced p -type S and can improve the power factor $S^2\sigma$ provided the radial curvature is not overly flattened.

5.4 Electronic Transport

Transport coefficients were obtained with **BoltzTraP2** using the converged DFT bands interpolated onto a dense $40 \times 40 \times 1$ grid [73]. We analyze the Seebeck coefficient $S(T)$, the electrical conductivity per relaxation time σ/τ , the electronic thermal conductivity per relaxation time κ_{el}/τ , and the power factor $\text{PF}/\tau = S^2(\sigma/\tau)$ at fixed nominal carrier concentrations $n, p = 10^{18}$ and 10^{19} cm^{-3} . A constant relaxation time $\tau = 10^{-14} \text{ s}$ is assumed across strains ($\Delta = 0, 2, 4, 6\%$) to isolate the role of band-structure changes; note that S is intrinsically independent of τ within CRTA. For readability, we align energies so that the VBM is at $E = 0$.

5.4.1 Seebeck Effect

Within the Mott relation,

$$S \approx \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln \sigma(E)}{\partial E} \right|_{E_F}, \quad (5.3)$$

A sharper DOS/transport onset at the band edge increases $|S|$, while higher carrier density (deeper E_F inside a band) lowers $|S|$ [80]. The strain trends for $S(T)$ should therefore mirror the Mexican-hat descriptors from Table 5.2: reduced anisotropy and a sharper DOS onset with increasing Δ , alongside a modest gap reduction.

Figures 5.3 show $S(T)$ for n -type and p -type SrHI at 10^{18} and 10^{19} cm^{-3} , respectively, for $\Delta = 0, 2, 4, 6\%$.

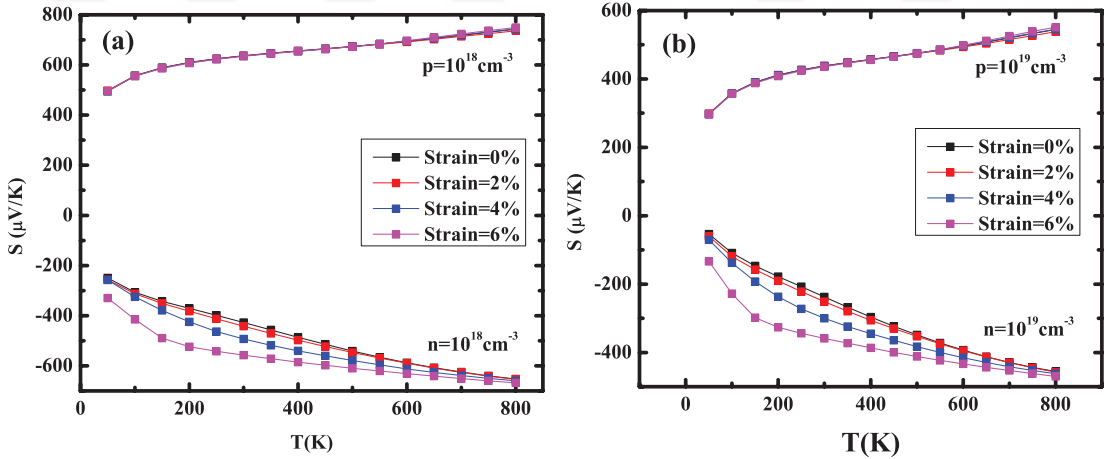


Figure 5.3: Seebeck coefficient $S(T)$ of monolayer SrHI at fixed carrier concentrations. (a) $n, p = 10^{18} \text{ cm}^{-3}$. (b) $n, p = 10^{19} \text{ cm}^{-3}$. Increasing Δ sharpens the valence-edge DOS onset, which raises $|S|$ for p -type; the n -type response changes more modestly.

For p -type, 10^{18} cm^{-3} in Fig. 5.3 (a). Across the entire temperature range, increasing Δ enhances $|S|$ and slightly steepens its rise with T . This is consistent with the progressive suppression of the Mexican-hat anisotropy and the sharpening of the DOS onset (Table 5.2): low degree of anisotropy in VBM ring increases

the angular degeneracy of the near-edge states, amplifying the energy derivative of the transport function at the VBM. Any differences among Δ become more visible at intermediate T , before potential bipolar effects set in at the highest T .

For p -type, 10^{19} cm^{-3} in Fig. 5.3 (b). Raising the hole density reduces $|S|$ overall (deeper E_F inside the valence manifold), but the *relative* ordering with strain persists: larger Δ yields larger $|S|$ at a given T . Because Δ also narrows the gap slightly, a weak high- T roll-off of $|S|$ may appear earlier at $\Delta = 6\%$ than at $\Delta = 0\%$ (onset of bipolar conduction). In the technologically relevant 300–700 K window, the net effect of strain remains beneficial for p -type S .

For n -type, 10^{18} cm^{-3} in Fig. 5.3 (c). Changes with Δ are smaller than in p -type because the conduction band of SrHI is less affected by the valence-side Mexican hat. Nevertheless, a mild, systematic evolution is typically visible: at fixed T , $|S|$ shifts modestly with strain due to subtle changes in conduction-band curvature and effective mass. Any high- T downturn is again linked to the slight gap reduction at larger Δ .

For n -type, 10^{19} cm^{-3} in Fig. 5.3 (d). With higher electron density, $|S|$ is reduced overall relative to 10^{18} cm^{-3} , and the strain dependence remains comparatively weak. Within errors from k -mesh and interpolation, the ordering with Δ is either nearly flat or shows a slight trend carried by conduction-edge curvature changes. In all cases the gap remains sufficiently open that bipolar suppression of $|S|$ is limited to the upper end of the temperature range.

5.4.2 Electrical Conductivity

The temperature-dependent electrical conductivity was obtained from the BoltzTraP2 interpolation on a dense $40 \times 40 \times 1$ grid within the constant-relaxation-time approximation (CRTA) [73, 43, 81]. Throughout we report σ/τ (multiply by $\tau = 10^{-14} \text{ s}$ to recover σ). σ reflects band velocities and state counts but is independent of the specific scattering model. Figure 5.4 collects $\sigma/\tau(T)$ for n -type and p -type doping at 10^{18} and 10^{19} cm^{-3} , overlaid for strains

$\Delta = 0, 2, 4, 6\%$.

For n -type carrier concentration, at both 10^{18} and 10^{19} cm^{-3} , the electrical conductivity increases with carrier concentration, while the strain dependence is modest across the temperature range. This reflects the fact that the conduction band of SrHI is only weakly perturbed by the strain-driven changes that primarily reshape the valence Mexican hat. With constant τ , σ/τ mainly follows the conduction-band velocities and their thermal activation around the band edge; small, nearly monotonic drifts with Δ track subtle curvature changes at the CBM. Any deviations at high- T are limited by the large gap, so bipolar effects remain minor in the plotted range.

For p -type in contrast, strain has a clearer impact because it targets the valence-band Mexican hat. As Δ increases, circularization and reduced anisotropy sharpen the DOS onset but also slightly flatten the radial curvature, which lowers group velocities on the VBM ring.

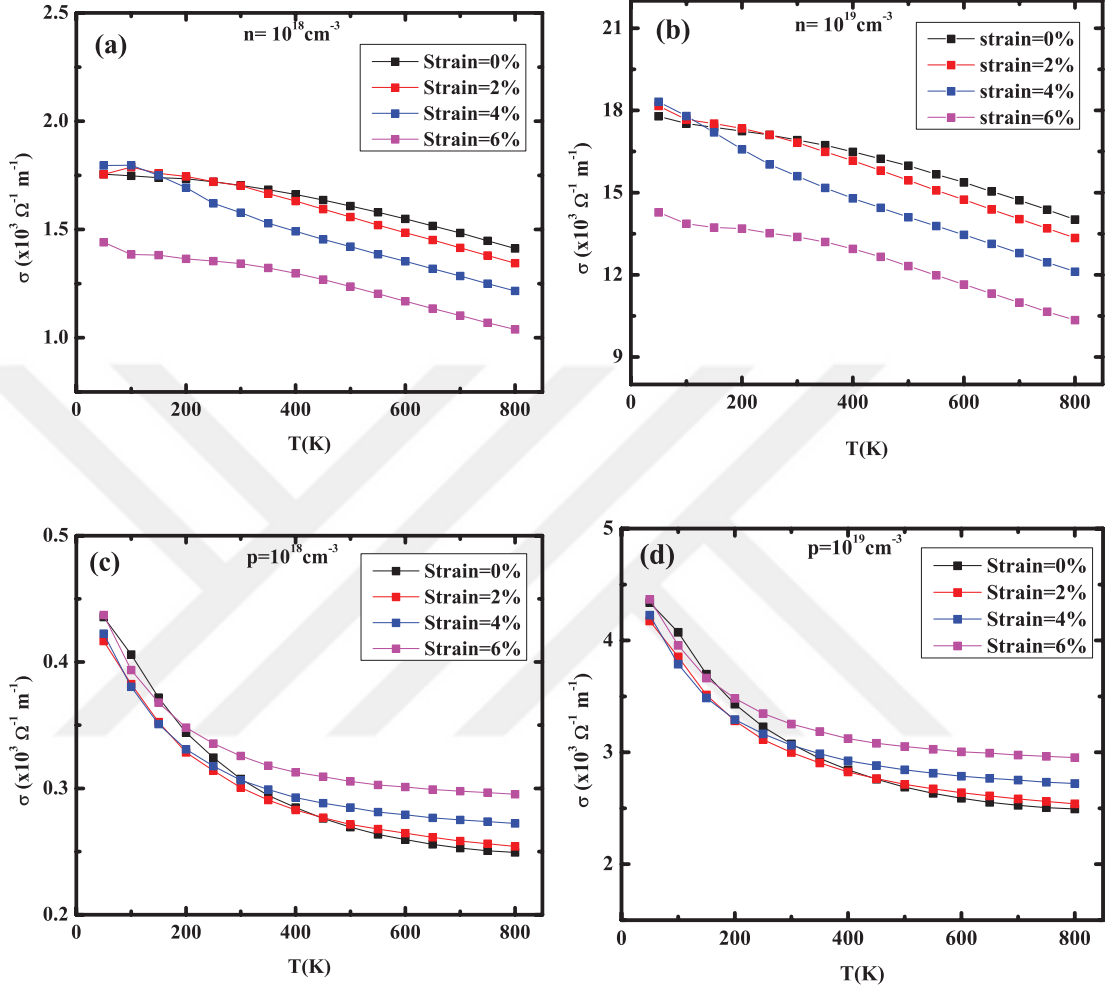


Figure 5.4: Electrical conductivity vs. temperature for SrHI at fixed carrier concentrations. (a) n -type 10^{18} and (b) 10^{19}cm^{-3} . (c) p -type 10^{18} and (d) 10^{19}cm^{-3} . Each plot overlays biaxial strain $\Delta = 0, 2, 4, 6\%$.

In CRTA, this translates to a gentle reduction of σ/τ with increasing Δ , most evident at lower doping (10^{18}cm^{-3}) and low to mid T . At 10^{19}cm^{-3} the difference between strains diminishes because the Fermi level samples deeper, more dispersive states where angular details matter less. Overall, the strain trend that benefits p -type S (sharper DOS onset) comes with a mild trade-off in p -type conductivity due to reduced radial velocities; the balance between these two governs the p -type power factor discussed later.

5.4.3 Electronic Thermal conductivity

The electronic contribution to the thermal conductivity, κ_{el} , quantifies heat carried by itinerant electrons/holes. Within the constant-relaxation-time approximation (CRTA) used here, we report κ_{el}/τ (multiply by $\tau = 10^{-14}\text{s}$ to obtain κ_{el}). κ_{el} is obtained from the same transport integrals as σ ; in the degenerate limit it follows the Wiedemann–Franz trend $\kappa_{\text{el}} \approx L_0 \sigma T$, so its strain and doping dependence generally mirrors that of σ with an additional linear-in- T scaling.

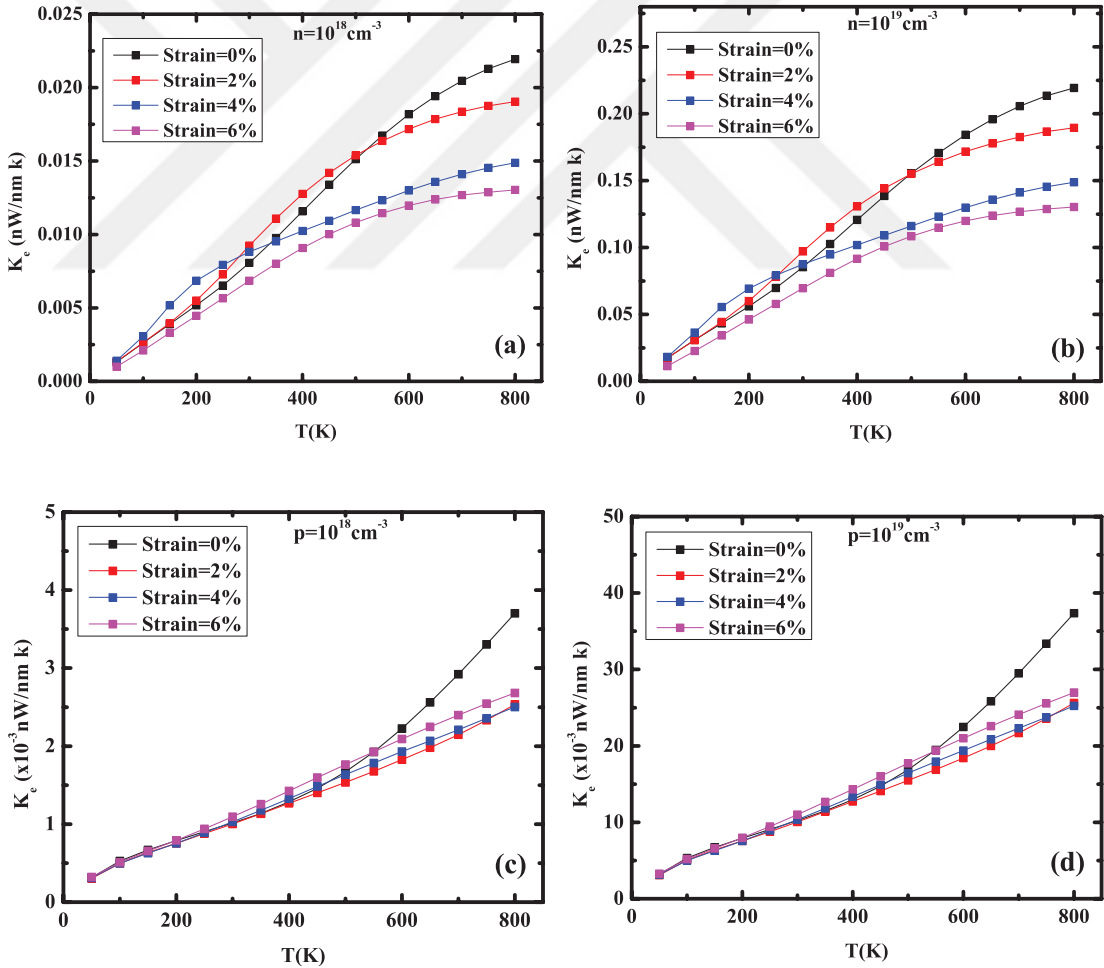


Figure 5.5: Electronic thermal conductivity versus temperature for SrHI at fixed carrier concentrations. (a) n -type 10^{18} and (a) 10^{19} cm^{-3} . (c) p -type 10^{18} and (d) 10^{19} cm^{-3} . Each plot overlays biaxial strain $\Delta = 0, 2, 4, 6\%$.

For n -type at both 10^{18} and 10^{19} cm^{-3} , κ_{el} increases with carrier concentration and approximately with T , consistent with $\kappa_{\text{el}} \sim \sigma T$. The strain dependence is modest across the range, reflecting the weaker impact of Δ on the conduction-band curvature relative to the valence-side Mexican hat. Small, nearly steady drifts with Δ track subtle CBM velocity changes.

For p -type Strain effects are more pronounced since Δ directly reshapes the Mexican-hat valence manifold. As Δ increases, the anisotropy reduces and slightly flattens the radial curvature on the VBM ring, lowering group velocities and yielding a gentle decrease of κ_{el} at a given T , most visible at 10^{18} cm^{-3} . At 10^{19} cm^{-3} the curves become closer because the Fermi level samples deeper, more dispersive states where angular details matter less. Overall, the same strain tuning that boosts p -type S entails a mild trade-off in κ_{el} (via σ), which will feed directly into ZT through the numerator–denominator balance.

5.4.4 Power Factor

The thermoelectric power factor is defined as $\text{PF} = S^2\sigma$ (units: $\text{W m}^{-1} \text{K}^{-2}$). It measures the electrical power output capability of a material under a thermal gradient and forms the numerator of ZT up to a factor of T ($ZT = \text{PF } T/\kappa$) [82]. The strain trends in PF reflect the competition between the DOS-driven changes in S and the group-velocity changes that enter σ .

For n -type, the power factor grows with carrier concentration and with temperature over the shown range, broadly tracking σ (since S is smaller in magnitude for electrons here). The impact of strain Δ is comparatively modest and largely steady: changes in PF with Δ mirror the small conduction-band curvature shifts seen in σ . Because the band gap remains wide across Δ , bipolar degradation at high T is limited, and the curves maintain their one-directional increase with temperature.

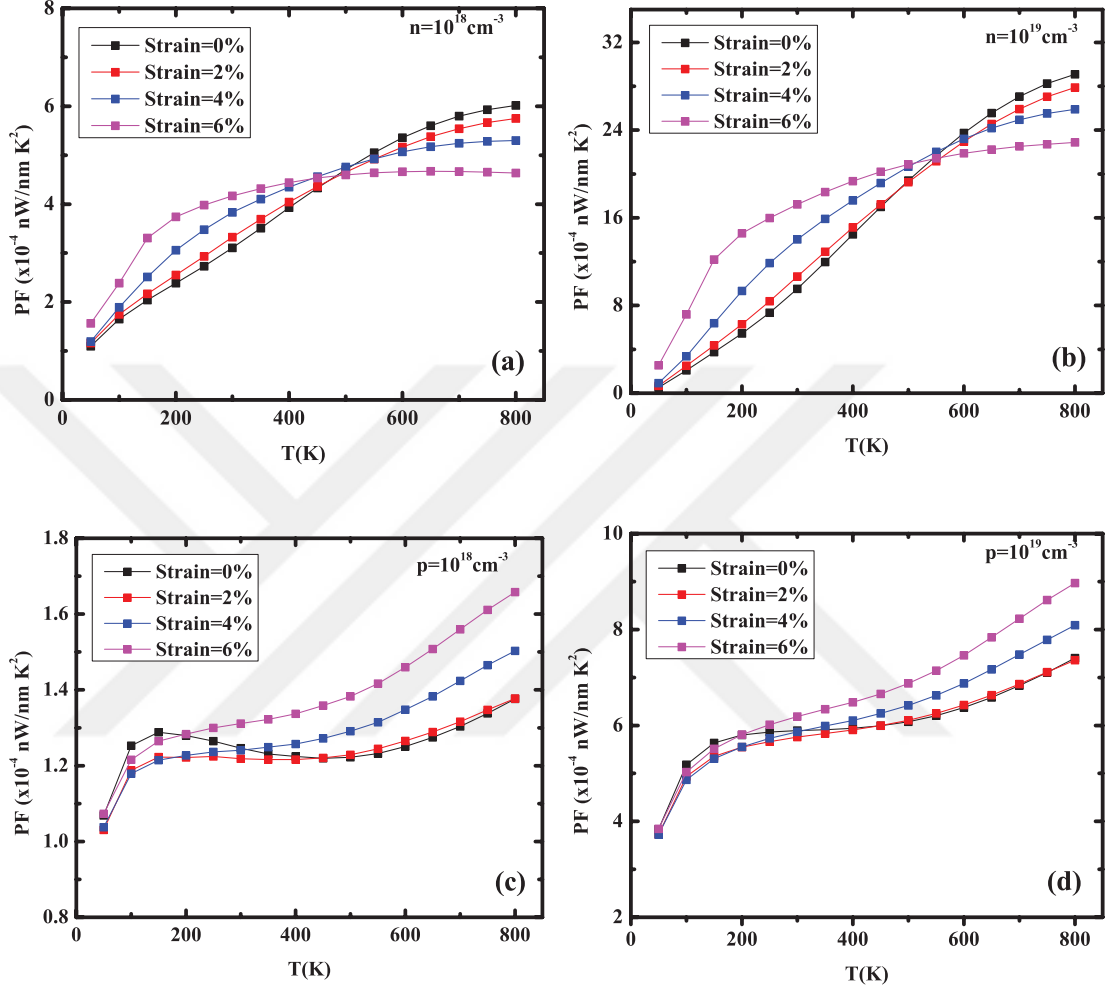


Figure 5.6: Power factor $PF = S^2(\sigma)$ versus temperature for SrHI at fixed carrier concentrations. (a) n -type 10^{18} and (b) 10^{19} cm^{-3} . (c) p -type 10^{18} and (d) 10^{19} cm^{-3} . Each plot overlays biaxial strain $\Delta = 0, 2, 4, 6\%$.

For p -type, strain has a clearer effect because it directly reshapes the Mexican-hat valence manifold. Increasing Δ sharpens the DOS onset (boosting S) but slightly reduces radial group velocities (lowering σ), so PF reflects a balance of these opposing tendencies. At 10^{18} cm^{-3} the gain in S typically outweighs the mild drop in σ , yielding an overall increase of PF with strain in the mid- T window. At 10^{19} cm^{-3} the differences between strains diminish because the Fermi level samples deeper, more dispersive states where angular details matter less; consequently the PF curves with different Δ tend to converge, with only gentle, systematic separations remaining. Overall, the same strain tuning that enhances

p -type S translates into an improved or at least maintained p -type power factor, provided the reduction in σ is not excessive—consistent with the conductivity trends reported above.

5.5 Lattice Transport Properties

We next investigate the lattice-governed (phononic) heat transport of monolayer SrHI under biaxial strain. In 2D crystals the lattice thermal conductivity κ_1 is carried by phonons—predominantly the acoustic LA, TA, and flexural ZA branches—and is controlled by a balance between their group velocities (set by the harmonic force constants) and lifetimes (limited by anharmonic three-phonon scattering). Biaxial tension (Δ) perturbs interatomic distances and bonding, which typically softens acoustic modes, can partially linearize the ZA branch, and enhances anharmonicity (larger Grüneisen parameters and three-phonon phase space). As a result, κ_1 often decreases with increasing Δ , though the magnitude is mode- and material-dependent. In the following, we quantify these effects by examining the phonon dispersion and phonon DOS at $\Delta = 0, 2, 4, 6\%$, and by computing $\kappa_1(T, \Delta)$ from second- and third-order force constants within the phonon Boltzmann transport framework.

5.5.1 Phonon dispersion under strain (harmonic IFCs)

The phonon dispersions were computed from second-order (harmonic) interatomic force constants obtained with `phonopy` + DFPT (VASP) using a $3 \times 3 \times 1$ supercell and a $7 \times 7 \times 1$ $\mathbf{k}$ -mesh at each biaxial strain $\Delta = 0, 2, 4, 6\%$ [66]. The same fractional high-symmetry path was used for all Δ to enable direct comparison. For all strain values, the spectra exhibit no imaginary branches along the high-symmetry lines, indicating dynamical stability within the explored window.

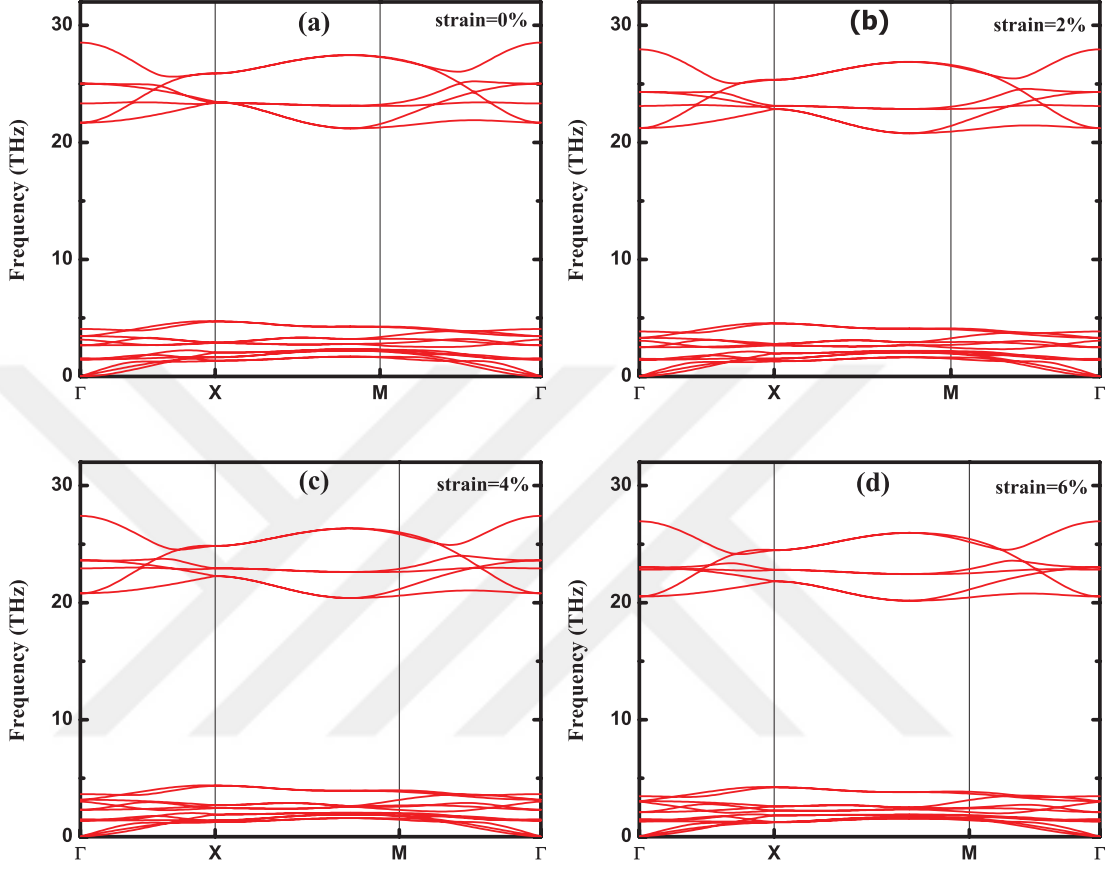


Figure 5.7: Phonon dispersion of monolayer SrHI at $\Delta = 0, 2, 4, 6\%$ (DFPT, harmonic IFCs). No imaginary branches are observed along the plotted paths, indicating dynamical stability for all strains. Tensile strain shifts modes to lower frequencies overall and slightly modifies the acoustic slopes and optical-acoustic separations.

With increasing Δ , the in-plane acoustic modes (LA/TA) soften modestly and their group velocities near Γ decrease slightly, consistent with lengthened bonds. The out-of-plane flexural mode (ZA) exhibits reduced quadratic curvature and a tendency toward partial linearization very close to Γ , as expected under tensile loading in a 2D membrane. These changes alter the balance of heat-carrying channels by lowering v_λ for long-wavelength modes and, together with increased anharmonicity (discussed with κ_1), tend to diminish the acoustic contribution to lattice thermal conductivity as Δ grows.

Tensile strain compresses the optical manifold and slightly narrows the optical–acoustic separation. The downward shift of low-lying optical branches enlarges three-phonon phase space (more channels satisfying energy–momentum selection), which promotes Umklapp scattering of acoustics at elevated temperatures. Because the optical modes also carry some heat at high T , their softening alone does not guarantee higher κ_1 ; the concurrent increase in scattering typically dominates, leading to an overall reduction of $\kappa_1(T, \Delta)$ with strain, consistent with the trends we report later from ShengBTE.

5.5.2 Phonon density of states (PDOS) under strain

The phonon density of states and its atomic projections were obtained from the harmonic IFCs (phonopy+DFPT) using the same settings at each biaxial strain $\Delta = 0, 2, 4, 6\%$. The PDOS is normalized so that the total number of modes equals $3N$ per unit cell, enabling a like-for-like comparison across strains.

Tensile strain red-shifts the vibrational spectrum: both acoustic and optical features move to lower frequencies, and the acoustic–optical gap (if present at $\Delta = 0\%$) narrows with increasing Δ . The enhanced low-frequency DOS arises from softening of long-wavelength acoustic modes (LA/TA and the ZA flexural branch), consistent with the dispersions. A reduced optical–acoustic separation enlarges the three-phonon phase space at finite T , which is expected to shorten lifetimes and lower κ_1 .

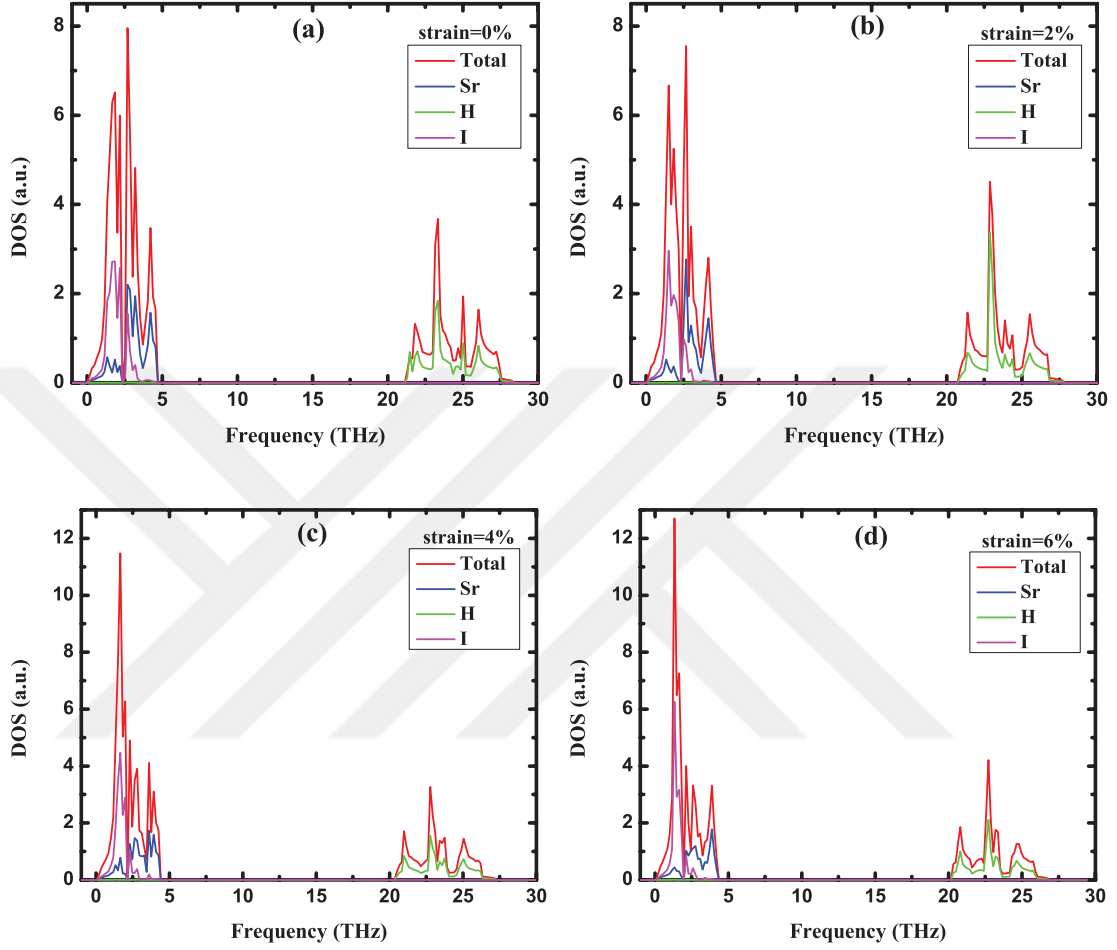


Figure 5.8: Total and partial phonon DOS of monolayer SrHI at $\Delta = 0, 2, 4, 6\%$. With increasing tensile strain, spectral weight shifts to lower frequencies (overall softening), the acoustic–optical separation narrows, and low-frequency DOS increases slightly due to softened acoustic branches.

The partial DOS indicates that heavy atoms (Sr and I) dominate the low-frequency acoustic sector, while the light H atom contributes predominantly to the high-frequency optical region. Under strain, Sr/I-dominated peaks shift downwards and broaden modestly, reflecting weakened restoring forces; the H-dominated optical peaks also red-shift, reducing their separation from the acoustic manifold. The progressive overlap between the lowest H-like optical modes and high-frequency acoustics increases three-phonon scattering channels (e.g., $A+A \leftrightarrow O$), further suppressing κ_1 with Δ . Overall, the PDOS trends softened

acoustics, narrowed optical–acoustic gap, and increased low- ω weight are consistent with the strain-induced reduction in lattice thermal conductivity reported later.

5.5.3 Lattice thermal conductivity under strain

The lattice thermal conductivity $\kappa_l(T)$ was computed by solving the phonon Boltzmann transport equation using second- and third-order interatomic force constants (IFCs) [73, 83]. For each strain $\Delta = 0, 2, 4, 6\%$, harmonic (second-order) IFCs were obtained with `phonopy`+DFPT (VASP), and the anharmonic (third-order) IFCs were generated with `thirdorder.py`+VASP. These IFCs were supplied to `ShengBTE`, and the phonon BTE was solved on a $16 \times 16 \times 1$ $\mathbf{q}$ -grid to yield $\kappa_l(T)$. For each Δ , we determined an effective monolayer thickness $t(\Delta)$ from the relaxed structure (excluding vacuum) and used it to convert the sheet conductivity to $\text{W m}^{-1}\text{K}^{-1}$. Thus, $\kappa_l(T)$ is reported with the strain-specific $t(\Delta)$, ensuring a consistent geometric normalization across strains.

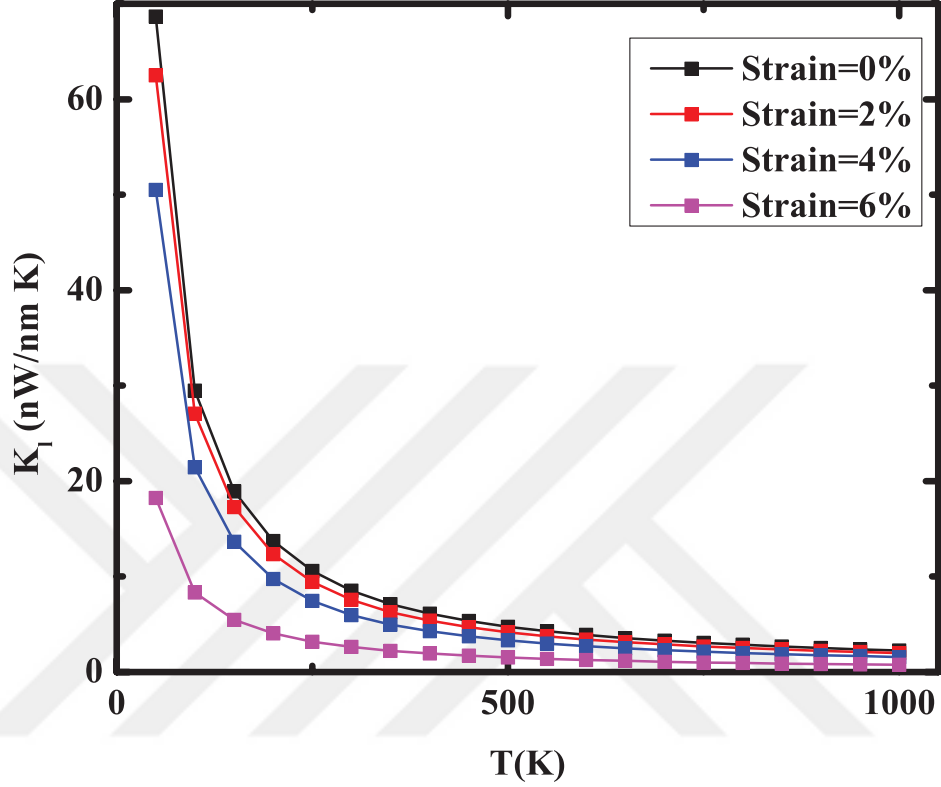


Figure 5.9: Lattice thermal conductivity $\kappa_l(T)$ of monolayer SrHI for $\Delta = 0, 2, 4, 6\%$ obtained from second-/third-order IFCs and **ShengBTE**. Tensile strain lowers κ_l across the temperature range.

Figure 5.9 shows that κ_l decreases steadily with increasing Δ at all temperatures. This trend follows directly from the harmonic and anharmonic changes seen in the phonon dispersion and PDOS. On the harmonic side, tensile strain softens the acoustic branches (LA/TA) and reduces their slopes near Γ , lowering group velocities v_λ that enter $\kappa_l \propto \sum C_\lambda v_\lambda^2 \tau_\lambda$. The flexural ZA mode also exhibits reduced quadratic curvature (partial linearization very close to Γ), which modifies long-wavelength heat transport in a way that does not compensate for the loss in in-plane acoustic velocities. On the anharmonic side, the partial DOS reveals a narrowing of the acoustic-optical separation and a red-shift of low-lying optical modes with strain, which enlarges the three-phonon phase space (more N/Umklaapp channels satisfy energy-momentum selection) and raises the effective Grüneisen parameters—both effects shorten phonon lifetimes τ_λ . Together, reduced v_λ and shorter τ_λ yield the observed suppression of $\kappa_l(T)$ as Δ increases.

The overall decrease of κ_l with T reflects increasing Umklapp scattering. Strain preserves this qualitative T -trend but shifts the absolute magnitude downward: for a given temperature, $\kappa_l(\Delta=6\%) < \kappa_l(\Delta=4\%) < \kappa_l(\Delta=2\%) < \kappa_l(\Delta=0\%)$. This hierarchy is consistent with the progressive acoustic softening and PDOS red-shift discussed above and underpins the ZT improvements anticipated on the lattice side when moving to higher Δ , provided electronic performance (PF) is maintained.

5.6 Figure of Merit

The dimensionless thermoelectric figure of merit is

$$ZT(T, \Delta) = \frac{S^2 \sigma T}{\kappa_{\text{el}} + \kappa_l},$$

where S is the Seebeck coefficient, σ the electrical conductivity, and $\kappa = \kappa_{\text{el}} + \kappa_l$ the total thermal conductivity (electronic + lattice). Within CRTA we evaluate S (independent of τ), σ/τ , κ_{el}/τ , and combine them with the first-principles $\kappa_l(T, \Delta)$ obtained from the phonon BTE. Biaxial strain Δ influences ZT through *all* channels: it sharpens the valence-edge DOS (boosting p -type S), mildly alters band velocities (affecting σ and thus $\kappa_{\text{el}} \sim L_0 \sigma T$), and reduces κ_l by softening the dispersions and enlarging anharmonic phase space. The net outcome reflects the balance of these effects.

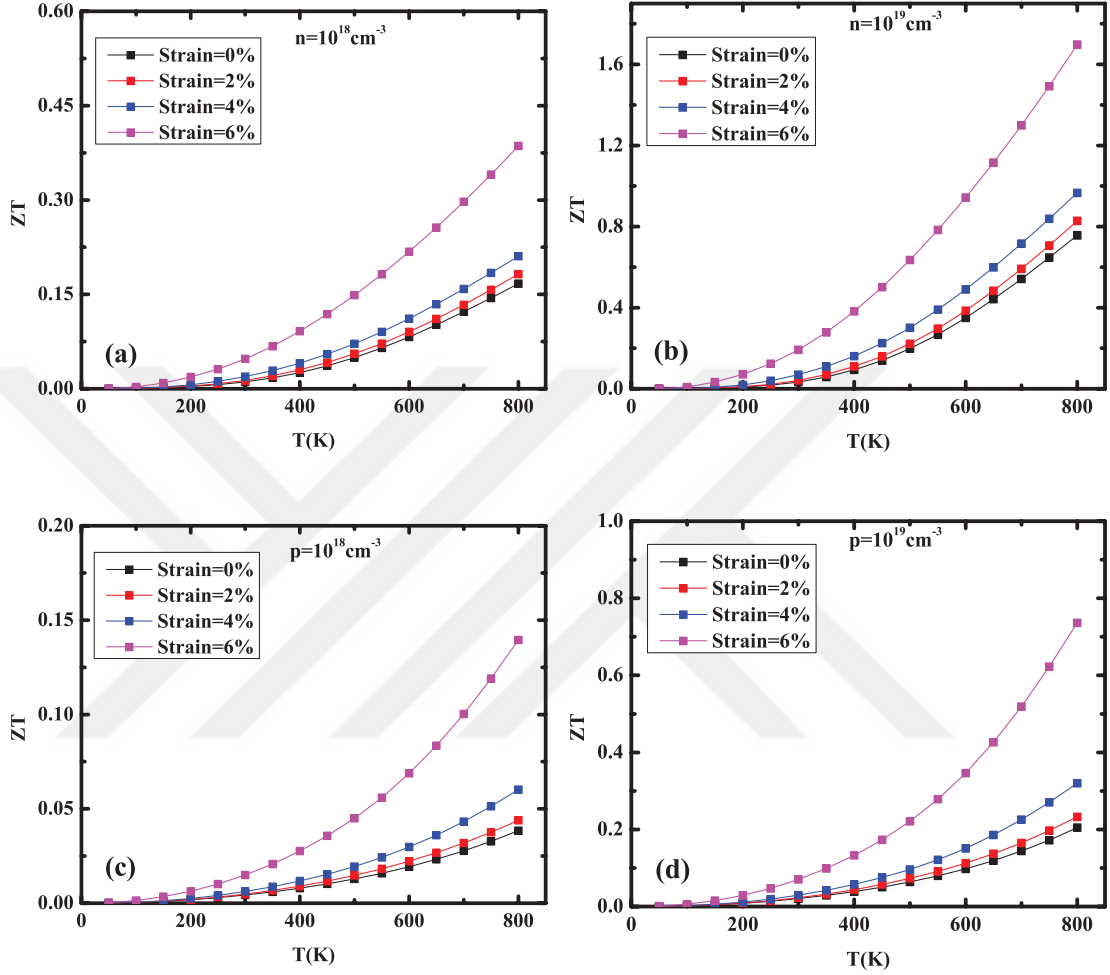


Figure 5.10: Figure of merit $ZT(T)$ for SrHI at fixed carrier concentrations. (a) n -type 10^{18} and (b) 10^{19} cm^{-3} . (c) p -type 10^{18} and (d) 10^{19} cm^{-3} . Each plot overlays biaxial strain $\Delta = 0, 2, 4, 6\%$.

For n -type carrier concentration, across both 10^{18} and 10^{19} cm^{-3} , ZT increases with temperature following the rise of $S^2\sigma T$ and despite the concurrent increase of κ_{el} . The strain dependence is moderate: since the conduction band is only weakly reshaped by Δ , S and σ change little, so the primary strain leverage on ZT comes from the reduction of κ_{l} (phonon softening and enhanced anharmonicity). Consequently, curves with larger Δ tend to sit slightly above those at smaller Δ , with the separation more visible at mid-high T where κ_{l} is an important denominator term.

For p -type carrier concentrations the strain impact is stronger because Δ directly affects the Mexican-hat valence manifold. Increasing Δ sharpens the DOS onset and enhances S , while slightly reducing radial group velocities and thus σ ; κ_{el} follows σ and does not offset the concurrent, strain-induced suppression of κ_{l} . The net effect is that ZT either improves or remains at least comparable as Δ grows, especially at 10^{18} cm^{-3} where the gain in S is most effective. At 10^{19} cm^{-3} the differences between strains narrow because the Fermi level samples deeper, more dispersive states (reducing the S -benefit), but the lower κ_{l} still supports equal or slightly higher ZT . Overall, the p -type trends are consistent with the electronic transport (enhanced S , mildly reduced σ) and the phonon picture (lower κ_{l}) established in the previous sections.

Chapter 6

Conclusions

This thesis examined thermoelectric transport in a family of 2D compounds that exhibit a Mexican-hat-like valence manifold, and demonstrated how *strain engineering* can tune the underlying band-structure descriptors to improve performance. The sharpness of the near-edge singularity in the electronic density of states (DOS) and the onset of the transport distribution are controlled primarily by the ring radius k_0 (the location of the valence-band maximum, VBM, in $\mathbf{k}$ -space), the hat height $\varepsilon_0 \equiv E_{\text{VBM}} - E_{\Gamma}$, and the azimuthal anisotropy of the ring (energy variation ΔE around the ring). Across the materials studied here, finite ΔE broadens the van Hove-like feature, shifts the DOS/transport onset to lower energies, and reduces the Seebeck coefficient S relative to the ideal, isotropic hat.

For the PbXF ($X = \text{Cl, Br, I}$) series, we quantified the role of spin-orbit coupling (SOC): including SOC *reduces* the effective valence-edge singularity and thus the p -type response, but can *enhance* the n -type response by sharpening conduction-edge features. Phonon spectra for all compounds show no imaginary modes, confirming dynamical stability. The lattice thermal conductivity κ_1 is intrinsically low, owing to soft optical branches and strong three-phonon scattering (large anharmonic phase space). Combining the electronic transport (BoltzTraP/BoltzTraP2 in CRTA) with first-principles κ_1 (second-/third-order IFCs + ShengBTE), we obtained room-temperature figures of merit consistent

with our band-structure analysis. As a representative summary at $T = 300$ K, the ZT values for 2D PbXF ($X = \text{Cl, Br, I}$), BaHI, BiOCl, and CaHBr are 0.68 (0.74), 0.567 (0.563), 0.53 (0.57), 0.66, 0.46, and 0.43, respectively, where values in parentheses indicate SOI for the PbXF compounds. Most materials follow the Mexican-hat-based trend (larger k_0 , larger ε_0 , and smaller $\Delta E \Rightarrow$ larger S and PF), with **PbIF** a notable exception: band crossing near the valence edge produces an unusually high DOS peak, and together with a very low κ_l yields a higher ZT than a naive trend would suggest.

We then applied biaxial tensile strain $\Delta = 0, 2, 4, 6\%$ to 2D-SrHI as a clean knob to *reduce* the Mexican-hat anisotropy while monitoring changes in ε_0 , k_c (ring radius), and the band gap E_g . From $\Delta = 0\%$ to 6% , ε_0 decreased by $\sim 30\%$ ($136.2 \rightarrow 95.3$ meV), k_c contracted by $\sim 5.6\%$ ($0.286 \rightarrow 0.270$ Å⁻¹), and the anisotropy energy dropped by $\sim 40\%$ ($37.2 \rightarrow 22.5$ meV), while E_g remained open and changed only modestly ($3.98 \rightarrow 3.85$ eV). In tandem, the DOS onset at the valence edge became progressively sharper. Consistent with the Mott relation, p -type $S(T)$ increased with strain at both 10^{18} and 10^{19} cm⁻³, whereas the n -type response changed only weakly (conduction bands are less affected by the hat). The trade-off for p -type is a small reduction in radial velocities on the VBM ring (slightly lower σ/τ), but the *net* effect on $\text{PF}/\tau = S^2(\sigma/\tau)$ is favorable in the mid- T window at 10^{18} cm⁻³, and largely maintained at 10^{19} cm⁻³. On the lattice side, tensile strain softened acoustic/optical branches and narrowed the acoustic-optical separation, increasing three-phonon phase space and lowering κ_l over the full T -range. Taken together, these electronic and phononic trends yield a *net* increase (or at least no loss) in p -type $ZT(T, \Delta)$ with strain, while n -type ZT benefits primarily from the reduction in κ_l .

- **Descriptors** The trio $(k_0, \varepsilon_0, \Delta E)$ compactly predicts the quality of a Mexican-hat valence edge for thermoelectrics: larger k_0 and ε_0 , and smaller ΔE , sharpen the near-edge DOS and favor large S .
- **SOC** In PbXF, SOC degrades p -type but can enhance n -type performance by reshaping band edges.

- **Strain is effective.** Modest biaxial tension circularizes the hat (reduces ΔE) without closing the gap, boosting p -type S and lowering κ_1 , thereby improving ZT within realistic ranges.
- **Phonons** Soft modes and strong anharmonicity keep κ_1 low; strain further suppresses it, which is beneficial for ZT provided the electronic power factor is preserved.

The results suggest several concrete paths forward:

1. **Beyond CRTA.** Replace the constant- τ approximation with energy, temperature, and carrier-type-dependent scattering, including polar optical phonons and charged impurities in 2D.
2. **Substrate & epitaxial strain.** Explore realistic strain fields from common substrates; assess dielectric screening, remote phonon scattering, and interfacial roughness on both PF and κ_1 .
3. **Alloying and chemical pressure.** Use isovalent alloying to tune $(k_0, \varepsilon_0, \Delta E)$ at fixed lattice mismatch; combine with disorder-limited κ_1 reduction.
4. **Nanostructuring for phonons.** Engineer the boundary and nanopore scattering to further suppress κ_1 with minimal impact on band curvature (e.g., quasi-ballistic electronic transport).
5. **Beyond PBE.** Validate key band-edge features with hybrid functionals or GW , especially where small gaps or band crossings (e.g., PbIF) control the DOS peak.
6. **Experimental validation.** Targeted growth of PbXF and SrHI-like monolayers under controlled strain, with transport measurements vs temperature and doping, would directly test the predicted polarity selective SOI effects and the strain-driven enhancement of p -type S and ZT .

In summary, this thesis establishes a descriptor-based understanding of Mexican-hat-driven thermoelectricity in 2D semiconductors and demonstrates that moderate biaxial strain can systematically improve performance by reducing azimuthal anisotropy while keeping the electronic gap open and the lattice thermal conductivity low. These design rules should generalize to a broader class of layered compounds, guiding the discovery of high-efficiency, room-temperature 2D thermoelectrics.



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Appendix A

Data



Appendix B

Code

