FIRST PRINCIPLES STUDY OF STRUCTURAL-MECHANICAL PROPERTY RELATIONSHIP OF TWO-DIMENSIONAL TRANSITION METAL DICHALCOGENIDES AND PHOSPHORENE ALLOTROPES

by

Pratyaksh Agrawal

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Mechanical and Industrial Engineering
University of Toronto

© Copyright by Pratyaksh Agrawal 2018
First Principles Investigation of Mechanical Properties of Transition metal dichalcogenides and Phosphorene Allotropes

Pratyaksh Agrawal
Master of Applied Science
Department of Mechanical and Industrial Engineering
University of Toronto
2018

Abstract

The structural and mechanical properties of four Transition metal dichalcogenides (TMDs): Rhenium disulfide (ReS$_2$), Rhenium diselenide (ReSe$_2$), Niobium disulfide (NbS$_2$), Niobium diselenide (NbSe$_2$) and nine phosphorene allotropes under large strains were investigated using first-principles density functional theory (DFT) calculations. A complete set of nonlinear elastic constants upto the fifth order were determined for four TMDs. NbSe$_2$ was found to withstand highest failure strain of 38% among four TMDs under uniaxial tension in armchair direction. The energy required to rotate a bond in NbSe$_2$ was found to be significantly smaller than bond stretching. Alpha phosphorene could sustain tensile strain upto 31% and 24% under uniaxial tension in armchair and zigzag directions, respectively. This enormous strain limit of alpha phosphorene resulted from its unique puckered structure. The tensile strain applied in x direction stretched the pucker of phosphorene, rather than significantly extending the P-P bond lengths.
Acknowledgments

I would like to express my sincere gratitude to Professor Chandra Veer Singh for his guidance, support and constant motivation. He has always pushed me to achieve more and do high impact research. I would also like to extend my sincere thanks to the members of the Computational Materials Engineering Laboratory, especially to Dr. Sankha Mukherjee and Hao Sun for their collaboration, guidance and valuable advice throughout my time with them. I thank my best friends, Saloni Bansal and Saloni Chhatwal for their consistent motivation and support. I would also like to thank my friends, Kartikay, Devansh, Raghav for their support. I would also like to thank the Mitacs and the Department of Mechanical and Industrial Engineering for funding this research. I would like to acknowledge Scinet, Calcul Quebec and Compute Canada for providing the computing resources for carrying out this research. At last, I would like to thank almighty God and my beloved parents for believing in me.
# Table of Contents

Acknowledgements iii
Table of Contents iv
List of Tables vi
List of Figures vii
List of Acronyms and Symbols ix

1 **Introduction**

1.1 Two dimensional materials 1
1.2 Phosphorene: 2D material 2
  1.2.1 Mechanical properties and Strain Engineering 3
1.3 Transition metal dichalcogenides 5
  1.3.1 Crystal Structure of TMDs 7
  1.3.2 Electronic Band structure 8
1.4 Thesis objectives 10
1.5 Outline of the Thesis 10

2 **Literature Review** 11

2.1 Mechanical Properties of TMDs 11
2.2 Strain Engineering in TMDs 13
  2.2.1 Strain effect on MoS<sub>2</sub> 14
  2.2.2 Strain effect on Rhenium dichalcogenides 16
2.3 Strain Engineering in Phosphorene 18
2.4 Mechanical Properties of Phosphorene 20
  2.4.1 Mechanical nonlinearity of phosphorene 22

3 **Methodology** 24

3.1 Density Functional Theory 24
3.2 Born-Oppenheimer approximation 25
3.3 Hartree-Fock approximation 26
3.4 Hohenberg-Kohn theorems and Kohn-Shan equations
3.5 Bloch’s theorem and supercell approximation
3.6 Pseudopotential approximation

4 Mechanical Properties of Transition Metal Dichalcogenides

4.1 Computational Details
4.2 Tensile stress-strain relationship
4.3 Nonlinear elastic constants
4.4 Mechanical response in NbS$_2$ and NbSe$_2$
4.5 Energetics of bond formation
4.6 Summary

5 Mechanical Properties of Phosphorene Allotropes

5.1 Introduction
5.2 Computational Details
5.3 Stress-strain response
5.4 Analysis of Mechanical Properties in Alpha Phosphorene
5.5 Mechanical Responses in Phosphorene Allotropes
5.6 Summary

Conclusion and Future work

6.1 Summary and Overall work
6.2 Future work

Bibliography
List of Tables

4.1 Calculated Lattice parameters \((a_0, b_0)\) of ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\). The calculated lattice parameters are compared with the values from literature \((a_0^*, b_0^*)\). 39

4.2 Nonlinear elastic constants \((N/m)\) of ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\) compared with graphene [1] & MoS\(_2\) [66] 42

4.3 The values of UTS and corresponding \(\eta_u\) for ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\) compared with graphene [1] MoS\(_2\) [66], GaS\(_2\) [135] & MoS\(_2^*\) [64] experimental values (for averages of maximum stress) 45

4.4 The values of Failure strain, Area of unit cell and Poisson’s Ratio in NbS\(_2\) and NbSe\(_2\) 49

5.1 \(E/\sigma_{\text{ideal}}\) for nine phosphorene allotropes. \(\sigma_{\text{ideal}}\) is the maximum strength a material can undertake, i.e. UTS in this case. 56

5.2 UTS \((N/m)\), corresponding \(\eta_u\), Young’s modulus \(E\) \((N/m)\) for 9 phosphorene allotropes 58

5.3 The bond lengths, puckered-layer distance, bond angles, and dihedral angles of the relaxed and strained monolayer phosphorene. The bond lengths \(r_1\) and \(r_2\), bond angles \(\theta_1\) and \(\theta_2\), puckered layer distance \(d\) are described in Figure 5.4 (a). \(\Phi_{1234}\) and \(\Phi_{1235}\) are the dihedral angles of the atoms 1-2-3-4 and 1-2-3-5 respectively. The values in the parentheses are the change percentages compared to that of relaxed phosphorene. 61
# List of Figures

1.1 Schematic illustration of different classes of 2D materials such as graphene, hexagonal boron nitride, TMDs, LDHs, MOFs, MXenes, oxides, metals and BP. [26]  
1.2 Structure of phosphorene (a,b) side views from the zigzag and the armchair direction, (c) top view, and (d) zoomed-in local atomic structure of the P–P bonding configuration [32]  
1.3 List of chalcogens and some transition metal atoms  
1.4 Crystal structures of (a) graphene [51], (b) phosphorene [52], and (c) MoS₂ bilayers [53], respectively (d) Schematic of the two most common TMDs phases, 2H and 1T [50]  
2.1 Simulated stress-strain curves for bi-axial strain and uniaxial strain along the zigzag (X) and armchair (Y) directions for a single-layer MoS₂. Insert shows the linear regression of the initial stress-strain curves used to extract elastic moduli. [60]  
2.2 Band gap of MoS₂ (a) MoSe₂ (b) monolayer as a function of the applied strain. The uniaxial tensile strain is applied in the x-direction (xx) and the y-direction (yy). The equal bi-axial tensile strain is applied in both x and the y-directions (xx+yy). Pure shear strain: expansion in the x-direction, and compression in the y-direction (xx-yy), and compression in the x-direction and expansion in the y-direction (yy-xx) with the same magnitude of strain. [80]  
2.3 The band structure of ReS₂ monolayer applied by 0%, 5% a-direction, 5% b-direction and 5% c-direction strain, respectively  
2.4 The band gap of phosphorene as a function of strain applied in the zigzag (a) and armchair (b) directions, respectively. Five strain zones were identified for the zigzag direction, and three for armchair direction, based on its distinct band structures. Zones I, III, V, and VII are corresponding to the direct band gap, while zones II, IV, VI and VIII to indirect band gap, correspondingly [111]  
2.5 (a) Stress as a function of tensile strain for phosphorene. Phosphorene can withstand a critical tensile strain up to 30% in the armchair direction [35] (b) Strain energy density of phosphorene as a function of uniaxial strain in the zigzag (red squares) and the armchair (blue triangles) direction [115]  
3.1 Schematic illustration of pseudoelectron (dash lines) and all electron (solid lines) potentials and their corresponding wavefunctions [122]  
4.1 Force on per atom during relaxation. The cell dimensions were fixed during this relaxation step  
4.2 Energy on per atom during relaxation. Energy per atom is decreasing with the increment in no. of scf cycles.  
4.3 Schematics of the atomic structure for (a) ReX₂, (X= S, Se) (b) NbX₂ (X= S, Se). The top and side view are also displayed. Atoms in dark blue colors and yellow colors represent  
4.4 (a) The Young’s modulus and (b) Poisson’s ratio as a function of the in-plane pressure  
4.5 Stress-strain curves for ReS₂, ReSe₂, NbS₂ & NbSe₂ (a) represent uniaxial tension in x direction (b) represent uniaxial tension in y direction (c) and (d) represent stress in x and y direction in biaxial tension. The UTS values are displayed in the figure with arrows pointing out the corresponding failure strain.
4.6 Energy-strain responses for ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$ (a) represent uniaxial tension in x direction (b) uniaxial tension in y direction and (c) uniaxial tension in biaxial direction respectively.

4.7 Evolution of bond length and bond angle for (a), (c) NbS$_2$ and (b), (d) NbSe$_2$ under the uniaxial-x, uniaxial-y, biaxial strains. The percentage values shown in figure indicate the percentage change in the bond length and angles with respect to the undeformed structure. Angle $\alpha$ and bond length, $d_1$, $d_2$ are marked in figure (e).

4.8 Evolution of buckling height for (a) NbS$_2$ and (b) NbSe$_2$ under the uniaxial-x, uniaxial-y, biaxial strains.

4.9 (a) Variation of bond strain and (b) Angle change as a function of tensile strain. Bond length and angle are shown in inset figure.

4.10 (a) $\Delta U_\phi(\eta)$ for the unit cell of NbSe$_2$ and $\Delta U_r(\eta)$ of one bond in NbSe$_2$ in uniaxial tension in x direction. $\Delta U_\phi(\eta)$ is smaller than $\Delta U_r(\eta)$, showing less energy is required to rotate a bond than bond stretching (b) Illustration of six bonds in the unit cell of NbSe$_2$, (c) Illustration of NbSe$_2$ structures under 1% and 10% triaxial strain. All the bonds are getting equally stretched without any significant change in angles.

5.1 Atomic topologies for the examined phosphorene allotropes. The periodic unit cells are highlighted in pink.

5.2 Stress-strain curves for all allotropes. (a) (b) represent uniaxial tension in x direction; (c), (d) represent uniaxial tension in y direction. UTS values and corresponding failure strain are shown with arrows.

5.3 Variation of UTS and corresponding strain for all allotropes under study: (a) uniaxial tension in x direction, (b) uniaxial tension in y direction.

5.4 Snapshots of a monolayer alpha phosphorene structure. In (a), atoms are labeled using the numbers 1-6. Bond lengths $r_1$ and $r_2$, bond angles $\theta_1$ and $\theta_2$ are denoted. The distance between puckered layers in z direction is labeled as d. (b) and (c) represent the geometry of alpha phosphorene under 30% tensile strain applied in uniaxial x and y directions, respectively.

5.5 (a) The evolution of bond strain with increase in strain for four phosphorene allotropes. (b) The degree of angle rotation $\Delta \theta$ for the four structures during deformation. All the angles and bonds are marked in subfigure (c).
# List of Acronyms and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
</tr>
<tr>
<td>TISE</td>
<td>time independent Schrodinger equation</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition metal dichalcogenides</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>N/m</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>$\nu$</td>
<td></td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\eta_u$</td>
<td></td>
<td>Critical strain</td>
</tr>
<tr>
<td>$\sigma_{\text{ideal}}$</td>
<td>N/m</td>
<td>Maximum strength</td>
</tr>
<tr>
<td>$\phi_{1234}$</td>
<td>$^\circ$</td>
<td>Dihedral angle</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

1.1 Two dimensional materials

Two dimensional (2D) materials are crystalline solids that have attracted a lot of attention in recent times due to their extraordinary physical properties, such as ultralow weight, high Young’s modulus (~ 1 TPa) [13], and high strength, exceptional electrical properties. In the past few years, graphene has been widely studied due to its unique electronic band structure [14], high carrier mobility (about 15000 cm2V-1s-1 at room temperature) [15], thermal conductivity and high transparency. Graphene consists of one atom thick sheet of sp2 bonded carbon atoms arranged in a honeycomb lattice. Even at one atom thickness, graphene has proved to be an excellent electronic and thermal conductor, and graphene based materials have been proposed for a variety of applications ranging from transparent conductors to thermal interface materials to barrister transistor like devices [16], [17]. In 2010, Novoselov and Geim were awarded the 2010 Nobel Prize in Physics for successfully obtaining an isolated graphene layer with sticky tape [13], [18]. The discovery of graphene in 2004 [18] and its unique properties have led to a scientific revolution as 2D materials were long thought to be thermodynamically unstable [19]. Since discovery of graphene, family of 2D materials has significantly expanded and now consists of hexagonal boron nitride (h-BN) [20], transition metal dichalcogenides (TMDs; e.g., MoS2, WSe2, MoSe2, WS2, etc.) [21]–[23], graphitic carbon nitride (g-C3N4) [24], layered metal oxides [25], layered double hydroxides (LDHs) [26], metal-organic frameworks (MOFs) [27], polymers [28], metals [29], black phosphorus (BP) [30], silicone [31] and MXenes [32]. Many of these 2D materials have exciting physical properties that are not available in their three-dimensional (3D) counterparts. Due to the unique combination of structural features and intriguing properties, 2D materials have
emerged as a leading class of materials in various branches of materials science, condensed matter physics and chemistry.

Pristine graphene has a zero band gap, [33] which makes its applications limited in certain fields requiring a semiconducting material. One of the possible solutions of band gap problem is to find other graphene like two dimensional materials that can be either insulators or semiconductors. As a potential substitute material of graphene, the transition metal dichalcogenides (TMDs, e.g., MoS$_2$, WSe$_2$) and black phosphorus (BP) with an intrinsic bandgap [23] have shown promising potential for electronics and optoelectronics applications [34], [35] and opened a new field for 2D materials.

![Figure 1.1: Schematic illustration of different classes of 2D materials such as graphene, hexagonal boron nitride, TMDs, LDHs, MOFs, MXenes, oxides, metals and BP. [36]](image)

1.2 Phosphorene: 2D material
Black Phosphorus (BP) is a single-elemental layered crystalline materials consisting of only phosphorene atoms [37]. It is the most stable allotrope of phosphorus and has a layered structure which is characterized by in-plane strong bonds along with weak van der Walls interlayer interaction [38]. In 2014, phosphorene, a single layer BP, was successfully synthesized from BP using a scotch tape based micro cleavage and since then has drawn an increased research interest due to its natural semiconducting properties [38]. The name ‘phosphorene’ was formulated as a generic term to introduce the 2D monolayer or a few-layer counterpart of bulk BP. Phosphorene is a single component 2D crystal following graphene and silicone. In contrast to graphene, which is a 2D zero band gap semiconductor, phosphorene is a 2D semiconductor with a finite band gap. The crystal structure of monolayer phosphorene is shown in Figure 1.2. Each phosphorus atom is covalently bonded to three adjacent phosphorus atoms. As shown in Figure 1.2, phosphorene has puckered structure along the armchair direction (Figure 1.2 (a)), but it emerges as a bilayer structure along the zigzag direction (Figure 1.2 (b)). The bond angle along the zigzag direction is 94.3° and the adjacent P-P bond length is 2.253 Å, which is smaller than the corresponding angle along the zigzag direction (103.3°). Such unique structural arrangement leads to the origin of anisotropic physical properties [39].

Phosphorene has high hole mobility, making it a p-type device material, which is complimentary to the n-type atomic layers like MoS$_2$ [40], [41]. Phosphorene has a direct band gap and displayed noticeable anisotropy due to the unique ridge structure of layers, distinguishing it from other 2D materials [38]. This band gap can be further optimized by the number of layers, strain, functionalization and defect engineering [2]. The unique puckered honeycomb structure of phosphorene leads to wide range of excellent chemical, physical, optical and mechanical properties making it a suitable candidate for optoelectronic and thermoelectric device applications, where the thermal gradient and the potential difference can be applied in two orthogonal directions [42]. It has been also found that optical properties of phosphorene could be beneficial for photo-energy-conversion processes including photocatalysis and solar cell applications [43]. All of these unique structural characteristics distinguishes phosphorene from other 2D materials.

1.2.1 Mechanical properties and Strain Engineering
Phosphorene has demonstrated fascinating mechanical properties and strong anisotropy due to its unique puckered structure. The structural anisotropy of phosphorene leads to anisotropic mechanical properties along the armchair and zigzag directions. Based on theoretical calculations, it has been found that single layer phosphorene can sustain tensile strains up to 27% and

30% along the zigzag and armchair directions, respectively [9]. The Young’s modulus of phosphorene was found to be 166 GPa along the zigzag direction and 44 GPa in armchair direction [9]. The difference in Young’s modulus can be contributed to variance in deformation modes under various strain conditions. Tensile strain in zigzag direction induces a larger P-P bond elongation while tensile strain in armchair direction stretched the pucker of phosphorene without significantly extending the P-P bond length [2]. Phosphorene has shown excellent flexibility and because of these remarkable mechanical properties, it has already been employed in nanoelectromechanical

Figure 1.2: Structure of phosphorene (a,b) side views from the zigzag and the armchair direction, (c) top view, and (d) zoomed-in local atomic structure of the P–P bonding configuration [2]
resonators [44]. This property is also useful in practical large-magnitude strain engineering of a variety of properties of phosphorene.

Strain engineering or application of pressure can be used to modify properties of 2D crystals like phosphorene, graphene, MoS$_2$ since these structures can sustain much larger strains than their bulk counterparts. Strain engineering is considered to be one of the most effective strategies to tune the band gap for tailored electronic and optical properties. Strain engineering does not lead to disorder or damage the structure unlike chemical functionalization or nano-structuring. Strain engineering can be most readily introduced by lattice mismatch, functional wrapping, material doping, and/or, direct mechanical application [43]. The impact of strain on phosphorene has been widely studied by theoretical simulations based on ‘first principle’ calculations. Due to the strong anisotropic structure of phosphorene, electronic conductivity and optical response of phosphorene has been found to be sensitive to the strain magnitude and orientation (tensile/compressive). Compressive strain in the direction normal to the plane of phosphorene changes its band structure from direct band gap semiconductor to indirect semiconductor, semimetal, and finally metal [45]. Liu et al. have shown that a compressive strain of 3% can trigger direct-to-indirect band gap transition [38]. Peng et al. have shown that 11.3% tensile strain or 10.2% compressive strain could change the phosphorene’s band gap from indirect to direct. Furthermore, Liu et al. showed that an external electric field can convert few-layer phosphorene into a topological insulator and eventually into a metal.

1.3 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are a large group of crystals with a generic chemical formula of MX$_2$, where M is a transition metal typically from groups 4-7, and X is a chalcogen atom such as S, Se or Te. Bulk TMDs have been widely studied over several decades because it is possible to formulate compounds with distinct electronic structures. In bulk form, TMDs form layered structures which has strong intralayer bonding and weak interlayer bonding (van der Waals forces). An individual layer of TMDs includes three atomic layers where transition metal is sandwiched between two chalcogen atoms. These chalcogen atoms are saturated and are not found to be highly reactive. All of these features leads to the attainment of individual layers of TMDs by
various exfoliation and vapor deposition methods. The isolation of monolayers of TMDs from their bulk counterparts results in the dramatic change in their properties. It could be due to the confinement of charge carriers in two dimensions (x- and y-directions) due to the absence of interactions in the z-direction. The single layered TMDs possess dramatically different fundamental properties from their bulk counterparts, making them extremely interesting for wide ranging applications such as catalysis, electronics and photonics. This has generated a tremendous amount of interest among research community in these promising materials.

![Figure 1.3: List of chalcogens and some transition metal atoms](image)

TMDs have a very long and rewarding history. The first structure of TMD was determined by Linus Pauling in 1923 [46]. By 1960s, around 60 TMDs were discovered and at least 40 of them were known to have a layered structure [47]. Adhesive tapes were used to produce ultrathin MoS$_2$ layers around 1963 and the first reports on the production of monolayer MoS$_2$ came around 1986 [48]. Reshef Tenne and colleagues reported the discovery of WS$_2$ nanotubes and nested particles
followed by the synthesis of MoS$_2$ nanotubes and nanoparticles [50]. The rapid growth in the research of graphene related fields that started in 2004 inspired the development of techniques favorable for working with layered materials, paving the way for new studies on TMDs. After the successful exfoliation of graphene, interest in two-dimensional materials has grown tremendously with our ability to control their synthesis [51], the characterization of their unique properties, and their initial use in devices [52].

1.3.1 Crystal Structure of TMDs

TMDs are layered materials containing a transition metal layer sandwiched between two chalcogen layers (X-M-X) (Figure 1.4). The d orbitals of M and the p orbitals of X are covalently bonded within an MX$_2$ monolayer. The atoms in monolayer are arranged in a hexagonal pattern when viewed from c-axis direction (Figure 1.4 (e)) and the individual layers are bonded by the weak van der Walls forces. At the basal surface, all the accessible orbitals of M and X are involved in the intralayer bonding and only the high-energy antibonding orbitals are left for interlayer bonding leading to a complete absence of dangling bonds [53]. The interlayer distances and intralayer bond lengths are generally found to increase with the size of M and X [54].

Polymorphism is one of the unique features of transition metal dichalcogenides. Monolayer graphene and hBN are the only true 2D crystals where all the atoms are covalently bonded in a hexagonal lattice and occupy the same plane (Figure 1.4 (a)). 2D materials such as phosphorene form buckled structures with the atoms distributed across more than one plane (Figure 1.4 (b)). TMDs exist in several structural phases because of different coordination positions of the transition metal atoms. In the bulk phase, TMDs crystallize as a layered structure with two main possible stacking structures: 1T structure, with tetragonal symmetry and octahedral coordination; 2H structure, with hexagonal closed packing and trigonal prismatic coordination (Figure 1.4 (d)). The in-plane lattice constants of various TMDs are in the range from 3.1 Å (VS$_2$) to 3.6 Å (TiTe$_2$), while the inter-layer spacing between the top and bottom chalcogen layers of two neighboring triple layers is approximately the same 3.6 Å [55]. The phase (2H or 1T) determines the properties of TMDs, e.g. MoS$_2$ exist either as 2H, which is a thermodynamically stable semiconducting phase with a bulk band gap of $\sim$1.2 eV, or as 1T, which is a metastable metallic phase [54]. The 2H and
IT phases can be transformed to one another by simple gliding of the atomic planes. It has been demonstrated by an in situ electron microscopy [56] and by chemical modification [57]. It was found that in MoS$_2$ monolayer [23] a selected region with 2H stacking can be turned into 1T structure by Li intercalation. The obtained heterostructure is stable after exfoliation and removal of Li atoms [23]. These two phases are coherently bonded to each other. The two phases exhibit quite different electronic structures due to the changes in the crystal symmetry. 2H phase is semiconducting [23], [55], [58] while the 1T phase is metallic [6]. Therefore, the obtained heterostructures are highly inhomogeneous, consisting of nanometer-sized semiconducting and metallic domains [23].

Figure 1.4: Crystal structures of (a) graphene [3], (b) phosphorene [4], and (c) MoS$_2$ bilayers [5], respectively (d) Schematic of the two most common TMDs phases, 2H and 1T [6].

1.3.2 Electronic Band structure
The diversity of chemical compositions and structural phases of TMDs results in a broad range of electronic properties, both from the point of view of the band structure character (metallic or insulating) and of the emergence of topological phases. In this section, the basic features of band structure of TMDs formed by group VI transition metals Mo and W combined with S and Se are discussed. The basic properties of TMD crystals have been studied for more than half a century. An individual monolayer of TMD consists of an X–M–X sandwich (Figure 1.4 c) with primarily covalent intra-layer bonding. Despite the structural similarity, layered TMDs can exhibit a wide range of electrical properties depending on the number of electrons in their non-bonding d orbitals and the coordination geometry of the metal atom [59].

Group 6 TMDs (MoS$_2$ and WSe$_2$) are semiconductors with an optical bandgap of 1–2 eV depending on the number of layers. Polymorphism or metal coordination are found to have a major influence on the electronic properties of TMDs. MoS$_2$ has found to be semiconducting in trigonal prismatic coordination (2H phase) whereas its octahedral phase is metallic [59]. This property drew attention of MoS$_2$ for electronic devices [6]. The semiconducting nature of trigonal prismatic MoS$_2$ is due to the completely filled d$_{z^2}$ and empty d$_{xy}$ and d$_{x^2-y^2}$ orbitals whereas the metallic nature is due to partially filled t$_{2g}$ band (d$_{xy}$, d$_{xz}$, d$_{yz}$) [59].

The number of layers also plays an important role on the electronic band structure. The materials with single layer are direct gap semiconductors, while multilayer materials display an indirect band gap due to interlayer orbital interactions. MoS$_2$ has found to change from indirect band gap semiconductor to direct band gap semiconductor while coming from bulk to monolayer due to change in the position of the valence and conduction band edges along with decreasing thickness [22], [60]. The calculated values for the bandgap of bulk and monolayer 2H-MoS$_2$ are 0.88 and 1.71 eV, respectively [61]. The valence band maximum and the conduction band minimum are found to be located at the two inequivalent high-symmetry points K and K’, corresponding to the corners of the hexagonal Brillouin zone. This property is common to monolayer 2H-MoS$_2$ (and other group VI monolayer 2H-TMDs) and to graphene, and enables the observation of valley-dependent physical phenomena and potential valleytronics applications [62].

Another important feature of TMDs is the absence of inversion symmetry in their monolayer structure. It results in a spin splitting of the electronic bands driven by the spin–orbit interaction.
This effect is particularly strong in the valence band, in which spin splitting values range from 0.15 eV in monolayer 2H-MoS$_2$ to 0.46 eV in 2H-WSe$_2$ [63]. This trend has been known by considering that the spin–orbit interaction is a relativistic effect, and hence is stronger for heavier elements.

1.4 Thesis objectives

The objective of this thesis is to study the mechanical properties of four TMDs: ReS$_2$, ReSe$_2$, NbS$_2$, NbSe$_2$ and nine phosphorene allotropes through density functional theory. Specifically:

**Study the mechanical properties of four TMDs: ReS$_2$, ReSe$_2$, NbS$_2$, NbSe$_2$**

- Determine the stress-strain behavior and evaluate non-linear elastic constants to investigate the insights into mechanical properties of 4 TMDs
- Study the effect of bond rotation and stretch on the flexibility of 4 TMDs

**Investigate the mechanical properties of phosphorene allotropes**

- Investigate the mechanical properties of nine phosphorene allotropes to find out a possible relation between mechanical and structural properties
- Study the effect of bond rotation on Young’s modulus of nine allotropes and how it is affecting their theoretical cohesive strength

1.5 Outline of the Thesis

In the second chapter, effect of strain on mechanical properties of MoS$_2$, ReS$_2$, phosphorene will be discussed. This chapter will also have a rigorous review of Strain engineering and the role of strain on the various properties of TMDs. The applications of TMDs in various nanoelectronic devices will be briefly discussed. This chapter will conclude with the brief description of mechanical properties of phosphorene and its allotropes.
In the third chapter, theoretical concepts behind the atomistic modeling techniques used for this work will be discussed. This will include an overview of the basics of density functional theory and the various theoretical concepts like Born-Oppenheimer Approximation. Fourth and fifth chapter will focus on the mechanical properties of various phosphorene allotropes and TMDs like Niobium disulfide, diselenide, Rhenium disulfide, selenide. The last chapter will talk about conclusion and scope of future wo
Chapter 2

Literature Review

In the previous chapter, we have discussed a brief outline of two-dimensional materials and their remarkable properties. This chapter will discuss a detailed insight into the properties, such as mechanical, electrical, thermal of various TMDs. This chapter will conclude with the understanding of mechanical properties of various phosphorene allotropes.

2.1 Mechanical Properties of TMDs

Similar to graphene, two-dimensional TMD materials are extremely thin, inherently flexible, and strong. The mechanical properties of TMDs are studied theoretically, by using first-principles methods [7], [64] and experimentally [34], [58]. The mechanical properties of single-layer MoS$_2$ has been recently measured in nanomechanical experiments [58], [64]. It was reported that single-layer MoS$_2$ breaks at the maximum tensile stress of 22 ± 4 GPa [64]. In this thesis, we will concentrate on the mechanical properties of TMDs through first-principles methods.

The single layer MoS$_2$, which has similar structure like graphene, has received enormous attention recently due to its striking optical, electronic, and mechanic properties [22], [58], [64]. Single-layer MoS$_2$ has a direct optical band gap of 1.8 eV [65]. The presence of this band gap makes it favorable for applications in flexible electronics where it would combine high performance with low cost. The study of the mechanical properties of MoS$_2$ is required for three reasons [66]. The knowledge of mechanical properties is important in designing structures for its practical applications. For example, MoS$_2$ requires integration with stretchable polymer substrates for application in high-end bendable electronics. Secondly, strain engineering is an important approach to tune the functional and structural properties of nanomaterials [67]. Recently, strain has been found to have a significant impact on the electronic, transport, and optical properties of semiconductor [7], [12], [62], [68], [69]. MoS$_2$ is sensitive to strain because of its monoatomic thickness. For instance, strain has been found in MoS$_2$ to come from the mismatch of lattice
constants. The lattice-mismatch between a deposited thick layer of HfO$_2$ and monolayer MoS$_2$ in a recent MoS$_2$ based transistor has been regarded comparable to tensile strain resulting in an increment in the carrier mobilities [70].

Figure 2.1: Simulated stress-strain curves for bi-axial strain and uniaxial strain along the zigzag (X) and armchair (Y) directions for a single-layer MoS$_2$. Insert shows the linear regression of the initial stress-strain curves used to extract elastic moduli. [7]

Li and coauthors calculated the mechanical properties of MoS$_2$ monolayer with Quantum-Espresso package [71] using Perdew-Burke-Ernzerhof functional [72] and Trouiller-Martins type norm-conserving pseudopotentials [73] with an energy cutoff of 100 Ry for the wave functions. They used a Monkhorst-Pack grid of $20 \times 20 \times 1$ to sample the first Brillouin Zone. The uniaxial and bi-axial strains were applied along the zigzag and armchair directions. As can be seen from Figure 1.4, at strain below 10%, the single-layer of MoS$_2$ is considered as a good approximation as an elastic isotropic 2D material. The stress-strain behavior becomes nonlinear with the increment in strain. In particular, along the armchair direction, both the maximum stress and its corresponding strain are higher than those along the zigzag direction, indicating that single layer MoS$_2$ is stronger along the armchair direction than along the zigzag direction [45]. The Young’s modulus is generally estimated as a slope of the stress-strain curve in the elastic regime. It was found to be 270 GPa [55], assuming that the effective monolayer thickness is 3.1 Å. The obtained Young’s
modulus was found to be close to the Young’s modulus of bi-layer MoS$_2$ (260 GPa) [55], bulk MoS$_2$ (238 GPa) [50], MoS$_2$ nanotubes (230 GPa) [74] and experimentally measured elastic moduli of freely suspended MoS$_2$ nano sheets (300 GPa) [58]. The monolayer Young’s modulus is slightly larger than the bulk modulus [58]. This anomalous behavior is possibly due to the presence of stacking faults in the bulk phase, which slightly weakens the mechanical properties of bulk MoS$_2$. The Young’s modulus of monolayer MoS$_2$ is higher than that of stainless steel (204 GPa) [75] or graphene oxide (207 GPa) [76] but weaker than that of hexagonal boron-nitride monolayer (∼820 GPa) [77] or graphene (∼1000 GPa) [78].

Flexural rigidity is another important mechanical characteristic of two-dimensional materials. Among typical 2D materials, it is relatively low for graphene (3.5 eV Å$^2$/atom) [79] and hexagonal boron-nitride (3.6 eV Å$^2$/atom) [80] but much higher for TMD materials MoS$_2$ (27 eV Å$^2$/atom) [81] and WS$_2$ (30 eV Å$^2$/atom) [81].

### 2.2 Strain Engineering in TMDs

Tuning the band gap is a common practice in electronic applications to enhance the carrier mobility in semiconductors, or to enhance the emission efficiency of light-emitting devices. It is generally done by external electric field, chemical functionalization, nanopatterning, or strain engineering. The strain engineering is regarded as one of the most effective strategies for band gap engineering. On contrary to chemical functionalization and nanopatterning, strain engineering does not contribute to disorder and damage in monolayers. Strain engineering is easy to implement- a strain can be applied either through lattice mismatch between TMD layers and substrates, or through bending of TMD layers on elastic substrates [82].

Two-dimensional TMDs can sustain strains of upto 10% before breaking [64] which makes them promising candidate for applications in strain engineering as high strain allows to induce considerable changes in the material properties. The three fold symmetry in TMDs allows them to vary the properties using lower strain unlike graphene, which has six-fold symmetry [83]. Several research results have suggested that tensile strain would reduce the bandgap of semiconducting TMDs, turning them into indirect semiconductors, eventually leading to closing of band gap at
baxial tensile strain of ~10% [84], [85]. In addition to the bandgap, strain is expected to modulate the charge carrier effective masses [86], thermal conductivity [87], [88], dielectric properties [87], spin–orbit coupling [89] and on-state currents in TMDs transistors [90].

Heterostructures formed by vertically stacking different TMDs are also strongly affected by strain [91], [92]. The strain possibly originates from the interlayer interactions and from lattice mismatch. In monolayers, strain could be used to modulate the bandgap of hybrid bilayers and multilayers [91]. Other theoretical studies have investigated the effect of strain on anisotropic TMDs [93], such as ReSe₂ and ReS₂. The distorted 1T phase structure of ReSe₂ and ReS₂ gives rise to a strong dependence of the strain response on the direction in which the strain is applied. The carrier mobility is also significantly enhanced if strain is applied in the direction perpendicular to the layers [62]. Thus, strain engineering has proved out to be a feasible approach for the realization of various types of electronic, optoelectronic, electromechanical and spintronic devices with tunable characteristics [94].

2.2.1 Strain effect on MoS₂

Molybdenum disulfide, MoS₂ , is a unique semiconductor with honeycomb structure that offers many exciting mechanical, optical and electronic properties [22], [58], [64], [66], [86], [88]. The three-dimensional bulk MoS₂ has been widely studied for promising application in tribology [95], hydrogen production [96], solar cells [97] and photocatalysis [98]. Theoretical research on the properties of monolayer and bulk MoS₂ has been widely done using first principles calculations, such as band gap (Johari & Shenoy 2012), functionalization through ad atom adsorption [55] and vacancy defect and stability of structures [55]. Strain is usually present in TMDs monolayers, depending on synthesis method, substrate, stacking, and several other conditions [100]. These materials have shown the flexibility and can tackle large strain without undergoing damage [64], leading for electronic structure engineering applications without any physical or chemical damage [62]. Different types of strain on different TMDs have shown many interesting effects. In many cases, the direct gap is turning into indirect with reduced value, to the point that the material is finally turning metallic under extreme strain. Detailed knowledge of the variation of electronic
band structure and variation of mechanical properties under strain is important. In this section, electronic and mechanical properties of monolayer and bulk MoS$_2$ will be discussed.

Recently, it has been shown that the indirect band gap of bulk MX$_2$ increases while it is reduced to few layers and eventually MX$_2$ becomes a direct band gap semiconductor in its monolayer, resulting in a dramatic increase in photoluminescence and in novel excitonic effects [35], [60]. In order to understand the broader aspects of strain engineering,

Figure 2.2: Band gap of MoS$_2$ (a) MoSe$_2$ (b) monolayer as a function of the applied strain. The uniaxial tensile strain is applied in the x-direction (xx) and the y-direction (yy). The equal bi-axial tensile strain is applied in the both x and the y-directions (xx+yy). Pure shear strain: expansion in the x-direction, and compression in the y-direction (xx-yy), and compression in the x-direction and expansion in the y-direction (yy-xx) with the same magnitude of strain. [80]

Johri and co-authors examined the effect of uniaxial tensile and pure shear strain on 2D TMDs. The tensile strain was applied in three different ways: uniaxial expansion of monolayer in x-direction (xx), y-direction (yy), and homogeneous biaxial expansion in both x and y-directions (xx+yy). The shear strain was applied in two ways by lengthing and compressing the monolayer in x- and y-directions (xx-yy), respectively, and by compressing it in x-direction and expanding in y-direction (yy-xx) with the same magnitude of strain. The band gap in graphene is insensitive to uniaxial and symmetrical bi-axial tensile strain. The combination of shear and uniaxial strain
can open and tune the band gap in graphene [101]. Using ab-initio simulations, Johri and co-workers demonstrated that the band gap of 2D TMDs can be widely tuned by applying tensile and shear strain (Figure 2.2). Initially, both MoS$_2$ and MoSe$_2$ exhibited a direct band gap with valence band maximum (VBM) and conduction band minimum (CBM) located at the high symmetry point K. The band gap of optimized monolayer MoS$_2$ and MoSe$_2$ was found to be 1.68 and 1.44 respectively. As shown in Figure 2.2, all three strains, uniaxial tensile, equal bi-axial tensile and shear strains result in the reduction of value of band gap. On the application of bi-axial tensile strain, the band gap decreases steeply, but slowly due to pure shear strain. The tensile strain induces the direct-to-indirect band gap transition while shear strain does not induce any transition and the band gap remains indirect. The band gap transitions depend on the type of chalcogenide atoms. The heavier chalcogenides requires more tensile strain and less shear strain to attain a direct-to-indirect band gap transition [84].

The band gap tuning of MoS$_2$ by applying strain has been observed in experiments [102], [103]. He and co-workers applied uniaxial tensile strain to the two-dimensional MoS$_2$ samples, deposited directly on a transparent thermoplastic substrate by mechanical exfoliation. The strain was applied by bending the flexible substrate in two perpendicular (armchair or zigzag) directions. The dependence of the electronic structure on strain was studied by optical absorption and photoluminescence spectroscopy. He and co-workers found out that the value of band gap can be increased by 70 meV per 1% of applied tensile strain for the direct band gap of MoS$_2$ monolayer. The observed effect was more pronounced for the indirect band gap in bi-layer MoS$_2$ [103]. In tri-layer of MoS$_2$ the band gap tunability was high at $\sim$ 300 meV per 1% of strain [102], which offers great band gap tunability in comparison to all bulk semiconductors under strain. These experimental results are in excellent agreement with first-principles calculations [102], [103].

### 2.2.2 Strain effect on Rhenium dichalcogenides

Rhenium dichalcogenides (ReX$_2$) are new members in the TMDs family and possess the same sandwich type structure like other TMDs, e.g. MoS$_2$ [58], [64], MoSe$_2$ [87], [104], WS$_2$ [23], [48]. ReX$_2$ have unique characteristics in such a way that they have unsubstantial interlayer coupling resulting from a distorted octahedral (1T) crystal structure with triclinic symmetry, which gives
ReX$_2$ have many robust properties, such as anisotropic electronic, optical and mechanical properties [105], [106].

Rhenium disulfide (ReS$_2$) has recently attracted attention on photoluminescence, Raman scattering response, and transconductive properties [68], [105], [107]. Due to the lack of interlayer registry and weak interlayer coupling arising from Peierls distortion of the 1T structure of ReS$_2$, the band renormalization is absent, and the bulk behaves as electronically and vibrationally decoupled monolayers [108]. The decoupled structures lead to a weakly tuned bandgap by the reduced layer number: $E_g = 1.5$ eV (bulk) and 1.6 eV (monolayer), respectively (Tongay et al. 2014). Yu and co-authors explicitly studied the anisotropic electronic and mechanical properties of ReS$_2$ monolayer by first-principle calculations. Yu and co-authors investigated ReS$_2$ structure with tensile strain which ranged from 0 to 5% at incremental step of 1%. The strain was applied along in-plane directions (a-direction, b-direction) and out-of-plane direction (c-direction). The band structure of ReS$_2$ monolayer under 0%, 5% strain applied along a-, b- and c-direction are displayed in Figure 1.6, respectively. They found out that ReS$_2$ is a direct band gap semiconductor from monolayers to bulk with monolayer having a direct bandgap of 1.50 eV (Figure 2.3) (Yu et al. 2016). However, a-direction strain induces indirect bandgap with the valence band shifting from $\Gamma$-point to [0.133, 0.133, 0] in Brillouin zone. This direct to indirect transition occurs at 1% a-direction strain. For strain along b- and c-directions, the bandgap remains direct with conduction band minimum (CBM) and valence band maximum (VBM) staying at $\Gamma$-point. The strain applied in different directions induced different elastic modulus, energy band structure, effective mass, and carrier mobility along different directions. Additionally, ReS$_2$ layered structures can have promising practical applications in photodetector, strain sensor, and field-effect transistors (FETs).
Figure 2.3: The band structure of ReS$_2$ monolayer applied by 0%, 5% a-direction, 5% b-direction and 5% c-direction strain, respectively

2.3 Strain Engineering in Phosphorene

Phosphorene is a single layer black phosphorous has a noticeable band gap unlike graphene and considerable anisotropy in the electro-optical and thermos-mechanical properties [38]. Phosphorene has high elasticity and superior flexibility. It can be stretched up to a strain of 30% [9], [110] which is higher than that of TMDs (ε~20%) [82], and significantly higher than that of typical semiconductors (ε~2%). The large strain range that phosphorene can withstand permits substantial tuning of its electronic and thermo-mechanical properties, thereby making it an ideal candidate for applications in flexible electronics [2]. With many benefits, phosphorene has some specific limitations too. Environmental instability is perhaps the most critical one. It takes upto one week for the degradation of few-layer phosphorene when exposed to ambient conditions such as water vapor, oxygen and light. However, this degradation time is sufficiently long for fabrication of devices, if operated in vacuum conditions [111].

Black phosphorous (BP) is a direct band gap semiconductor with band gap value between 0.33-0.39 eV [111]. A few-layer phosphorene, exfoliated from BP, also remains to be a direct band gap semiconductor [112]. The value of the band gap increases when the number of layers decreases to a single layer due to the quantum confinement effects [112]. The band gaps of black phosphorus and phosphorene have values between those of graphene (zero band gap) and the semiconducting TMDs. Liu et al. were the first to measure the band gap of phosphorene experimentally [38]. They
examined photoluminescence (PL) of exfoliated monolayer phosphorene in the visible wavelengths. For thick black phosphorus flakes, PL signal was not detected within the selected range of the visible spectrum since its band gap ($E_g \sim 0.3$ eV) is in the infrared region. In contrast, a very pronounced PL signal centered at $E_g \sim 1.45$ eV was detected for phosphorene. The observed PL peak confirms that the band gap in phosphorene is significantly larger than in bulk BP. Recently, using high resolution scanning tunneling microscopy and spectroscopy, Liang et al. measured and refined the value of the band gap of phosphorene to be $E_g \sim 2.05$ eV [113].

Carvalho et al. studied the effect of strain on the electronic properties of phosphorene [114]. They found that compressive strain in the direction normal to the plane of phosphorene changes its band structure, causing phosphorene to transform from nearly direct band gap semiconductor to indirect semiconductor, semimetal, and finally metal.

Figure 2.4: The band gap of phosphorene as a function of strain applied in the zigzag (a) and armchair (b) directions, respectively. Five strain zones were identified for the zigzag direction, and three for armchair direction, based on its distinct band structures. Zones I, III, V, and VII are corresponding to the direct band gap, while zones II, IV, VI and VIII to indirect band gap, correspondingly [8]

Peng et al. calculated the band gap of phosphorene as a function of strain applied along the zigzag (ZZ) and arm-chair (AC) directions (Figure 2.4) [8]. They found that the band gap is very sensitive to the applied strain. As shown in Figure 2.4 (a) a sequence of alternating direct-indirect band gap transitions occurs when the uniaxial strain is applied along the ZZ direction. The band gap was found to vanishes at a critical tensile strain of $\epsilon = 13\%$. A similar direct-indirect band gap
transitions also occur when the uniaxial strain is applied along the AC direction (Figure 2.4 (b)).
Liu et al. also reported the sensitive dependence of the band gap on the in-layer stress, and showed that a critical compressive strain of \( \epsilon = -5\% \) triggers the direct-to-indirect band gap transition [38].

### 2.4 Mechanical Properties of Phosphorene

Phosphorene has superior mechanical flexibility and strong anisotropy due to its unique puckered structure. It can be stretched up to \( \sim 40\% \) along the AC direction, which is largely attributed to the unfolding of the puckers, rather than to bond stretching [9]. The Young’s modulus of phosphorene is highly anisotropic: It is more ductile along the AC direction. Although the Young’s modulus of phosphorene is smaller than that of graphene and MoS\(_2\), it is still larger than those of many conventional materials [82]. The electronic properties of phosphorene are anisotropic. Similarly, the puckered structure of phosphorene leads to anisotropy of its mechanical properties. The mechanical properties of phosphorene monolayer subjected to uniaxial strain were studied by Jiang et al. using first-principles calculations [110]. They found that the Young’s modulus (Y) and the related effective two-dimensional Young’s modulus is considerably smaller in the AC direction (\( Y = 41.3 \) GPa, \( E = 21.9 \) Nm\(^{-1}\)) than in the ZZ direction (106.4 GPa, \( E = 56.3 \) Nm\(^{-1}\)). Peng et al. found out the similar results with Young’s modulus (Y) and the related effective two-dimensional Young’s modulus as 44 GPa and 166 GPa respectively. The effective 2D Young’s modulus of phosphorene is 56.3 Nm\(^{-1}\), half of the effective Young’s modulus of the single-layer MoS\(_2\) [82], which is 120 Nm\(^{-1}\). The effective 2D Young’s modulus of phosphorene is smaller than the effective Young’s modulus of single-layer hexagonal boron-nitride [115][131], \( E = 292.1 \) Nm\(^{-1}\) and that of graphene [116], E = 335.0 Nm\(^{-1}\). The smaller value of 2D Young’s modulus of phosphorene is due to its weaker P-P bond strength [12]. In contrast to the isotropic Young’s modulus of graphene and MoS\(_2\), the Young’s modulus of phosphorene is direction-dependent. Wei et al. found that the maximal Young’s modulus of \( Y = 166 \) GPa is in the zigzag direction and the minimal one of 44 GPa is in the armchair direction. The average value of the Young’s modulus over all directions is \( Y = 94 \) GPa.

The mechanical properties of phosphorene can be tuned by functionalization. The 2D Young’s modulus of phosphorene can be modified by sodiation (adsorption of sodium atoms on
phosphorene) [117]. Kulish et al. found that the effective two-dimensional Young’s modulus reduces with increasing the concentration of Na atoms. This softening effect is attributed to the decrease in P-P bond strength after sodiation. The two-dimensional Young’s modulus along the armchair direction decreases by 43% at the highest Na concentration, while Young’s modulus along the zigzag direction changes less than 4%. These results again indicate towards the high anisotropy nature of phosphorene.

Figure 2.5: (a) Stress as a function of tensile strain for phosphorene. Phosphorene can withstand a critical tensile strain up to 30% in the armchair direction [9] (b) Strain energy density of phosphorene as a function of uniaxial strain in the zigzag (red squares) and the arm-chair (blue triangles) direction [10]

The Poisson’s ratio is a fundamental mechanical property that relates the resulting transverse strain to applied axial strain. A stretching in the axial direction is accompanied by compression in a transverse direction [82]. For phosphorene, stretching in the armchair direction results in compression in the transverse out-of-plane Z direction and in plane Y direction. While stretching in armchair direction, the Poisson’s ratio in z and y direction is 0.046 and 0.4 respectively. The stretching in zigzag direction results in a contraction along the transverse in plane X direction. While stretching in zigzag direction, the Poisson’s ratio in x direction was found to be 0.7-0.93 [8], [110], which is about two times larger than the Poisson’s ratio in the armchair-direction. This indicates that Poisson’s ratio is anisotropic in phosphorene monolayer.
2.4.1 Mechanical nonlinearity of phosphorene

Using DFT, Jiang et al. studied the behavior of phosphorene monolayer under uniaxial strain [10]. They found that the strain energy density of phosphorene is very asymmetric with respect to compression and tension deformation (Figure 2.5 (b)). This asymmetric behavior of phosphorene indicates towards a strong mechanical nonlinearity. Using first-principles calculations, Kou et al. found that a compressive strain applied to phosphorene is able to lead to highly anisotropic ripple formation. The ripple formation happens only along the ZZ direction (in the strain range up to ~10%), but not along the AC direction. This direction-sensitive ripple formation is due to the puckered structure of phosphorene. The ripple formation in phosphorene was also found to change its electronic properties and thus influence its application in nanoelectronics [118].

The anisotropic mechanical properties of phosphorene is also illustrated in the difference in the maximal tensile strain along the two principal (armchair and zigzag) directions [119]. Jiang et al. found that the phosphorene can be stretched upto a strain of 48% in the zigzag direction, indicating its high ductile nature, while it can be strained upto a strain of 11% in zigzag direction. Wei et al. found that phosphorene can withstand a tensile strain of 30% along the armchair direction and a strain of 27% in the zigzag direction (Figure 2.5 (a)) [9]. The substantial ductility of phosphorene along the armchair direction is explained by its puckered structure. The tensile strain along the armchair direction unfolds the puckers resulting in bond rotation imparting high failure strain in armchair direction. In comparison, MoS$_2$ can sustain a strain upto 23% [7] and graphene upto 25% [116].

To conclude, in this chapter we have discussed the mechanical properties of TMDs and phosphorene. MoS$_2$ can withstand high strain and corresponding stress in armchair direction, making it more stronger in armchair direction than zigzag direction [45]. The Young’s modulus of MoS$_2$ is 270 GPa [55] closer to experimentally measured elastic moduli of freely suspended MoS$_2$ nano sheets (300 GPa) [58]. Phosphorene can be stretched upto a strain of 48% in the zigzag direction resulting in high ductility. The puckered structure of phosphorene results in bond rotation imparting high failure strain in armchair direction. We have also discussed the strain engineering in TMDs such as MoS$_2$, ReS$_2$ and phosphorene. MoS$_2$ becomes a direct band gap semiconductor
in its monolayer from indirect in bulk. The tuning of band gap also depends on the type of applied strain. The shear strain does not induce any band gap transition and band gap remains indirect. The band gap transitions also depend on the type of chalcogenide atoms. Heavier chalcogenide atoms require more tensile strain for the tuning of band gap. ReS$_2$ remains a direct band gap semiconductor from monolayers to bulk with monolayer having a direct bandgap of 1.50 eV. Black phosphorous (BP) is a direct band gap semiconductor with band gap value between 0.33-0.39 eV [111]. The band gap of phosphorene was found to be very sensitive to the applied strain. The band gap goes through a sequence of alternating direct-indirect band gap transitions when subjected to uniaxial strain in zigzag direction.
Chapter 3
Methodology

The research presented in this thesis utilized the computational technique of Density Functional Theory (DFT), which allows for the atomic scale modelling of materials with the inclusion of electron effects in a relatively efficient manner. The DFT technique was used to calculate the ground state energies of systems with various compositions and configurations. The basic idea of DFT theory is that any property of the ground state of a system can be described as a functional of the ground state electron density. The Quantum Espresso software [71] suite was used to carry out all DFT simulations in this work. The following sections will explain the theoretical basis for the mentioned techniques.

3.1 Density Functional Theory

The Schrodinger equation can fully describe the quantum state of a particular set of atoms. The solution of the Schrodinger equation gives information about various processes and phenomena occurring in complex systems. The complexity of the solution increases with the increasing number of particles in the system. However, solving the partial differential equation for most systems is infeasible, as the equation becomes a many body problem with an enormous number of dimensions. With a number of approximations, DFT can solve the non-relativistic time-independent Schrodinger equation (TISE) by greatly reducing the number of dimensions. DFT can reasonably predict the ground state (lowest energy) quantum properties for a wide variety of systems in a practical period. The basic form of TISE is:

\[ \hat{H}\Psi = E\Psi \]  

Equation 2.1 consists of a Hamiltonian operator \( \hat{H} \), eigenvectors \( \Psi \) (which represent wavefunctions) and eigenvalues \( E \) (which represent system energy). The Hamiltonian is composed of the following terms:
\[ \hat{H} = T_e(r) + T_N(R) + V_{eN}(r,R) + V_{NN}(R) + V_{ee}(r) \]  \hspace{1cm} (2.2)

The terms mentioned in equation 2.2, describes a set of atoms with interacting nuclei (with spatial coordinates represented by \( R \)) and electrons (with spatial coordinates represented by \( r \)). In equation 2.2, the first term on the right represents the kinetic energy of electrons, the second term represents kinetic energy of nuclei, the third term represents electron-nuclei interactions, the fourth term represents nuclei-nuclei interactions and the last term represents electron-electron interactions. The main difficulty in solving equation 2.2 arises because of the electron-electron interaction. The multiple body problem ingraind in TISE makes it very difficult to solve. Since the exact solution is not possible, various attempts have been made to get approximate solutions of the Schrodinger equation. The next section will briefly discuss the various approximations and theories developed to solve the Schrodinger equation.

### 3.2 Born-Oppenheimer approximation

The Born-Oppenheimer (BO) approximation separates an atom’s wavefunctions into nuclei and electrons components respectively. The wavefunction is expressed as a product of its individual components, \( \Psi(r, R) = \Psi(r; R) \chi(R) \). The proton-to-electron mass ratio is about 1836 showing that nuclei are more massive than electrons. Due to massive mass, nuclei have a much smaller velocity compared to that of electrons. The motion of electron can be considered occurring on a timescale where the nuclei are almost stationary. Based on this fact, one can consider that nuclei is “freeze” at fixed positions and take into account only the movement of electrons under a static potential induced by the fixed nuclei. This is known as Born-Oppenheimer adiabatic approximation [120]. The position of nuclei is fixed and the wavefunctions describing electronic motion within the field of the nuclei are determined for their lowest ground state energy. As the nuclei are fixed, \( R \) acts as a parameter for the electronic component of the wavefunction:

\[ \Psi(r, R) = \Psi(r; R) \chi(R) \]  \hspace{1cm} (2.3)
The stationary nuclei also mean that the $T_N(R)$ and $V_{NN}(R)$ terms of the Hamiltonian in Equation 2.2 can be neglected for further Hamiltonian formulations. Thus, the many-particle Schrodinger equation is reduced to a many-electron Schrodinger equation

$$\hat{H} = T_e(\mathbf{r}) + V_{en}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r})$$

$$E\Psi = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j)$$

(2.4)

The first term on right in equation (2.4) represents the kinetic energy of electrons, the second term represents electron-nuclei interactions and the last term represents electron-electron interactions for a system with N electrons. Here, wavefunction, $\Psi$ generally represents electronic wavefunction ($\Psi(\mathbf{r})$). All constants, such as $\chi(\mathbf{R})$ comes under E term. It is still impossible to solve the many-electron Schrodinger equation due to the complexity of the Coulomb interaction potentials. One of the possible solution could be to use an effective potential of a mean-field to replace the Coulumb interaction potentials so that the many-electron Schrodinger equation can be further reduced to a tractable single-electron Schrodinger equation. These approximations were proposed by Hartree [121] and Fock [122].

### 3.3 Hartree-Fock approximation

The electronic wavefunction is still a function of the coordinates of all electrons in the system. The Hartree product assumes that the electronic wavefunction can be expressed a product of individual electron wavefunctions. For N electrons:

$$\Psi = \Psi_1(\mathbf{r}_1)\Psi_2(\mathbf{r}_2), \ldots, \Psi_N(\mathbf{r}_N)$$

(2.5)

The individual electronic wavefunctions can be solved independently of each other. The separation of functional would greatly help to reduce the mathematical complexity and reduce the computational time. The simple Hartree product does not always satisfy the antisymmetry principle. The antisymmetry principle states that the wavefunction should change sign whenever any two electrons are exchanged. The Hartree-Fock approximation create an anti-symmetric product of non-interacting wavefunctions by approximating the electronic wavefunction with a
Slater determinant. For N electrons, slater determinant consists of a determinant of a N x N matrix of individual electron wavefunctions producing a sum of N! Hartree products each with individual electron wavefunctions in a different order and has the following form:

\[ \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(r_1) & \Psi_2(r_1) & \cdots & \Psi_N(r_1) \\ \Psi_1(r_2) & \Psi_2(r_2) & \cdots & \Psi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(r_N) & \Psi_2(r_N) & \cdots & \Psi_N(r_N) \end{vmatrix} \]  

(2.6)

In equation 2.6, each electron can be assumed to move independently of other electrons. The wavefunction variational principle is used to solve for the energy and wavefunction solution of the problem. The exact ground-state wave-function minimizes the expectation value of the Hamiltonian, ˆH:

\[ E[\psi] = \frac{\langle \psi|\hat{H}|\psi \rangle}{\langle \psi|\psi \rangle} \]  

(2.7)

\[ \langle \psi|\hat{H}|\psi \rangle = \int \psi^* \hat{H} \psi \, d\mathbf{r} \]  

(2.8)

By varying the wavefunction parameters, energy is minimized for a particular system to find its ground state energy and get the actual wavefunctions. These true wavefunctions minimizes the energy.

### 3.4 Hohenberg-Kohn theorems and Kohn-Shan equations

Hohenberg and Kohn presented two theorems that allowed the transformation of many-body wavefunctions to one in terms of electronic density. The electron density of the system is a spatial quantity defined as a function of individual wavefunctions:

\[ n(r) = 2 \sum_i \Psi_i^*(r)\Psi_i(r) \]  

(2.9)
The first theorem stated that the ground state energy in the Schrodinger equation of system is a unique functional of the electron density. It expresses the Schrodinger equation in terms of the electron density which only depends on three spatial coordinates, reducing the electronic description of the system to a three dimensional problem instead of the 3N dimensions needed previously for N electrons. The second theorem stated that the ground state energy can be obtained by finding the variational minimum of the energy functional \( E[\rho] \), where the corresponding \( \rho \) is the ground state electron density. The energy functional, in terms of electron density \( n(r) \), can be written as:

\[
E(n) = T_e(n) + V_{\text{ext}}(n) + V_H(n) + E_{xc}(n)
\] (2.10)

The first term on right side in equation 2.10, include electron kinetic energy, second and third term represents coulombic interactions between and amongst nuclei and electrons respectively. Last term, \( E_{xc}(n) \) is known as the exchange-correlation functional and includes the effects of exchange interaction and correlation between electrons as well any other effects, such as self-interaction corrections, which are not included in the earlier known terms. The exact form of the exchange-correlation functional for any system other than the free electron gas is unknown. Many approximate forms have been proposed over the years to represent exchange-correlation functional. Local Density Approximation (LDA) is one of the earliest and simplest functionals which uses the local density of the exactly known uniform electron gas to define the exchange-correlation functional. Generalized Gradient Approximation (GGA) is another most widely used functional which incorporates both the local density and the local gradient of the electron gas. There are many diverse specific implementations of these functionals as well more complex and hybrid functionals with additional terms available.

Kohn and Sham proposed to group all the many body terms which make the theory untreatable into an exchange-correlation potential \( V_{xc} \). Kohn and Sham used the energy functional in equation 2.9 to reformulate Time Independent Schrodinger equation in terms of electron density as:

\[
\left[ \frac{-\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{xc}(r) \right] \Psi_i(r) = \mathcal{E}_i \Psi_i(r)
\] (2.11)
Equation 2.11 contains similar terms to those in Equation 2.4. The second term on the left defines interaction between an electron and nuclei and the third term describes interaction between an electron and total electron density with the following form:

$$V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3 r'$$  \hspace{1cm} (2.12)$$

Equation 2.19 differs from the original TISE in a way that it involves only electron density and single electron wavefunctions of three spatial variables on the left side of equation. On the other hand, summation terms on the left side of original TISE included the effects of all other electrons.

The Kohn-Sham equations can now be iteratively solved in a self consistent manner to find the ground state electron density, single-particle wavefunctions and ground-state system energy.

### 3.5 Bloch’s theorem and supercell approximation

Based on Density functional theory, many body problem has been reduced to single non interacting electrons where all the terms in Schrodinger equation are known. It is still out of reach for any computational power to solve single-electron Schrodinger equations of more than $10^{23}$ particles in solids. Fortunately, Bloch theorem can be used to solve the Schrodinger equation, which uses the periodically repeating system space known as the supercell. This would greatly reduce computational efforts and make DFT calculation possible. The Bloch theorem states that the Schrodinger equation solution can be expressed as a sum of terms where the wavefunction has the following form:

$$\psi_K(r) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_K(r)$$  \hspace{1cm} (2.13)$$

where $u_K(r)$ is periodic in space with the same periodicity as the supercell. It means that Schrodinger equation can solved for each value of k independently. The k vectors are part of k-space, also known as the reciprocal space used in crystallography and solid state physics fields. This approach is commonly used with periodic systems and makes solving DFT calculations easier. Such methods are known as plane wave calculations as functions with the form of the
exponent on the right hand side of Equation 2.13 are known as plane wavefunctions. Calculations in k-space involve integrating functions of k vectors over the primitive cell of the system in reciprocal space known as the Brillouin zone. The periodic $u_k(r)$ term in Equation 2.13 can be further expanded in terms of a special set of plane waves:

$$\Psi_k(r) = \sum_G c_G \exp i(G.r)$$  \hspace{1cm} (2.14)

Combining this equation with Equation 2.13 results in an expression involving summation over an infinite number of G vector values. During calculations, one should always make sure to have a large enough kinetic energy cutoff ($E_{cut} = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_{cut}|^2$) of plane-wave basis sets to include a sufficient large number of plane-wave basis sets to expand the wave function. The infinite sum of the G vector expressions is truncated to solutions which have kinetic energies below a certain cutoff energy. This then reduces the expression for the solutions to the following form:

$$\Psi_k(r) = \sum_{|G|<|G_{cut}|} c_{G+K} \exp [i(k + G)r]$$  \hspace{1cm} (2.15)

The cutoff energy is an important parameter that must be selected in most DFT implementations. Due to the Bloch’s theorem, one needs only to integral over the k-points of the 1st Brillouin zone (1BZ) to obtain a certain quantity instead of over the whole space of a periodic system. One of the most popular way of k-point sampling is the Monkhorst-Pack scheme [123] in which $N_1 \times N_2 \times N_3$ equally spaced k-points in 1BZ are generated following the rule

$$k = \sum_{i=1}^{3} \frac{2n_i - N_i - 1}{2N_i} b_i$$  \hspace{1cm} (2.16)

Where $n_1,n_1$ and $n_3 = 1, \ldots, N_i$.

In practical calculations, one should always ensure to have a dense enough k-point mesh so that the total energy of the system can be well converged.

### 3.6 Pseudopotential approximation
In most of the cases, physical and chemical properties depend on valence electrons. The core electrons of atoms are not important for physical interactions between atoms, such as those involving chemical bonding or electronic conductivity. Moreover, these core electrons require very large energy cutoffs to model in plane wave calculations due to their small length scale oscillations. A weaker pseudopotential can be used to replace the strong Coulomb potential from the core electrons and nucleus. In this way the pseudo wave function becomes much more smooth and thus it is easier to be expanded. Consequently, pseudopotentials are used to approximate core electrons as illustrated in Figure 1.9. Pseudopotentials use the frozen core approach in which the electron density for core electrons up to a certain radial cutoff is replaced with an effective density which matches the density calculated from an all electron simulation. This allows the usage of much lower energy cutoffs as only valence electron plane waves are solved in each calculation and thus reduces computational expense.

Figure 3.1: Schematic illustration of pseudoelectron (dash lines) and all electron (solid lines) potentials and their corresponding wavefunctions [11]

The three common types of pseudopotentials are ultrasoft pseudopotentials (USPP), projected augmented wave (PAW) and norm-conserving. Norm-conserving pseudopotentials [124] use the norm conserving condition:
\[ \int_0^\infty |\Psi_{n,k}^{PS}(r)|^2 dx = \int_0^\infty |\Psi_{n,k}^{AE}(r)|^2 dr \] (2.17)

to make sure the pseudopotentials generated from isolated atoms are transferable to all kinds of chemical environments. Vanderbilt et al. proposed the ultrasoft pseudopotentials to use less plane-wave to expand the wave function and be softer where norm-conserving condition is relaxed and an auxiliary wave function is used to make the pseudopotentials as soft as possible [125]. This method is supposed to tremendously improve the computational efficiency. The projector augmented-wave (PAW) method [126], developed by Bloch in 1994 combines accuracy with efficiency for electronic structure calculations. PAW offers almost the same accuracy as all electron calculations but only requires similar computational efforts as ultrasoft pseudopotentials. We have used PAW method to study the mechanical properties of phosphorene allotropes and TMDs.

To conclude, we have described the theory behind DFT. Several approximations are used in DFT to solve the multiple body Schrodinger equation. The Born-Oppenheimer (BO) approximation considers that nuclei is “freeze” at fixed positions and take into account only the movement of electrons. This eliminates the kinetic energy of nuclei and nuclei-nuclei interactions terms from Hamiltonian (equation 2.2). Hartree-Fock approximation assumes that the electronic wavefunction can be expressed a product of individual electron wavefunctions. These individual electronic wavefunctions can be solved independently of each other. Hohenberg and Kohn presented two theorems that allowed the transformation of many-body wavefunctions to one in terms of electron density. The first theorem stated that the ground state energy in the Schrodinger equation of system is a unique functional of the electron density. The second theorem stated that the ground state energy can be obtained by finding the variational minimum of the energy functional \( E[\rho] \), where the corresponding \( \rho \) is the ground state electron density. Kohn and Sham used the energy functional to reformulate Time Independent Schrodinger equation in terms of electron density which involved only electron density and single electron wavefunctions of three spatial variables. Pseudopotential considers that core electrons do not participate in chemical bonding and thereby replaces the strong Coulomb potential by a weaker pseudopotential.
Chapter 4

Mechanical Properties of Transition Metal Dichalcogenides

The separation of atomically monolayers from bulk materials has attracted a wide range of interest in two-dimensional (2D) family [18]. The atomically thin sheets separated from materials such as boron nitride, graphite, and molybdenum disulfide exhibit novel electronic and mechanical properties, different from their bulk, three-dimensional (3D) counterparts [86], [127]. The layered materials such as Molybdenum disulfide, and Transition metal Dichalcogenides (TMDs) has been profoundly studied over the past few decades as catalysts [96], lubricants [128] and materials for solar cells [47]. Layered materials having weak van der Waals interactions between the layers can be possibly used to fabricate various low dimensional systems such as nanoplatelets and nanosheets [55], [87], [129]. The properties of these low dimensional systems not only differ from each other but also show distinct behavior with respect to their three dimensional (3D) counterparts [55], [87], [129], [130]. Since properties of graphite has been studied extensively in two dimensional form there has been an increased interest in exploring the properties of other layered materials. Transition metal dichalcogenides (TMDs) exhibit layer type structure, similar to graphite, with chemical formula MX$_2$, where M stands for transition metal (Nb, Re, Mo, etc.) and X for chalcogenides (S, Se, Te etc). These structures generally possess a sandwich type of structure with metal atom located between two layers of chalcogen atom as shown in Figure 4.4. Atoms within these layers are covalently bonded, while individual sheets are bonded via weak van der Walls interaction, which makes the properties of these materials extremely anisotropic. The unique physical properties of these new class of materials result from quantum confinement and these properties can be tuned by the number of multi layers as well as on the application of strain.

This work studies the mechanical properties of four different TMDs: Rhenium disulfide (ReS$_2$), Rhenium diselenide (ReSe$_2$), Niobium disulfide (NbS$_2$), Niobium diselenide (NbSe$_2$). First principle DFT calculations were performed to extensively study the stress-strain responses under uniaxial and biaxial loading. The non-linear elastic constants were estimated by fitting the stress–strain data to the fourth order continuum elasticity theory. The nonlinear elastic constants and other mechanical properties were compared with other TMDs as well as with the experimental values.
4.1 Computational Details

The mechanical properties of TMDs were studied using first principles methods based on density functional theory (DFT). The DFT calculations were performed with Quantum-Espresso [71] package with a plane-wave pseudopotential approach. The generalized gradient approximation (GGA) functional described by Perdew-Burke-Ernzerhof (PBE) [72] was used to describe the exchange-correlation of electrons. Kinetic energy cutoffs of 60 Ry and 480 Ry were used for the calculation of wavefunction and charge density, respectively.

The convergence criterion for the self-consistent field (SCF) procedure was set to $1.0 \times 10^{-6}$ Ry. The Brillouin zone was sampled using a Monkhorst–Pack grid of $[123] \times [13] \times [3]$ k-points. A 20 Å vacuum layer was added to the simulation box to avoid any inter-layer interactions. Each system was initially relaxed with variable cell sizes using conjugate gradient minimization technique until the magnitude of the residual Hellman–Feynman force on each atom was less than 0.001 Ry per Bohr. As shown in Figure 4.1 and Figure 4.2, magnitude of force and energy on initial structures is quite high and keeps coming down with the number of scf cycles. The unit cells of ReS$_2$ and ReSe$_2$ had 13 atoms, and NbS$_2$ and NbSe$_2$ had 3 atoms respectively. After the initial relaxation, the unit cells were subjected to different magnitudes of uniaxial, equal-biaxial strains in the x and y directions (i.e. 1 and 2 directions, respectively). The structures were deformed by incrementally dilating the unit cells along the loading direction and applying an equal affine transformation to the atomic positions, followed by an energy minimization routine. During this relaxation step, the cell dimensions were fixed to preserve the overall strain loading on the deformed configuration. The atomic positions and charge density were visualized using the XCrySDen package [131].

The calculated lattice parameters, $a_0$, $b_0$, shown in Figure 4.3 are compared with the literature values in Table 4.1. It can be seen from Table 4.1 that our calculated lattice parameters are in close agreement with the literature.
Figure 4.1: Force on per atom during relaxation. The cell dimensions were fixed during this relaxation step.

Figure 4.2: Energy on per atom during relaxation. Energy per atom is decreasing with the increment in no. of scf cycles.
4.2 Tensile stress-strain relationship

The structures of ReX$_2$ and NbX$_2$ (X=S, Se) are shown in Figure 4.4. In this study, we have considered the mechanical deformation of ReX$_2$ and NbX$_2$ at ground energy state. The true stress versus Lagrangian strain responses for ReX$_2$ and NbX$_2$ are shown in Figure 4.5. The simulations result show that nonlinear relationships between the stress and strain exist for all four TMDS, i.e. ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$. All of these 4 structures were found to follow a linear stress-strain response for strains smaller than 10%. For strain larger than 10%, strain started behaving non-linearly with strain. The mechanical instability takes place in all the structures upon reaching UTS. A slow decrease in stress against increasing magnitudes of strain can be observed in all the structures after UTS.

The nonlinear elastic constants were calculated after fitting the stress strain data until the UTS point in equations 2.18-2.26. The second nonlinear elastic constants were used to calculate the Young’s modulus (E) and Poisson’s ratio (ν) using the following:

\[ E = \frac{C_{11}^2 - C_{12}^2}{C_{11}}, \quad \nu = \frac{C_{12}}{C_{11}} \]  

(2.18)

The magnitudes of UTS, the strain corresponding to UTS point (\(\eta_u\)), Young’s modulus (E) and Poisson’s ratio (ν) and area density of ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$ along with graphene are listed in Table 4.2. All the four TMDs were found to have inferior values of UTS and Young’s modulus compared to graphene. Graphene was found to have highest Young’s modulus (E) of 348.64 N/m [1] while NbS$_2$ had the lowest Young’s modulus (E) of 72.29 N/m. NbS$_2$ has lowest UTS of 9.67 N/m , which is approximately 20 N/m lower than that of graphene. As compared to ReSe$_2$, ReS$_2$ is found to be stronger in x and y directions. NbSe$_2$ is found to be comparatively Stronger than NbS$_2$ in x and y directions. All TMDs were found to withstand higher elongation at peak stress (\(\eta_u\)) under uniaxial tension (x & y directions) than biaxial tension. For instance, NbS$_2$ has \(\eta_u = 0.27\) under y- uniaxial tension ( Table 4.2) but only 0.19 for biaxial tension (Table 4.2). NbX$_2$ (X=S, Se) have larger \(\eta_u\) than that of graphene under uniaxial tension. Interestingly, under uniaxial –x tension, NbSe$_2$ was found to have higher elongation of 38% at peak stress than graphene (23%) and highest among all other TMDs listed in Table 4.2. The higher \(\eta_u\) of NbSe$_2$ can be due to
increased bond rotation. The next sections of this chapter will discuss about it in detail. Additionally, area density of all TMDs is smaller than that of graphene, leading to fewer bond connections and hence smaller UTS and E. This observation that graphene has higher UTS and Young’s modulus than TMDs is in the sync with the fact that graphene has higher area density than TMDs and hence stronger bond connection.

The strain energy per unit area, \( E_s = (E_{\text{tot}} - E_0)/A \), where \( E_{\text{tot}} \) is the total energy of the strained system, \( E_0 \) is the total energy of the strain-free system, and \( A \) is the area of the unit cell. The strain energy is a size independent quantity and has been used for comparison between different systems. Figure 4.6 shows strain energy per unit area versus lagrangian strain under uniaxial and biaxial tension for ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\). In all of the materials, the strain energy obeys a quadratic relation with \( \eta \) for strains smaller than 0.1. This result suggest that a linear relationship exists between stress and strain for small deformations, \( \eta < 10\% \). However, for \( \eta >10\% \), all the materials were found to follow a nonlinear elastic behavior.

Figure 4.3: Schematics of the atomic structure for (a) ReX\(_2\), (X= S, Se) (b) NbX\(_2\) (X= S, Se). The top and side view are also displayed. Atoms in dark blue colors and yellow colors represent Transition metal (Re, Nb) and chalcogen (S, Se) respectively. \( a_0, b_0 \) are lattice parameters.
Table 4.1: Calculated Lattice parameters \((a_0, b_0)\) of ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\). The calculated lattice parameters are compared with the values from literature \((a_0^*, b_0^*)\). Our calculated lattice parameter values are in good agreement with literature.

<table>
<thead>
<tr>
<th>Structures</th>
<th>(a_0) (Å)</th>
<th>(b_0) (Å)</th>
<th>(a_0^*) (Å)</th>
<th>(b_0^*) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbS(_2)</td>
<td>3.38</td>
<td>3.38</td>
<td>3.33 [133]</td>
<td>3.33 [133]</td>
</tr>
<tr>
<td>NbSe(_2)</td>
<td>3.48</td>
<td>3.48</td>
<td>3.48 [87]</td>
<td>3.48 [87]</td>
</tr>
</tbody>
</table>

4.3 Nonlinear elastic constants

The fifteen nonzero independent elastic constants of 4 TMDs, ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\) are presented in Table 4.1. The nonlinear elastic constants are evaluated by performing a least squares fitting to the 2nd P-K stress–strain data following the continuum description of nonlinear elasticity of graphene proposed by Wei et al. The mechanical response of TMDs under uniaxial lagrangian strain \((\eta)\) along the x direction (i.e., 1 direction) can be represented using the Voigt notation, which is given by

\[
\Sigma = J F^{-1} \sigma (F^{-1})^T, \quad J = \text{det}(F)
\]  

\[
\Sigma_1 = C_{11} \eta_1 + \frac{1}{2} C_{111} \eta_1^2 + \frac{1}{6} C_{1111} \eta_1^3 + \frac{1}{24} C_{11111} \eta_1^4
\]  

\[
\Sigma_2 = C_{12} \eta_1 + \frac{1}{2} C_{112} \eta_1^2 + \frac{1}{6} C_{1112} \eta_1^3 + \frac{1}{24} C_{11112} \eta_1^4
\]
\[ \Sigma^x_6 = 0 \]  

In the case of uniaxial loading along the y direction, where \( \eta_1 = 0, \eta_2 \geq 0, \eta_6 = 0 \), the mechanical response follows:

\[
\Sigma_1^2 = c_{12} \eta_2 + \frac{1}{2} (c_{111} - c_{222} + c_{112}) \eta_2^2 + \frac{1}{6} (c_{1111} + 2c_{1112} - c_{2222}) \eta_2^3 + \frac{1}{24} c_{12222} \eta_2^4 \tag{2.23}
\]

\[
\Sigma_2^2 = c_{11} \eta_2 + \frac{1}{2} c_{222} \eta_2^2 + \frac{1}{6} c_{2222} \eta_2^3 + \frac{1}{24} c_{22222} \eta_2^4 \tag{2.24}
\]

\[
\Sigma_6^2 = 0 \tag{2.25}
\]

Under equi-biaxial loading, the constitutive equations are

\[
\Sigma_{1\text{b}} = (c_{11} + c_{12}) \eta + \frac{1}{2} (2c_{111} - c_{222} + 3c_{112}) \eta^2 + \frac{1}{6} (\frac{3}{2} c_{1111} + 4c_{1112} - \frac{1}{2} c_{2222} + 3c_{1122}) \eta^3 + \frac{1}{24} (3c_{11111} + 10c_{11112} - 5c_{12222} + 10c_{11122} - 2c_{22222}) \eta^4 \tag{2.26}
\]

\[
\Sigma_{1\text{b}} = \Sigma_{2\text{b}} \tag{2.27}
\]

eqn (2.18)–(2.26) are valid for finite strains under arbitrary in-plane tensile loading when the bending stiffness is negligible.

The fifteen fourth-order elastic constants of 4 TMDs, ReS\(_2\), ReSe\(_2\), NbS\(_2\) & NbSe\(_2\) were calculated by fitting the simulated stress–strain responses to eqn (2.19)–(2.27). The magnitudes of the elastic constants of these 4 TMDs are listed in Table 4.1. Additionally, for comparison nonlinear elastic constant values of graphene are also presented in Table 4.1. The third order elastic constants \((c_{111}, c_{222}, c_{112})\) are negative for most of the structures, leading to mechanical softening of the structures at large strains. The magnitudes of \(c_{11}\) and \(c_{22}\) are of the same order for all the structures, implying isotropic mechanical behavior along the x and y directions. It can be observed from Table 4.1 that ReS\(_2\) and NbS\(_2\) possess the highest and lowest magnitudes of \(c_{11}\) and \(c_{22}\) respectively, among all the TMDs illustrated in Table 4.1. This observation is consistent with the fact that ReS\(_2\) has highest UTS and Young’s modulus (Table 4.2) while NbS\(_2\) has lowest UTS and Young’s modulus among all the TMDs studied here.
We have also calculated the pressure-dependent second-order elastic constants \((\tilde{C}_{11}, \tilde{C}_{12}, \tilde{C}_{22})\) using the following expressions [134]:

\[
\begin{align*}
\tilde{C}_{11} &= C_{11} - (C_{111} + C_{112}) \frac{1 - \nu}{E} P \\
\tilde{C}_{12} &= C_{12} - C_{112} \frac{1 - \nu}{E} P
\end{align*}
\]

(2.28) (2.29)

where \(P\) is the in-plane pressure, \(p_{mm} = -P \delta_{mm}\), \(\delta_{mm}\) is the Kronecker-delta function. The pressure-dependent second-order elastic moduli, Young’s modulus and Poisson’s ratio of all 4 TMDs are plotted in Figure 4.3 as a function of the in-plane pressure (P).

![Figure 4.4](image)

Figure 4.4: (a) The Young’s modulus and (b) Poisson's ratio as a function of the in-plane pressure

The effect of pressure on Young’s modulus and Poisson’s ratio is presented in Figure 4.4 (a) and (b), respectively. The Young’s modulus increases linearly in all the TMDs as a function of pressure. The rate of increase of elastic moduli is the highest in ReS\(_2\) compared to three other allotropes. The absolute value of Poisson’s ratio decreases with an increasing in-plane pressure for all the 4 TMDs. Generally, the absolute value of Poisson’s ratio decreases with an increasing in-plane pressure for most of the two-dimensional structures, suggesting that 2D materials are more easily compressed than sheared for increased in-plane pressures. As shown in Table 4.2
and Figure 4.5, ReS$_2$ was found to possess highest Young’s modulus while NbS$_2$ had the lowest Young’s modulus. However, an opposite trend was observed in Poisson’s ratio of these two materials. This suggest that Transition metal dichalcogenides with different structures tend to have different Young’s moduli and Poisson’s ratio.

Table 4.2: Nonlinear elastic constants (N/m) of ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$ compared with graphene [1] & MoS$_2$ [66]

<table>
<thead>
<tr>
<th>TMDs</th>
<th>ReS$_2$</th>
<th>ReSe$_2$</th>
<th>NbS$_2$</th>
<th>NbSe$_2$</th>
<th>MoS$_2$</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{11}$</td>
<td>144.23</td>
<td>130.28</td>
<td>80.25</td>
<td>84.08</td>
<td>128.4</td>
<td>358.1</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>16.19</td>
<td>29.65</td>
<td>25.27</td>
<td>27.21</td>
<td>32.6</td>
<td>60.4</td>
</tr>
<tr>
<td>C$_{22}$</td>
<td>143.71</td>
<td>132.10</td>
<td>79.66</td>
<td>83.62</td>
<td>N/A</td>
<td>358.1</td>
</tr>
<tr>
<td>C$_{111}$</td>
<td>-1792.88</td>
<td>-1257.54</td>
<td>-552.79</td>
<td>-806.44</td>
<td>-1460.0</td>
<td>-2817</td>
</tr>
<tr>
<td>C$_{112}$</td>
<td>246.96</td>
<td>-242.41</td>
<td>-205.82</td>
<td>-357.36</td>
<td>48.0</td>
<td>-337.1</td>
</tr>
<tr>
<td>C$_{222}$</td>
<td>-1473.03</td>
<td>-1129.26</td>
<td>-459.92</td>
<td>-632.55</td>
<td>-1238.2</td>
<td>-2693.3</td>
</tr>
<tr>
<td>C$_{1111}$</td>
<td>19166.16</td>
<td>11831.77</td>
<td>2378.16</td>
<td>7389.22</td>
<td>13327</td>
<td>13416.2</td>
</tr>
<tr>
<td>C$_{1112}$</td>
<td>1862.75</td>
<td>6150.33</td>
<td>1645.57</td>
<td>-2116.93</td>
<td>505</td>
<td>759</td>
</tr>
<tr>
<td>C$_{1122}$</td>
<td>-8227.60</td>
<td>-3814.73</td>
<td>901.75</td>
<td>1044.04</td>
<td>-1467</td>
<td>2582.8</td>
</tr>
<tr>
<td>C$_{2222}$</td>
<td>18567.86</td>
<td>7610.17</td>
<td>691.64</td>
<td>4290.16</td>
<td>10452</td>
<td>10358.9</td>
</tr>
<tr>
<td>C$_{11111}$</td>
<td>-115119.13</td>
<td>-113137.80</td>
<td>-6894.94</td>
<td>-41455.73</td>
<td>-57311</td>
<td>-31383.8</td>
</tr>
<tr>
<td>C$_{11112}$</td>
<td>-89647.77</td>
<td>-104553.46</td>
<td>-8128.90</td>
<td>-1132.63</td>
<td>972</td>
<td>-88.4</td>
</tr>
<tr>
<td>C$_{11222}$</td>
<td>-11247.27</td>
<td>-11649.48</td>
<td>8272.04</td>
<td>17884.76</td>
<td>-19630</td>
<td>-13046.6</td>
</tr>
<tr>
<td>C$_{22222}$</td>
<td>-207115.44</td>
<td>-53241.43</td>
<td>5687.47</td>
<td>-21357.79</td>
<td>-68555</td>
<td>-33446.7</td>
</tr>
</tbody>
</table>
Figure 4.5: Stress-strain curves for ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$ (a) represent uniaxial tension in x direction (b) represent uniaxial tension in y direction (c) and (d) represent stress in x and y direction in biaxial tension. The UTS values are displayed in the figure with arrows pointing out the corresponding failure strain.
Figure 4.6: Energy-strain responses for ReS₂, ReSe₂, NbS₂ & NbSe₂ (a) represent uniaxial tension in x direction (b) uniaxial tension in y direction and (c) uniaxial tension in biaxial direction respectively.

Generally, the energy variation with respect to Lagrangian strain can be classified into four strain regions: harmonic, anharmonic, plastic, and failure region [66]. The anharmonic region is the range of strain where the linear stress–strain relationship is not valid and higher order terms cannot be neglected. The maximum strain in the anharmonic region is known as the critical strain. The region between $\eta=0$ and critical strain is known as the elastic region and strain energy monotonically increases in this region, and the structure of system is preserved. The system returns to its original
state at $\eta=0$ after the release of tension. At $\eta$ larger than critical strain, system is in plastic region and undergoes irreversible structural changes where structures might undergo phase transition or may fail.

Table 4.3: The values of UTS and corresponding $\eta_u$ for ReS$_2$, ReSe$_2$, NbS$_2$ & NbSe$_2$ compared with graphene [1] MoS$_2$ [66], GaS$_2$ [135] & MoS$_2$* [64] experimental values (for averages of maximum stress)

<table>
<thead>
<tr>
<th></th>
<th>$x$-axial UTS (N/m)</th>
<th>$y$-axial UTS (N/m)</th>
<th>Biaxial UTS (N/m)</th>
<th>$x$-axial $\eta_u$</th>
<th>$y$-axial $\eta_u$</th>
<th>Biaxial $\eta_u$</th>
<th>Area density ($\text{Å}^{-2}$)</th>
<th>Poisson’s Ratio (v)</th>
<th>Young’s modulus (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReS$_2$</td>
<td>12.32</td>
<td>12.97</td>
<td>9.15</td>
<td>0.17</td>
<td>0.16</td>
<td>0.13</td>
<td>0.3291</td>
<td>0.21</td>
<td>142.41</td>
</tr>
<tr>
<td>ReSe$_2$</td>
<td>10.62</td>
<td>12.28</td>
<td>8.72</td>
<td>0.16</td>
<td>0.17</td>
<td>0.12</td>
<td>0.3021</td>
<td>0.22</td>
<td>123.53</td>
</tr>
<tr>
<td>NbS$_2$</td>
<td>9.67</td>
<td>10.43</td>
<td>8.23</td>
<td>0.23</td>
<td>0.27</td>
<td>0.19</td>
<td>0.3030</td>
<td>0.31</td>
<td>72.29</td>
</tr>
<tr>
<td>NbSe$_2$</td>
<td>11.71</td>
<td>10.42</td>
<td>9.81</td>
<td>0.38</td>
<td>0.25</td>
<td>0.24</td>
<td>0.2859</td>
<td>0.32</td>
<td>75.27</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>11.9</td>
<td>12.6</td>
<td>15.1</td>
<td>0.24</td>
<td>0.37</td>
<td>0.26</td>
<td>N/A</td>
<td>0.25</td>
<td>120.1</td>
</tr>
<tr>
<td>MoS$_2^*$</td>
<td>15±3</td>
<td>15±3</td>
<td>15±3</td>
<td>0.06-0.11</td>
<td>0.06-0.11</td>
<td>0.06-0.11</td>
<td>N/A</td>
<td>0.27</td>
<td>180±60</td>
</tr>
<tr>
<td>GaS$_2$</td>
<td>8.62</td>
<td>10.46</td>
<td>8.83</td>
<td>0.24</td>
<td>0.47</td>
<td>0.27</td>
<td>N/A</td>
<td>0.18</td>
<td>334.77</td>
</tr>
<tr>
<td>Graphene</td>
<td>31.2</td>
<td>29.26</td>
<td>33.11</td>
<td>0.23</td>
<td>0.18</td>
<td>0.23</td>
<td>0.3790</td>
<td>0.17</td>
<td>348.64</td>
</tr>
</tbody>
</table>

4.4 Mechanical response in NbS$_2$ and NbSe$_2$

The bond lengths ($d_1,d_2$) and bond angle ($\alpha$) of NbX$_2$ (X=S, Se) as a function of lagrangian strain, $\eta$ are plotted in Figure 4.7. In NbS$_2$, AB and AC bonds behave in a similar fashion under uniaxial and biaxial strains. When the strain is applied in biaxial direction, the bond lengths $d_1$-$d_2$ increase under increasing strains, extending by about 22% at $\eta=0.3$ followed by 16% in uniaxial y direction. In all the three cases, bond lengths monotonically increases until $\eta=0.3$. In NbSe$_2$, AB and AC bonds were found to behave differently under uniaxial and biaxial strains. The bond length $d_1$ extended by about 28% while $d_2$ increased by about 15% at 40% strain in uniaxial –x direction. Few bond lengths, $d_2$ under uniaxial- y direction was found to decrease slightly with the strain.
The evolution of bond angle, $\alpha$ with strain was examined under uniaxial and biaxial strains (Figure 4.7 (c), (d)). In NbS$_2$, bond angle, $\alpha$ monotonically increases with increasing strain under uniaxial–x direction. While in NbSe$_2$, bond angle, $\alpha$ constantly increases with strain in uniaxial –y direction. The bond angle, $\alpha$ is reduced from 83° to 64°, which is 22% reduction under uniaxial tension in x direction in NbSe$_2$. Similarly, there is decrement in $\alpha$ of about 20% under uniaxial –y direction in NbS$_2$ respectively. Due to this bond rotation, NbS$_2$ and NbSe$_2$ can sustain higher ultimate strain upto 27% and 38% in uniaxial –y and x directions respectively.

The buckling height is an important parameter to characterize the corrugation of the surfaces [9]. The tensile strain decreases the buckling height in a complex function. Both in NbS$_2$ and NbSe$_2$, the buckling height decreases with increasing strains under both uniaxial and biaxial strains. In NbS$_2$, uniaxial and biaxial strains have the same effect on the buckling height upto $\eta = 0.2$. The biaxial strain has a stronger effect on the buckling height, approximately twice the uniaxial strains. There is a sudden drop in buckling height after $\eta = 0.2$ under biaxial strain.

### 4.5 Energetics of bond formation

From Table 4.2 and Figure 4.5, it can be seen that NbSe$_2$ has ultimate strain ($\eta = 0.38$) in the uniaxial –x direction, highest among all the materials listed in Table 4.2 under all the directions. NbS$_2$ has $\eta = 0.23$ under uniaxial strain, approximately 65% smaller than NbSe$_2$. The increase in ultimate strain in NbSe$_2$ under uniaxial strain is due to the increased bond rotation. Initially, bonds undergo rotation followed by bond stretching under uniaxial tension in x direction. Under uniaxial tension, the bonds, which are not parallel or perpendicular to the loading direction undergo rotation [136]. As seen in Figure 4.7 (b) and Figure 4.7 (d), the bond lengths in NbSe$_2$ are smaller under uniaxial tension in x direction as compared to biaxial tension followed by drastic change in angle, upto 22% reduction, in uniaxial tension. This is due to the bond rotation, which leads to the relaxation of bond stretching, resulting in an increment in ultimate strain.
Figure 4.7: Evolution of bond length and bond angle for (a), (c) NbS$_2$ and (b), (d) NbSe$_2$ under the uniaxial-$x$, uniaxial-$y$, biaxial strains. The percentage values shown in figure indicate the percentage change in the bond length and angles with respect to the undeformed structure. Angle $\alpha$ and bond length, $d_1$, $d_2$ are marked in figure (e).
Figure 4.8: Evolution of buckling height for (a) NbS$_2$ and (b) NbSe$_2$ under the uniaxial-x, uniaxial-y and biaxial strains.

The bond strain ($\varepsilon$) and change in bond angle ($\omega$) with lagrangian strain are shown in Figure 4.9. It can be seen from Figure 4.9 (b) that the change in bond angle under uniaxial tension is greater than biaxial tension showing that more bond rotation is happening in former case. Due to this bond rotation, the bond strain is partially relaxed. Consequently, bond strain under uniaxial tension is smaller than biaxial tension. The smaller bond strain is leading to higher strain corresponding to failure and hence higher ductility.

The interaction between individual atoms play a key role in describing the mechanics of structures, which may also be characterized by a force field based on classical mechanics. According to molecular mechanics theory, this force field depends on relative positions of individual atoms. When a structure is deformed, the energy stored in the structure is a sum of several individual energy sources, e.g. bond stretch, bond rotation, van der walls interactions etc. For our systems, the total stored energy can be written as:

$$\Delta U(\eta) = \Delta U_r(\eta) + \Delta U_\omega(\eta)$$

(2.30)
Figure 4.9: (a) Variation of bond strain and (b) Angle change as a function of tensile strain in NbSe$_2$. Bond length and corresponding angle are shown in inset figure.

Table 4.4: The values of Failure strain, Area of unit cell and Poisson’s Ratio in NbS$_2$ and NbSe$_2$.

<table>
<thead>
<tr>
<th>Structures</th>
<th>$x$ - $\eta_u$</th>
<th>Area of unit cell ($\text{Å}^2$)</th>
<th>Poisson’s Ratio (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbS$_2$</td>
<td>0.23</td>
<td>9.9</td>
<td>0.31</td>
</tr>
<tr>
<td>NbSe$_2$</td>
<td>0.38</td>
<td>10.5</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Figure 4.10: (a) $\Delta U_\phi(\eta)$ for the unit cell of NbSe$_2$ and $\Delta U_r(\eta)$ of one bond in NbSe$_2$ in uniaxial tension in x direction. $\Delta U_\phi(\eta)$ is smaller than $\Delta U_r(\eta)$, showing less energy is required to rotate a bond than bond stretching (b) Illustration of six bonds in the unit cell of NbSe$_2$, (c) Illustration of NbSe$_2$ structures under 1% and 10% triaxial strain. All the bonds are getting equally stretched without any significant change in angles.
Where $\Delta U_r(\eta)$ and $\Delta U_\theta(\eta)$ represent the energy increase due to bond stretching and bond angle bending. In order to decouple the influence of $\Delta U_r$ and $\Delta U_\theta$, we calculated $\Delta U(\eta)$ for NbSe$_2$ under uniaxial and triaxial deformation. As shown in Figure 4.10 (a) & (b), during triaxial tension, bond angle doesn’t change significantly and only bond stretching takes place. Therefore, for triaxial loading, $\Delta U(\eta)$ of the unit cell can be written as:

$$
\Delta U(\eta) = \sum_{i=1}^{6} \Delta U_r(\eta_i^i) = 6\Delta U_r(\eta)
$$

(2.31)

Where $\eta_i^i = (l' - l_o)/l_o$ is the lagrangian strain in the i-th bond, $l_o$ is the initial length and $l'$ is the bond length for externally applied strain, $\eta$. Both bond stretch and bond rotation takes place during uniaxial tension in zigzag direction. We calculated $\Delta U_\theta$ for the unit cell of NbSe$_2$ under uniaxial tension by using the magnitudes of $\Delta U_r(\eta_i^i)$ of the same bond under triaxial tension calculated using equation (2.31), with strain values equal to the corresponding bond strain in uniaxial tension. Therefore, $\Delta U_\theta$ in the unit cell of NbSe$_2$ is given by, $\Delta U_\theta = \Delta U(\eta) - \sum_{i=1}^{6} \Delta U_r(\eta_i^i)$. In figure 4.10 (a), we have plotted both energy required to stretch one bond, $\Delta U_r(\eta)$ and energy change in the unit cell due to bond rotation, $\Delta U_\theta$ as a function of $\eta$, the applied uniaxial lagrangian strain. It can be clearly seen from the figure that, stress and strain follows a linear relationship for small magnitudes of strain. As mentioned before, nonlinear elastic behavior becomes dominant as the magnitude of applied strain is increased. However, the magnitude of $\Delta U_\theta$ is significantly smaller than $\Delta U_r(\eta)$. This means that for a certain amount of work done by a NbSe$_2$ bond during tensile deformation, the amount of energy stored by bond stretching is significantly larger than the elastic energy retained by bond rotation. The energy required to rotate a bond is less than bond stretching, resulting in increased bond rotation and hence higher ductility in uniaxial direction in NbSe$_2$. From Table 4.4, it can be seen that NbSe$_2$ has greater unit area and Poisson’s ratio than NbS$_2$. The electrons are farther away from each other in larger unit area cell structure, leading to less repulsive force and making it easier to contract. It is comparatively easier for bonds in greater area NbSe$_2$ structure to undergo rotation, leading to higher failure strain.
4.6 Summary

This work looked at the mechanical properties of four TMDs: ReS$_2$, ReSe$_2$, NbS$_2$, NbSe$_2$. A linear relationship existed between stress and strain in all the 4 structures for strains smaller than 10%. A non-linear behavior became dominant for larger strains. All the four TMDs were found to have inferior values of UTS and Young's modulus when compared with graphene. NbS$_2$ had lowest UTS and Young’s modulus of 9.67 N/m and 20 N/m respectively. All TMDs were found to withstand higher elongation at peak stress (η$_u$) under uniaxial tension (x & y directions) than biaxial tension. The area density of all TMDs is smaller than that of graphene, leading to fewer bond connections and hence smaller UTS and E. NbSe$_2$ was found to have the highest elongation of 38% at peak stress under uniaxial tension in x direction, higher than graphene and other TMDs. The higher elongation in uniaxial tension was due to greater bond rotation. The change in bond angle with strain was found to be significantly greater in uniaxial –x direction than biaxial tension. The energy required for bond rotation was significantly lower than the bond stretching, resulting in larger bond rotation and hence greater elongation.
5.1 Introduction

In recent years, the investigation of phosphorene based structures has emerged after the possibility of obtaining two-dimensional monolayer systems from black-phosphorus [30]. The crystal structure of black-phosphorus consists of quasi-planar corrugated layers that interact by van der wall forces, in a way similar to graphite. Phosphorene is a monolayer system of black-phosphorus that has been fabricated using mechanical exfoliation [38]. Phosphorene distinguishes itself from other 2D materials through its unique structural characteristics of puckered structure. It has a puckered structure along the armchair direction but appears as a bilayer configuration along the zigzag direction (Figure 5.1). The structural anisotropy in phosphorene arises from its local bonding configuration. Kou et al. reported that the bond angle in phosphorene along the zigzag direction is 94.3° and adjacent P-P bond length is 2.253 Å while the corresponding dihedral angle along the zigzag direction is 103.3° and connecting bond length is 2.287 Å [2]. The lattice constants along the two perpendicular directions are 3.30 and 4.53 Å, respectively [38]. The unique structural arrangement in phosphorene is the origin of the anisotropic physical [38] and mechanical properties [9], [110].

The mechanical properties of phosphorene monolayer subjected to uniaxial strain were recently studied by Jiang et al. using first-principles calculations [110]. They found that the Young’s modulus (Y) and the related effective two-dimensional Young’s modulus is considerably smaller in the armchair direction (Y = 41.3 GPa, E = 21.9 Nm⁻¹) than in the zigzag direction (106.4 GPa, E = 56.3 Nm⁻¹). Peng et al. found out the similar results with Young’s modulus (Y) and the related effective two-dimensional Young’s modulus as 44 GPa and 166 GPa respectively. The effective 2D Young’s modulus of phosphorene is 56.3 Nm⁻¹, half of the effective Young’s modulus of the single-layer MoS₂ [82], which is 120 Nm⁻¹. The effective 2D Young’s modulus of phosphorene is smaller than the effective Young’s modulus of single-layer hexagonal boron-nitride [115]131, E = 292.1 Nm⁻¹ and that of graphene [116], E = 335.0 Nm⁻¹.
Due to these features, other 2D phosphorene allotropes have been explored. (Guan, Zhu, and Tománek 2014; Zhu and Tomnek 2014). In this work, we have studied the mechanical properties of 9 different phosphorene allotropes. Using first principle DFT calculations, we simulated the stress-strain responses under strain loading in uniaxial x and y directions. We found that some of the allotropes were exceeding the Griffith strength estimate of E/9. We have analysed the various bond properties to find out a suitable explanation for this finding.

### 5.2 Computational Details

The mechanical properties of phosphorene allotropes were studied using first principles methods based on density functional theory (DFT) with Quantum-Espresso [71] package. The Perdew-Burke-Ernzerhof (PBE) [72] exchange-correlation functional along with the projector-augmented wave (PAW) potential [126] were employed for the self-consistent total energy calculations and geometry optimization. Kinetic energy cutoffs of 60 Ry and 480 Ry were used for the calculation.
of wavefunction and charge density, respectively. The Brillouin zone was sampled using a Monkhorst–Pack grid of $[123]13 \oplus 13 \oplus 3$ k-points. A 20 Å vacuum layer was added to the simulation box to avoid any inter-layer interactions. Each system was initially relaxed with variable cell sizes using conjugate gradient minimization technique until the magnitude of the residual Hellman–Feynman force on each atom was less than 0.001 Ry per Bohr.

Subsequently, the cells were subjected to differing magnitudes of uniaxial strains in the $x$ direction. The strains were applied by dilating the unit cells along the loading direction and applying an equal affine transformation to the atomic positions. The deformed topology was then subjected to an energy minimization routine to obtain its ground state configuration. The true (Cauchy) stress ($\sigma$) for prescribed levels of strain was obtained for each optimized structure from the pressure tensor. The deformation experiment in Griffith’s theory was carried out in a condition where there is tensile or compressive stress in one direction and no stress in the other directions. Therefore, we have performed simulations with free boundary method [139]. With each axial strain applied, the lattice constant in the transverse direction was fully relaxed through the technique of energy minimization to ensure the force in the transverse direction is a minimum.

### 5.3 Stress-strain response

The true stress versus Lagrangian strain for the phosphorene allotropes studied for strain loading in uniaxial $x$ (Figure 5.2 (a), (b)) and $y$ direction (Figure 5.2 (c), (d)) are shown in Figure 5.2. The simulation results show that for strains smaller than 0.1, all the allotropes follow a linear stress strain response. For strains larger than 0.1, a nonlinear relationship exist between stress and strain for all the allotropes. The mechanical instability takes place in all the structures upon reaching UTS. The results show that alpha can sustain large strains, 0.31, 0.24 in uniaxial $x$ and $y$ directions respectively, highest among all the allotropes studied here. This is mainly due to the bond rotation happening during the tensile strain in uniaxial $x$ direction. The tensile strain in uniaxial $x$ direction leads to the bond rotation, flattening the pucker like structure, rather than extensively extending the P-P bond lengths and opening the bond angles.
Table 5.2 shows the ultimate tensile strength (UTS in N/m) and corresponding strain, $\eta_u$, Young’s modulus $E$ (N/m), $E/\sigma_{\text{ideal}}$ for 9 phosphorene allotropes studied here. The initial slope of the stress-strain curve is considered as Young’s modulus $E$ here. $\sigma_{\text{ideal}}$ is the maximum strength a material can undertake, i.e. UTS in our case. The ideal strength, $\sigma_{\text{ideal}}$, is often approximated by its relation with Young’s modulus since it is much easier to measure Young’s modulus in the experiment than to measure ideal strength. Based on Griffith’s groundbreaking work [140], Orowan [141] and other scientists found a universal approximation between the ideal strength and Young’s modulus, $\sigma_{\text{ideal}} \sim E/9$, which is supposed to be valid for any material. Graphene has been found to reach a strength of $E/11$ [1] to $E/9$ [116] through nano-indentation. Experimental measurement of the ideal strength of monolayer MoS$_2$ range between $E/10$ and $E/15$ [64].

Table 5.1: $E/\sigma_{\text{ideal}}$ for nine phosphorene allotropes. $\sigma_{\text{ideal}}$ is the maximum strength a material can undertake, i.e. UTS in this case.

<table>
<thead>
<tr>
<th>$E/\sigma_{\text{ideal}}$</th>
<th>alpha</th>
<th>epsilonP</th>
<th>ptetra</th>
<th>tetra</th>
<th>Alpha6</th>
<th>beta</th>
<th>Beta6</th>
<th>psi</th>
<th>zeta</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-dir</td>
<td>5.04</td>
<td>9.70</td>
<td>6.27</td>
<td>6.60</td>
<td>10.40</td>
<td>9.81</td>
<td>9.20</td>
<td>9.06</td>
<td>11.31</td>
</tr>
<tr>
<td>y-dir</td>
<td>6.34</td>
<td>9.76</td>
<td>6.26</td>
<td>6.61</td>
<td>12.61</td>
<td>10.02</td>
<td>12.99</td>
<td>7.39</td>
<td>8.54</td>
</tr>
</tbody>
</table>

Recently, Shi and Singh found that the ideal strength of two-dimensional stanene can reach upto $E/7$ [142], even higher than the traditional approximation $E/9$. Table 5.1 shows the $E/\sigma_{\text{ideal}}$ values for 9 phosphorene allotropes in uniaxial x and y direction. From Table 5.1, Alpha, ptetra and tetra were found to exceed the Griffith strength limit of $E/9$. This unusual behavior is due to the bond rotation. Bond rotation decreases the Young’s modulus significantly than $\sigma_{\text{ideal}}$, therefore decreasing the ratio of $E/\sigma_{\text{ideal}}$. The next section of this chapter will discuss the bond rotation in detail.
Figure 5.2: Stress-strain curves for all allotropes. (a) (b) represent uniaxial tension in x direction; (c), (d) represent uniaxial tension in y direction. UTS values and corresponding failure strain are shown with arrows.
Table 5.2: UTS (N/m), corresponding $\eta_u$, Young’s modulus $E$ (N/m) for 9 phosphorene allotropes

<table>
<thead>
<tr>
<th></th>
<th>x-axial UTS (N/m)</th>
<th>y-axial UTS (N/m)</th>
<th>x-axial $\eta_u$</th>
<th>y-axial $\eta_u$</th>
<th>No. of atoms per unit cell</th>
<th>Area of unit cell ($\text{Å}^2$)</th>
<th>Area density ($\text{Å}^{-2}$)</th>
<th>$E_x$ (N/m)</th>
<th>$E_y$ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha</td>
<td>5.17</td>
<td>11.67</td>
<td>0.31</td>
<td>0.24</td>
<td>4</td>
<td>15.27</td>
<td>0.26</td>
<td>26.1</td>
<td>74.0</td>
</tr>
<tr>
<td>epsilon P</td>
<td>4.90</td>
<td>4.87</td>
<td>0.22</td>
<td>0.22</td>
<td>8</td>
<td>29.15</td>
<td>0.27</td>
<td>47.5</td>
<td>47.5</td>
</tr>
<tr>
<td>ptetra</td>
<td>4.56</td>
<td>4.56</td>
<td>0.18</td>
<td>0.18</td>
<td>12</td>
<td>43.95</td>
<td>0.27</td>
<td>28.58</td>
<td>28.5</td>
</tr>
<tr>
<td>tetra</td>
<td>6.18</td>
<td>6.15</td>
<td>0.20</td>
<td>0.20</td>
<td>8</td>
<td>41.75</td>
<td>0.19</td>
<td>40.76</td>
<td>40.6</td>
</tr>
<tr>
<td>Alpha6</td>
<td>3.74</td>
<td>5.32</td>
<td>0.12</td>
<td>0.12</td>
<td>6</td>
<td>24.22</td>
<td>0.25</td>
<td>38.91</td>
<td>67.1</td>
</tr>
<tr>
<td>beta</td>
<td>7.88</td>
<td>8.48</td>
<td>0.18</td>
<td>0.14</td>
<td>4</td>
<td>18.82</td>
<td>0.21</td>
<td>77.34</td>
<td>85.0</td>
</tr>
<tr>
<td>Beta6</td>
<td>6.01</td>
<td>6.24</td>
<td>0.15</td>
<td>0.10</td>
<td>12</td>
<td>48.23</td>
<td>0.25</td>
<td>55.27</td>
<td>81.1</td>
</tr>
<tr>
<td>psi</td>
<td>5.98</td>
<td>4.86</td>
<td>0.14</td>
<td>0.21</td>
<td>10</td>
<td>48.2</td>
<td>0.21</td>
<td>54.17</td>
<td>35.9</td>
</tr>
<tr>
<td>zeta</td>
<td>6.76</td>
<td>5.23</td>
<td>0.13</td>
<td>0.19</td>
<td>8</td>
<td>36.3</td>
<td>0.22</td>
<td>76.44</td>
<td>44.7</td>
</tr>
</tbody>
</table>
Figure 5.3: Variation of UTS and corresponding strain for all allotropes under study: (a) uniaxial tension in x direction, (b) uniaxial tension in y direction.

Figure 5.3 shows the relationship between UTS and corresponding strain for the phosphorene allotropes. The calculated strain values corresponding to UTS values for all the allotropes in uniaxial x direction are found to be inferior to phosphorene (Figure 5.3 (a)). Alpha has highest UTS of 11.67 N/m in uniaxial y direction while beta has highest UTS of 7.88 N/m in uniaxial x direction. Under uniaxial tension in x direction, Alpha phosphorene has highest strain corresponding to failure, $\eta_u = 0.31$, due to the greater bond rotation. The next section will give more insights into the bond rotation.
Figure 5.4: Snapshots of a monolayer alpha phosphorene structure. In (a), atoms are labeled using the numbers 1-6. Bond lengths $r_1$ and $r_2$, bond angles $\theta_1$ and $\theta_2$ are denoted. The distance between puckered layers in $z$ direction is labeled as $d$. (b) and (c) represent the geometry of alpha phosphorene under 30% tensile strain applied in uniaxial $x$ and $y$ directions, respectively.

5.4 Analysis of Mechanical Properties in Alpha Phosphorene

The ideal strengths of alpha phosphorene are 5.17 N/m and 11.67 N/m (see Table 5.2), respectively, for uniaxial tensions in $x$ and $y$ directions. The corresponding critical strains are 31% and 24%. To understand this enormous critical strain, we have examined its crystal structure under 30% tensile strain in $x$ and $y$ directions and compared it with the relaxed structure. Figure 5.4 shows the structure of alpha phosphorene in (a) relaxed configuration (b), (c) under 30% tensile strain applied in uniaxial $x$ and $y$ directions, respectively. The parameters, such as bond lengths
(r₁, r₂), bond angles (θ₁, θ₂) and dihedral angles (φ₁₂₃₄, φ₁₂₃₅) are marked in Figure 5.4 (a) and values are presented in Table 5.3. φ₁₂₃₄ and φ₁₂₃₅ are dihedral angles of the atoms 1-2-3-4, and 1-2-3-5, and d is the distance between the puckered layers of phosphorene in z direction. For the relaxed phosphorene, the bond lengths are r₁ = 2.21 Å and r₂ = 2.25 Å. The puckered layer distance d = 2.15 Å. The bond angles θ₁ and θ₂ are 96° and 103°, respectively. The dihedral angles are φ₁₂₃₄ = 73.8° and φ₁₂₃₅ = 36.5°.

Under the tensile strain loaded in y direction, bond length r₂ and angle θ₂ which do not lie in xy plane demonstrate smaller changes with 0.4% and 1.9% reduction, respectively. The change percentages of dihedral angles are also less than 5%. A different situation occurs in the uniaxial x direction. The puckered layer distance d and dihedral angles Φ₁₂₃₄ and Φ₁₂₃₅ experience significant reduction. The distance d is reduced from 2.15 Å to 2.01 Å, which is 6.5% reduction. This implies that the tensile strain in uniaxial x direction significantly flattens the pucker of phosphorene through bond rotation, shown in Figure 5.4 (b), rather than extensively extending the P-P bond lengths and opening the bond angles. The flattening of pucker leads to higher critical strain corresponding to failure and lower stiffness during the tensile strain in uniaxial x direction.

Table 5.3: The bond lengths, puckered-layer distance, bond angles, and dihedral angles of the relaxed and strained monolayer phosphorene. The bond lengths r₁ and r₂, bond angles θ₁ and θ₂, puckered layer distance d are described in Figure 5.4 (a). Φ₁₂₃₄ and Φ₁₂₃₅ are the dihedral angles of the atoms 1-2-3-4 and 1-2-3-5 respectively. The values in the parentheses are the change percentages compared to that of relaxed phosphorene.

<table>
<thead>
<tr>
<th>System</th>
<th>r₁ (Å)</th>
<th>r₂ (Å)</th>
<th>d (Å)</th>
<th>θ₁ (°)</th>
<th>θ₂ (°)</th>
<th>Φ₁₂₃₄ (°)</th>
<th>Φ₁₂₃₅ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxed</td>
<td>2.21</td>
<td>2.25</td>
<td>2.15</td>
<td>96</td>
<td>103</td>
<td>73.8</td>
<td>36.5</td>
</tr>
<tr>
<td>εₓ = 30%</td>
<td>2.19 (-0.9%)</td>
<td>2.39 (6.2%)</td>
<td>2.01 (-6.5%)</td>
<td>94 (-2.0%)</td>
<td>114 (10.6%)</td>
<td>71.66 (-2.8%)</td>
<td>29 (-20.5%)</td>
</tr>
<tr>
<td>εᵧ = 30%</td>
<td>2.23 (0.9%)</td>
<td>2.24 (-0.4%)</td>
<td>2.17 (0.9%)</td>
<td>97 (1.0%)</td>
<td>101 (-1.9%)</td>
<td>76 (2.9%)</td>
<td>38 (4.1%)</td>
</tr>
</tbody>
</table>

The ideal strength in the uniaxial y direction is more than doubled compared to that in the uniaxial x direction (11.67 N/m versus 5.17 N/m). The Young’s modulus in the y direction is almost three times larger than along the x direction. The lower stiffness in the x direction results from the smaller alternation of the in-plane crystal structure under the same amount of tensile strain. For
example, 30% tensile strain in the x direction is primarily due to bond rotation to stretch the pucker of phosphorene, shown by large changes in $d$, $\theta_2$, $\phi_{1234}$ and $\phi_{1235}$ listed in Table 5.3. The changes in xy plane in-plane structural parameters, such as the bond lengths $r_1$ and angle $\theta_1$ are negligible (0.9% and 2.0% reduction, respectively). These compromised dihedral angles significantly reduces the required strain energy.

5.5 Mechanical Responses in Phosphorene Allotropes

As discussed in Section 5.3, alpha, tetra and ptetra were found to exceed the traditional Griffith strength limit of $E/9$. In Figure 5.5, we have plotted the bond strain and the degree of angle rotation $\Delta \theta$ with strain for alpha, tetra and ptetra, and compared with zeta phosphorene. $E/\sigma_{\text{ideal}}$ for zeta is around 11 and 9 in x and y directions, respectively, which is within the Griffith strength limits. The magnitude of change in bond angles for alpha, tetra and ptetra is greater than zeta, shown in Figure 5.5 (b). This implies that there is more bond rotation happening in these three allotropes as compared to other allotropes, leading to $E/\sigma_{\text{ideal}} < 9$.

The energy cost of bond rotation is much smaller than that of bond stretch [136]. It is much easier to rotate a bond than to stretch a bond. Bond rotation changes the bond’s orientation to accommodate the strain which cannot be achieved only by bond stretch, e.g. the compression due to Poisson’s ratio effect. Bond rotation can also help to reduce the total amount of strain undertaken by bond stretch since rotation can introduce increment in tension direction. Bond rotation also enables the relaxation of bond stretching [136]. The smaller bond strain in to alpha, tetra and ptetra, shown in Figure 5.5 (a) as compared to zeta leads to higher bond rotation. The higher bond rotation in these allotropes decreases the Young’s modulus leading to $E/\sigma_{\text{ideal}} < 9$.

In the relaxed structure of alpha, the bond lengths a and b are 2.21 Å and 2.25 Å respectively. Similarly, in the relaxed structure of tetra, the bond lengths c and d are 2.27 Å and 2.25 Å respectively. In alpha and tetra, the bond strain of bond a and c is larger than bond b and d respectively. This is because electrostatic forces tend to be stronger in bonds with smaller bond lengths, making them stronger and harder to stretch leading to higher bond strain than bonds with larger bond lengths.
Figure 5.5: (a) The evolution of bond strain with increase in strain for four phosphorene allotropes. (b) The degree of angle rotation $\Delta \theta$ for the four structures during deformation. All the angles and bonds are marked in subfigure (c)
5.6 Summary

In this work, we have studied the mechanical properties of nine phosphorene allotropes through first principles DFT calculations. For strains smaller than 0.1, all the allotropes followed a linear stress strain response. For strains larger than 0.1, a nonlinear relationship existed between stress and strain for all the allotropes. The mechanical instability took place in all the structures upon reaching UTS. Alpha phosphorene demonstrated highest mechanical flexibility amongst all the allotropes studied here. Alpha phosphorene can withstand stress upto 5.17 N/m and 11.67 N/m in uniaxial x and y directions, respectively. It can hold critical strain upto 31% in uniaxial x direction. This higher strain limit is due to its unique puckered structure. In the uniaxial x direction, tensile strains effectively flattens the pucker of phosphorene through bond rotation, rather than extensively extending the P-P bond lengths. Three allotropes, alpha, tetra and ptetra was found to exceed the traditional Griffith’s strength limit of $E/\sigma_{\text{ideal}} \sim 9$. The degree of angle rotation $\Delta \theta$, is higher in these allotropes resulting in higher bond rotation. The greater bond rotation reduces the bond strain, decreasing the Young’s modulus, therefor decreasing the ratio $E/\sigma_{\text{ideal}}$. 
Chapter 6

Conclusion and Future work

6.1 Summary and Overall work

This work aimed to use first principles based Density Functional Theory (DFT) to study the mechanical properties of Transition metal dichalcogenides (TMDs) and various phosphorene allotropes to explore the possible relation between structure and mechanical properties.

The mechanical properties of four TMDs, Rhenium disulfide (ReS$_2$), Rhenium diselenide (ReSe$_2$), Niobium disulfide (NbS$_2$), Niobium diselenide (NbSe$_2$) were studied in Chapter 4. The non linear elastic constants and pressure-dependent second-order elastic constants were also calculated for four TMDs. Young’s modulus (E) and Poisson’s ratio (ν) were calculated using the second nonlinear elastic constants. The variation of bond length and bond angle under uniaxial tension was studied to understand the effect of strain on bond geometry. The variation of bond strain and degree of angle rotation under uniaxial and biaxial strain was analyzed to understand the superior mechanical flexibility in NbSe$_2$. Finally, the energy required to stretch a bond and rotate a bond was studied in uniaxial direction to understand the higher ductility in NbSe$_2$.

The mechanical properties of nine phosphorene allotropes were studied in Chapter 5. The stress-strain curves for nine phosphorene allotropes were studied under uniaxial tension in free boundary conditions. The structure of monolayer alpha phosphorene was studied in detail to understand the higher mechanical flexibility. The bond lengths, bond angles, puckered-layer distance and dihedral angles were calculated for relaxed and strained monolayer alpha phosphorene. The evolution of bond strain and the degree of angle rotation $\Delta \theta$ under uniaxial tension were studied in four phosphorene allotropes, alpha, tetra, ptetra and zeta.
The main conclusions of this work are following:

- A linear relationship existed between stress and strain in all the TMDs and phosphorene allotropes studied in this thesis for strains smaller than 10%. A non-linear behavior was found to become dominant for larger strains.

- All the TMDs were found to withstand higher elongation at peak stress ($\eta_u$) under uniaxial tension (x & y directions) than biaxial tension.

- All the four TMDs were found to have inferior values of UTS and Young's modulus when compared with graphene. This observation is in agreement with the fact that the area density of all TMDs is smaller than that of graphene, leading to fewer bond connections and hence smaller UTS and E.

- NbSe$_2$ demonstrated superior mechanical flexibility of 38% under uniaxial tension in x direction. This strain limit of NbSe$_2$ is possible due to bond rotation. The energy cost of bond rotation was found to be much smaller than that of bond stretch, resulting in larger bond rotation, and hence higher ductility.

- Amongst all phosphorene allotropes studied in this thesis, alpha phosphorene demonstrated highest mechanical flexibility. It can withstand a critical strain of upto 31% under uniaxial tension in x direction. This higher strain limit is due to its unique puckered structure.

- Three allotropes, alpha, tetra and ptetra were found to exceed the traditional Griffith’s strength limit of $E/\sigma_{\text{ideal}} \sim 9$.

- The degree of angle rotation $\Delta \theta$, is higher in these three allotropes resulting in higher bond rotation. The greater bond rotation reduces the bond strain, decreasing the Young’s modulus, therefor decreasing the ratio $E/\sigma_{\text{ideal}}$.
6.2 Future work

The research presented in this thesis has been performed to look at one specific part of larger research process. There are additional details that must be obtained to further understand mechanical properties. The following avenues of investigation could be further explored in the future:

- **Mechanical properties of TMDs under defects and after introduction of new elements**
  - Study the effect of defects on mechanical properties of TMDs
  - Study the effect of foreign element on mechanical properties of TMDs

- **Exploring the possibility of structure-mechanical property relationship among phosphorene allotropes**
  - A comprehensive study of phosphorene allotropes could be done to find out a relation between structural and mechanical properties of phosphorene allotropes.
Bibliography


thermoelectric properties of few layers to bulk MoS$_2$,” Nanotechnology, vol. 25, no. 46,

[89] H. Rostami, R. Roldán, E. Cappelluti, R. Asgari, and F. Guinea, “Theory of strain in
Nov. 2015.

[90] A. Sengupta, A. Chanana, and S. Mahapatra, “Phonon scattering limited performance of

electronic properties of two-dimensional hybrid bilayers of transition-metal

[92] H. Kumar, D. Er, L. Dong, J. Li, and V. B. Shenoy, “Elastic Deformations in 2D van der waals Heterostructures and their Impact on Optoelectronic Properties: Predictions from a

electrical conductance in ReS2 monolayer,” Appl. Phys. Lett., vol. 108, no. 19, pp. 1–6,
2016.

[94] J. Feng, X. Qian, C.-W. Huang, and J. Li, “Strain-engineered artificial atom as a broad-

vol. 5, p. 3631, Apr. 2014.

“Identification of Active Edge Sites for Electrochemical H$\textsubscript{2}$ Evolution from MoS$\textsubscript{2}$ Nanocatalysts,” Science (80-. ), vol. 317, no. 5834, p. 100 LP-102, Jul. 2007.


monolayer, few-layer, and bulk ReSe2: An anisotropic layered semiconductor,” ACS Nano, 2014.


[140] “Griffith1921fracture.pdf.”
