# Ab-initio Investigation of Mechanical Properties of MX2(M=Zr, Hf; X=S, Se, Te) Transition Metal Dichalcogenides Nano Tubes (TMDNTs)

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**Abstract** –Miniaturization of bulk crystals in any direction down to nanometer dimensions leads to the emergence of quantum confinement phenomenon, which is technologically favorable. Transition Metal Dichalcogenides (TMDs) are important mechanical materials that have a layered structure. In addition, ach layer consists of three atomic layers. TMD Nano Tubes (TMDNTs) can be created by rolling such a layer. This study investigates structural, mechanical, and bonding properties of TMDNTs. In particular, two important quantities, Young's modulus and Poisson's ratio, are calculated for 6 zigzag $MX_2$ (M=Zr, Hf; X=S, Se, Te) nanotubes and the results are compared with those of other known nanotubes. The computed value of Young's modulus is greater than that of blue Phosphorus and, in some cases, higher than those of $WS_2$ nanotubes (which are experimentally synthesized). Given the increase in the bond length between M and X atoms, the ratio of Young's modulus to Poisson's increases as the atomic number X is reduced. However, there is no significant difference in the aforementioned quantity for $ZrX_2$ and $HfX_2$ nanotubes due to the close bond lengths of Zr-X and Hf-X. The band gap confirms this finding. A Mulliken charge analysis was conducted to investigate the amount of charge transfer between M and X atoms to observe the strength of bond lengths.

**Keywords**: Transition metal dichalcogenides, Young's modulus; Poison's ratio; Density functional theory; Mechanical properties.

## 1. Introduction

Nanotubes have been the focus of many research studies due to their enhanced electronic, thermoelectric, and mechanical properties [1],[2]. Theoretically, these nanotubes can be synthesized in terms of their two-dimensional structures and their stability is predicted thanks to first-principles Density Functional Theory (DFT) calculations [3] and molecular dynamics simulations [4]–[8]. Following the experimental realization of carbon nanotubes in the year 1991 [9], many more distinct nanotubes have continued to be synthesized because they can be constructed in accordance with their two-dimensional counterparts. First synthesis of inorganic fullerene-like nanoparticles and nanotubes (IF) was reported back in 1992 [9]. Thousands of nanotubes have been simulated using ab-initio methods and their properties have been predicted [10]. Mechanical properties of crystalline solids may completely change in the course of any stress applied due to the presence of surfaces, defects, boundaries, and dislocations that determine fracture and ductility of material. However, nanotubes have a simple and precise atomic morphology and can provide us with rich information about quantum effects on nano-sized scales [6],[7]. The strength of materials is only partially determined by their intrinsic mechanical properties, i.e., the strength of their chemical bonds. TMDs are being actively researched in terms of their applicability in the material industry. The largest number of materials synthesized belongs to this family of materials up until now [1],[2],[10]. Tuning electronic properties through the application of mechanical strains and loads is an interesting feature of these materials. In this work, an attempt is made to study and predict mechanical properties of 6 zigzag $MX_2$ (M=Zr,Hf; X=S,Se,Te) nanotubes and, in particular, calculated Young's modulus and Poisson's ratio at their equilibrium diameter. It was found here that Young's modulus followed a decreasing trend as X atomic number increased in $MX_2$ tubes. In the earlier research work, the current author has extensively investigated electronic, bonding, and thermoelectric properties of TMDNTs. The rest of this paper is constructed as in the following manner. In the section on computational details, the ab-initio code, pseudo potentials, basis functions, and geometry structure

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of the nanotubes used in calculations are discussed. To establish a viable methodology fit to the purpose of this study, a theory on which our calculations are based is proposed in the methodology section. The results and discussion section present and analyzes computational results. Finally, important findings of our calculations are summarized in conclusion.

## 2. Materials and methods

### 2.1 Computational details

To simulate the $MX_2$ (M=Zr,Hf; X=S,Se,Te) TMD nanotubes, OpenMx software was used [11]. The Generalized Gradient Approximation (GGA) exchange-correlation functional was the preferred choice given its better accuracy over LDA. The Perdew-Burke-Ehrzernhof version of this functional was applied [12]. PAOs (Pseudo Atomic Orbitals) were used as basis functions for solving the Kohn-Sham equations[13]. These PAOs are denoted by Hf9.0-s3p3d2f1, Zr7.0-s3p2d2f1, S7.0-s3p2d2f1, Se7.0-s3p2d2f1, and Te7.0-s3p3d2f1. The numbers represent the atomic cut-off radii in Bohr. A mesh cutoff of 300 Ry was chosen to discretize real space and calculate wave functions. Monkhorst-Pack mesh grids of (15×1×1) k-points were employed for sampling the Brillouin zone so as to optimize the geometry and calculate the band energies [14]. Force error threshold for geometry optimization of the nanotubes was kept below 0.01 eV/A to get reasonable results ($10^{-6}$Hartree and $10^{-4}$Hartree/Bohr). VESTA program was used to visualize unit cells.

The proposed armchair nanotubes are made of transition-metal dichalcogenides family with a chemical formula of $MX_2$ (M=Hf, Zr; X=S, Se, Te). Similar to CNTs, notations (*m,n*) can be used to characterize single-wall TMDNTs. Given that all the proposed materials share the same space group, a rectangular cell consisting of six atoms was chosen to make the tube. Thus, a small unit cell was selected to speed up the DFT calculation task. A similar approach mentioned in [15] was adopted to build TMD nanotubes. These nanotubes are generated by first repeating the rectangular unit cell five times along the armchair direction and then, rolling it up to make a cylinder. The diameter (d) of the tube can be simply calculated as $n\times|\boldsymbol{r}_1| = \pi d$. The top and side views of TMDNTs are given in Figure 1(a,b).

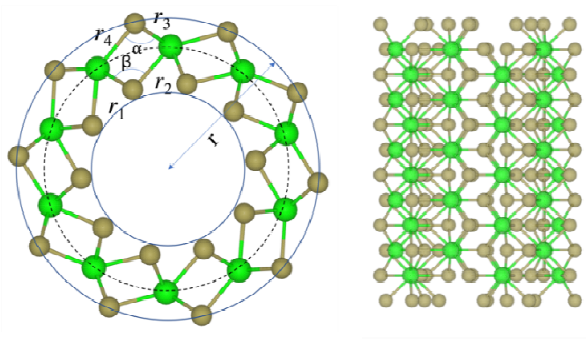



**Fig. 1.** (a) top and (b) side view of $MX_2$ (M=Hf, Zr; X=S, Se, Te) TMDNTs.

### 2.2 Method

From linear elasticity theory [16], the usual definition of Young's Modulus involves the second derivative of energy with respect to applied axial strain $\epsilon$ at $\epsilon = 0$ [5],[6],[10],[17]

$$Y = \frac{1}{V_0}\frac{\partial^2 E}{\partial \epsilon^2}, \epsilon = 0 \quad (1)$$

where $V_0$ is equilibrium volume and E is the total energy. The second derivative of energy measures how rapidly energy grows as the system is distorted out of its equilibrium configuration. However, volume is a vague parameter for pseudo 1d systems as in the case of TMDNTs. Some may adopt a rather different definition for Young's Modulus; for instance, Yakobson [6] used 'surface' instead of 'volume' in the definition for nanotubes. Thus, we define volume as $V_0 = 2\pi R L_0 \Delta$; R as the tube radius; $L_0$ as the equilibrium tube length at zero axial strain. Δ is the shell thickness and is chosen as Van der Waals distance in accordance to common conventions in the literature [18],[19]; $\epsilon = \frac{(L-L_0)}{L_0}$ is the axial strain. Atomic coordinates under axial strain are optimized by fixing tube length and allowing the cross-section coordinates to be fully relaxed. Another interesting mechanical quantity is Poisson's ratio $\vartheta$, which is defined here as the nanotubes under axial strain:

$$\vartheta = \frac{-1}{\epsilon}\left(\frac{R(\epsilon)-R(0)}{R(0)}\right) \quad (2)$$

where $R(\epsilon)$ is the radius of strained tube and $R(0)$ is the

radius of unstrained tube($\epsilon = 0$). It can also be obtained by dividing the transverse strain by axial strain as defined below [6]:

$$\epsilon_{radial} = -\vartheta\epsilon_{axial} \quad (3)$$

In the following, the Mulliken population analysis [20]method is used to determine the amount of charge transferred between the atoms to find a clearer mindset about the bonding between the atoms.

## 3. Results and discussion

The results in the range of -0.02 < ε < 0.02 and variation of axial strain with respect to the strain energy for the structures of all nanotubes are calculated. Young's modulus is obtained for different structures and the values are given in Table 1.

**Table 1**. Interlayer van der Waals distance and Young's modulus of $MX_2$ nanotubes.

| Material | Interlayer van der Waals distance | Young's modulus (GPa) |
|---|---|---|
| $ZrS_2$ | 3.42 | 176.0 |
| $ZrSe_2$ | 3.48 | 153.8 |
| $ZrTe_2$ | 3.39 | 149.7 |
| $HfS_2$ | 3.32 | 212.7 |
| $HfSe_2$ | 3.62 | 157.7 |
| $HfTe_2$ | 3.44 | 126.9 |

Based on the comparison of Young's Modulus values with carbon nanotubes [6]–[8],[21] and blue phosphorus [18], it can be seen that these values are on average 7.7 times less than CNTs, but higher than blue phosphorus in value. Young's modulus value for a zigzag PNT (phosphorus nanotube) (R = 5 A; Van der Waals distance Delta=5.6A) is about 117 Gpa[18], and for a CNT (Delta=3.4A) is 1260 Gpa [6]. Also, the experimental/theoretical value of $WS_2$ nanotube is respectively 171/150 GPa, showing good agreement with our calculated values [9],[22]. The computed values of the modulus for TMD nanotubes indicate a decreasing trend for $ZrX_2$ and $HfX_2$ structures. That is, as the atomic number X decreases, so does the value of the Young's modulus. This decrease in value can be attributed to the increase in the distance between the Zr-X and Hf-X bonds. Also, the values computed for $MX_2$ nanotubes suggest that $HfS_2$ has the highest value of Young's modulus among others. This can be very explained by that fact that bond lengths of $HfS_2$ are stronger and shorter.

Based on this referenced literature piece [23], Pugh's ratio of bulk $MX_2$ exhibits brittle behavior which we expect to be the case in nanotubes. Another important elastic parameter being somehow similar in concept to Pugh's ratio is Poisson's ratio. It states the brittleness and ductility similarly. A dimensionless Poisson's ratio of 0.5 indicates that no changes in volume occur during axial load or elastic deformation, which is a definition of ductility. Any values less/greater than the critical value of 0.26 are brittle and ductile, respectively. The computed values in [23],[24] suggest that $MX_2$ bulk materials are brittle and less than 0.26. As shown in Table 2, all the calculated values are higher than 0.26 and behave in a more ductile manner. Moreover, it is inferred that bondings are rather ionic than covalent. This is the small diameter that results in such quantum confinement effects. The larger the radius, the smaller the effect. In $ZrX_2$ and $HfX_2$ nanotubes, as the radius of the X atoms increases, Poisson's ratio decreases. However, because Zr-X and Hf-X bonds are close to each other, Poisson's ratios are very close. Poisson's ratio of armchair (n,n) carbon nanotubes is about 0.14 (0.12-0.16) and slightly higher for other chiralities close to 0.19 [6], suggesting stronger covalent bonding between carbon atoms. The calculated data indicate that TMD nanotubes are more ductile to axial load. Poisson's ratio of TMDNTs is 0.05-0.2 greater than BNNTs and CNTs values, which makes them more plastic [6].

**Table 2.** Interlayer van der waals distance and Young's modulus of $MX_2$ nanotubes.

| Material | Poisson's ratio |
|---|---|
| $ZrS_2$ | 0.327 |
| $ZrSe_2$ | 0.323 |
| $ZrTe_2$ | 0.285 |
| $HfS_2$ | 0.324 |
| $HfSe_2$ | 0.312 |
| $HfTe_2$ | 0.306 |

Based on DOS plots (Figure 2), all nanotubes, even $ZrTe_2$ and $HfTe_2$, are non-metallic with a tiny band gap. Other nanotubes have a decreasing band gap from larger X to smaller one, implying that the smaller the bond lengths, the wider the band gap.

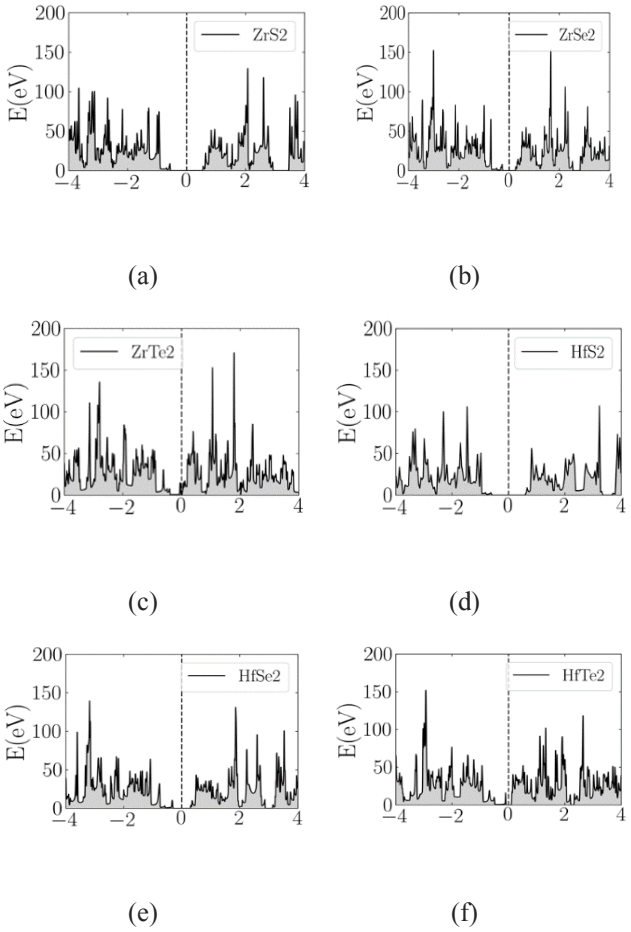
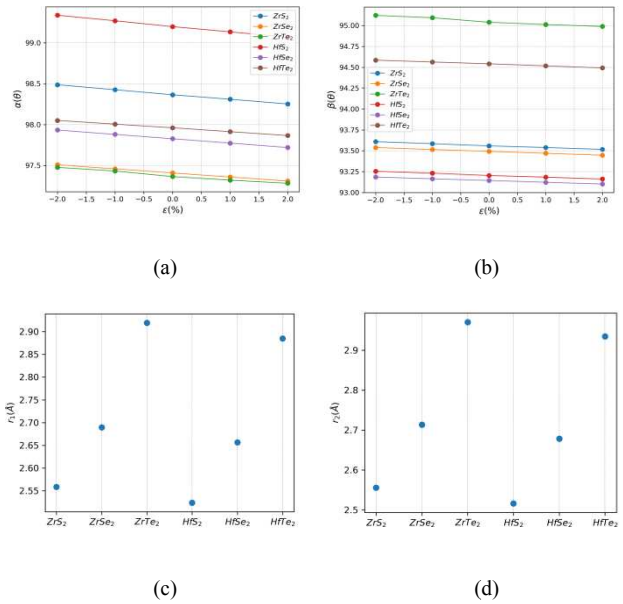



**Fig 2.** Density of electronic states of (a) $ZrS_2$ (b) $ZrSe_2$ (c) $ZrTe_2$ (d) $HfS_2$ (e) $HfSe_2$ (f) $HfTe_2$ nanotubes.



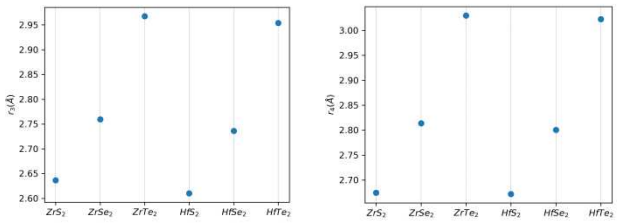




**Fig 3.**bond angles (a) $\alpha(\theta)$(b) $\beta(\theta)$ and bond lengths (c)$r_1(Å)$ (d)$r_2(Å)$ (e) $r_3(Å)$ (f)$r_4(Å)$ shown in figure 1(a) of $MX_2$(M=Zr,Hf; X=S,Se,Te)

As seen earlier, bond lengths of $HfX_2$ tubes are slightly smaller than those of $ZrX_2$ for common Xs. Also, as the atomic number of X elements increases, the length of the bonds increases. Moreover, bond lengths of $MS_2$ and $MSe_2$ are closer in value than that of $MTe_2$. Generally, the shorter bond length results in stronger bonds.

Based on the conducted Mulliken population analysis, each Zr atom gives 0.40e, 0.37e, and 0.40e on average to S, Se, and Te atoms. Similarly, Hf atom gives 0.43e, 0.34e, and 0.36e to S, Se, and Te atoms. Based on Figure 3 and Table 3, for $ZrX_2$(X=S,Se) and $HfX_2$(X=S,Se) structures, upon increasing the atomic number of X, the bond length increases while the charge transfer from Zr and Hf atoms to X atoms weakens. Thus, the strength of their atomic bond is reduced. In the cases of $ZrTe_2$ and $HfTe_2$ tubes, the bond length between atoms Zr(Hf) and Te increases to an extent that the charge transfer from Zr and Hf atoms to Te atoms (with 16 electron valences, unlike S and Se, which have 6 valence electrons) cannot hold the bonds tight.

Among $MX_2$ nanotubes, bond lengths of $MS_2$ tubes are quite close. However, charge transfer in HfS2 is slightly greater, resulting in stronger bonds.

**Table 3.** decomposed Mulliken populations

| Material | atoms | Mulliken population |
|---|---|---|
| $ZrS_2$ | Zr | -0.80 |
| | S | 0.40 |
| $ZrSe_2$ | Zr | -0.74 |
| | Se | 0.37 |
| $ZrTe_2$ | Zr | -0.80 |
| | Te | 0.40 |
| $HfS_2$ | Hf | -0.86 |
| | S | 0.43 |
| $HfSe_2$ | Hf | -0.68 |
| | Se | 0.34 |
| $HfTe_2$ | Hf | -0.72 |
| | Te | 0.36 |

## 4. Conclusion

In this paper, structural, electronic, elastic, and bonding properties of $MX_2$ nanotubes were investigated and it was demonstrated that these nanotubes were mechanically robust tubes with high Young's modulus and Poisson's ratio. This study particularly focused on calculating Young's modulus and Poisson's ratio. The values of Young's modulus for TMD nanotubes indicated a decreasing trend for $ZrX_2$ and $HfX_2$ structures. That is, as the atomic number X increased, the value of Young's modulus decreased. This decrease in value could be attributed to the increase in the distance between theZr-X and Hf-X bonds. $HfS_2$ had the highest Young's modulus value among others due to shorter bond lengths. Another important quantity was Poisson's ratio which decreased following an increase in atomic number X in ZrX2 and HfX2. Also, based on our electronic calculations, the band gaps followed a similar decreasing trend, as shown in DOS plots. The calculated data indicated that TMD nanotubes were more ductile to axial load. Poisson's ratio of TMDNTs was 0.05-0.2 greater than BNNTs and CNTs values. The values of Poisson's ratio ranged between 0.28 and 0.33. The bonding in materials with a value of 0.33 was purely ionic and 0.1 was covalent. Thus, TMDNTs possessed mostly ionic bonds and, in some cases, a mixture of ionic and covalent bonds. This puts them in ductile and elastic materials. Another observation shows that bulk ZrTe2 and HfTe2 incorporates a zero band gap, but their nanotubes exhibit a very small finite size gap. Also, the Mulliken population analysis illustrated that the charge transfer from Hf to S atoms was slightly higher than other tubes which yielded stronger bonds, being consistent with the results of Young's modulus and Poisson's ratio.

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