Effect of strain on electronic and thermoelectric properties of few layers to bulk MoS$_2$

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Abstract

The sensitive dependence of the electronic and thermoelectric properties of MoS$_2$ on applied strain opens up a variety of applications in the emerging area of straintronics. Using first-principles-based density functional theory calculations, we show that the band gap of a few layers of MoS$_2$ can be tuned by applying normal compressive (NC) strain, biaxial compressive (BC) strain, and biaxial tensile (BT) strain. A reversible semiconductor-to-metal transition (S-M transition) is observed under all three types of strain. In the case of NC strain, the threshold strain at which the S-M transition occurs increases when the number of layers increase and becomes maximum for the bulk. On the other hand, the threshold strain for the S-M transition in both BC and BT strains decreases when the number of layers increase. The difference in the mechanisms for the S-M transition is explained for different types of applied strain. Furthermore, the effect of both strain type and the number of layers on the transport properties are also studied using Botzmann transport theory. We optimize the transport properties as a function of the number of layers and the applied strain. 3L- and 2L-MoS$_2$ emerge as the most efficient thermoelectric materials under NC and BT strain, respectively. The calculated thermopower is large and comparable to some of the best thermoelectric materials. A comparison among the feasibility of these three types of strain is also discussed.

Keywords: electronic structure, thermoelectric, density functional theory

1. Introduction

Semiconducting two-dimensional (2D) materials are very promising for nanoelectronics and nanophotonics applications. Semimetallic graphene, although it was the first 2D material to be synthesized and studied [1], cannot be used in these applications because efforts to open the band gap have not yet been successful. Due to the presence of an intrinsic band gap, molybdenum disulphide (MoS$_2$), which is a layered material, has been explored extensively. The possibility of experimentally obtaining freestanding layer (either single or a few) [1–8] with excellent optical absorption and photoconductivity [2, 9] has attracted recent interest in MoS$_2$. Bulk MoS$_2$ is an indirect band gap semiconductor with a band gap of 1.23 eV [10]. The band gap of MoS$_2$ increases when the number of layers decrease [11], and becomes direct [12] with a value of 1.9 eV [13] for the monolayer. This semiconducting behaviour has been exploited in various applications such as field-effect transistors with high room-temperature current on/off ratios [14] and higher on-current density [15, 16], integrated circuits [17], sensors [18, 19], memory cells [20], and phototransistors [21].

Many electronic and photonics applications require band gap tuning. For MoS$_2$, band gap tuning has been achieved through the application of strain [22, 23] and electric field [24, 25]. The semiconductor-to-metal (S-M) transition was observed in bilayer MoS$_2$ under normal compressive (NC) strain, [22] as well as in mono layer and bilayer MoS$_2$ under biaxial compressive (BC) and biaxial tensile (BT) strains [23, 26–28]. Also, for bulk MoS$_2$, application of hydrostatic
pressure has shown to reduce resistivity [29]. Recently, it has been experimentally shown for the first time that few-layered MoS₂ undergoes a complete S-M transition under applied hydrostatic pressure [30].

Apart from the band gap, strain has also been shown as a potential method for tuning the thermoelectric properties of various layered materials [31–35]. Recent studies have shown that the thermoelectric properties of Bi₂Te₃ [32] and Sb₂Te₃ [31] can further be improved by the application of strain. Pardo et al reported that strain can optimize the thermoelectric properties of hole-doped La₂NiO₄⁺δ [33]. MoS₂ and other members of the dichalcogenides family are regarded as promising candidates for the next generation of thermoelectric devices. They have several advantages, including good environmental compatibility, high thermal and chemical stability [36], and abundance in nature. They possess high power factors, which are comparable to that of commercially available thermoelectric materials such as Bi₂Te₃ [37] and PbTe [34, 38–40]. The theoretical study of Zhang et al showed that the thermoelectric performance of bulk MoS₂ can be enhanced by the application of hydrostatic pressure [34]. Recent studies on thermoelectric properties as a function of the number of layers for MoS₂ predicted the possibility of tuning thermoelectric performance by optimizing the layer thickness [38, 39]. Another important advantage of using few layers is their lower thermal conductivity compared to bulk [41], which is the most important parameter for efficient thermoelectric performance.

The ability to tune both the band gap and the thermoelectric properties by the application of strain shows great potential for using this 2D material as an electromechanical and thermoelectric device. However, to the best of our knowledge, no studies have investigated the strain-induced S-M transition or the change in thermoelectric properties of MoS₂ as a function of applied strain and layer thickness. In this paper, we study the effect of strain and the number of layers on the electronic and thermoelectric properties of MoS₂. Using first-principles density functional calculations and Boltzmann transport theory, a comprehensive study is performed to understand the origin of S-M transition under various types of applied strains and its dependence on number of layers. We report that the S-M transition is independent of the number of layers for all the strain types. Although the trend in change of the band gap remains the same for all the multilayers under the same strain, it is quite distinct for each different type of strain. The critical strain for S-M transition increases (decreases) for normal (biaxial) strain. The S-M transition significantly improves electrical conductivity while keeping a large value of thermopower (250–350 μV/K) for all the multilayers studied here, giving rise to enhanced thermoelectric transport properties. We optimized the thermoelectric properties with respect to number of layers and strain, and found that 3L- and 2L-MoS₂ are the best materials for thermoelectric applications under 0.08 NC and 0.05 BT strain, respectively, for both p- and n-type doping.

2. Method

The calculations were performed using ab-initio density functional theory (DFT) in conjunction with All-electron projector augmented wave potentials [42, 43] and the Perdew-Burke-Ernzerhof [44] generalized gradient approximation to the electronic exchange and correlation, as implemented in the Vienna Ab initio Simulation Package (VASP) [45]. A well-converged Monkhorst-Pack K-point set (15 × 15 × 1) was used for the Brillouin zone sampling, and a conjugate gradient scheme was employed to optimize the geometries until the forces on every atom were ≤ 0.005 eV/Å. Sufficient vacuum was used in perpendicular to few-layered MoS₂ to avoid spurious interaction among the periodic images. Grimme’s DFT-D2 method [46], as implemented in VASP, was used to incorporate the weak van der Waals (vdW) interaction. In Grimme’s method, a semi-empirical dispersion potential (D) was added to the conventional Kohn-Sham DFT energy through a pair-wise force field.

For transport calculations, Boltzmann transport theory [47, 48] was used to enable calculation of the temperature and doping-level-dependent thermopower and other transport parameters from the electronic structure. All the transport properties were calculated within the constant scattering time approximation (CSTA) [47, 48]. The CSTA is based on the assumption that the scattering time does not vary strongly with energy. It also does not consider either temperature or the doping-level dependence of the scattering time. Within the CSTA, the energy dependence of transport function is described through both the density of states and the carrier velocity. In this theory, the motion of an electron is treated semiclassically, and its group velocity in a specific band is given by

\[
\nu_\alpha(i, k) = \frac{1}{\hbar} \frac{\partial c(i, k)}{\partial k_\alpha}.
\]

where \(c(i, k)\) and \(k_\alpha\) are the \(\alpha\)th energy band and \(\alpha\)th component of wavevector \(k\), respectively. From group velocity \(v_\alpha(i, k)\), the thermopower and electrical conductivity can be obtained as

\[
S_{\alpha\beta}(T, \mu) = \frac{1}{eT} \int \nu_\alpha(i, k) \nu_\beta(i, k) (e - \mu) \left[ -\frac{\partial f_T(T, e)}{\partial e} \right] de.
\]

\[
\sigma_{\alpha\beta}(T, \mu) = \frac{1}{V} \int e^2 \nu_\alpha(i, k) \nu_\beta(i, k) \left[ -\frac{\partial f_T(T, e)}{\partial e} \right] de.
\]

where \(e, T, V, \tau, \) and \(f_\mu\) are the electronic charge, temperature, the volume of the unit cell, the relaxation time, and the Fermi-Dirac distribution function, respectively. The Brillouin zone was sampled by a well-converged 50 × 50 × 1 Monkhorst-Pack \(k\)-mesh [49]. Subsequently, the group velocities were obtained by Fourier interpolation [50] of band energies on the converged denser \(k\)-grid. These values are used in equations (2) and (3) to calculate the transport properties as implemented in BoltzTraP code [51]. This approach has been
shown to provide a good estimate of thermopower as a function of temperature and carrier concentration in a variety of thermoelectric materials without any adjustable parameters [52–56].

3. Results and discussion

The optimization of the lattice parameters was completed using the primitive unit cell of bulk MoS2. The calculated values of $a$ (3.21 Å) and $c$ (12.42 Å) are very close to other reported theoretical [57] and experimental [58] results. The multilayered structures were obtained by arranging MoS2 layers one over another to form AB stacking (figure 1(a)) and named as $nL$-MoS2, where $n$ is the number of MoS2 layers. The NC strain was applied perpendicular to the plane of the multilayers and along the $c$ axis for the bulk case (figure 1(a)). The upper and lower layers were constrained to move along the normal direction at each NC strain for the multilayers. For the biaxial cases, equal strain was applied along the $a$ and $b$ axes of the multilayers, as shown in figure 1(b). However, no constraint was used while applying the biaxial strain, allowing the layers to optimize their interlayer distance in each strain. The change in electronic structure and angular momentum resolved density of states (LDOS) under the application of strain was also analyzed for each multilayer MoS2.

Unstrained MoS2 with more than one layer and bulk has an indirect band gap with valence band maxima (VBM) and conduction band minima (CBM) at $\Gamma$- and K-points of the Brillouin zone, respectively, as shown in figure 1(c) for $nL$-MoS2 with $n$ = 2, 3, 4, and 5. The band structures of all these multilayers show that the number of bands forming VBM and CBM increases and is equal to the number of layers. These bands are nearly degenerate at the K-point and completely split at the $\Gamma$-point. Furthermore, the spacing between the VBM and VBM−1 at the $\Gamma$-point decreases as the number of layers increases. This nature of the band structure has important implications under the applied strain.

3.1. Normal compressive strain

First, we study the effect of NC strain on the electronic structure and thermoelectric properties of few-layered MoS2. The calculated band gap as a function of NC strain is plotted in figure 2(a) for $nL$-MoS2 with an increasing number of layers. The applied NC strain leads to S-M transition for all the multilayers and bulk MoS2. The band gap reduces smoothly and becomes zero at a threshold strain, $\varepsilon_{th}$, the magnitude of which increases as the number of layers increase and converges towards the bulk limit (i.e., −0.16, as seen in the figure 2(a) inset). The change in the electronic structure under the application of strain was analyzed for each multilayer and is shown for 3L-MoS2 (which is the best case in terms of thermoelectric performance, as shown below) in figure 2(b). With the increase in normal compression, the degenerate bands begin to split (figure 2(b)). The splitting is observed to be more prevalent in the valence band (VB) than it is in the conduction band (CB). Both the VBM and the CBM start to move towards the Fermi level with strain, reducing the band gap smoothly, as shown in figure 2(a). An S-M transition occurs when the VBM crosses the Fermi level at the $\Gamma$-point. Upon removal of NC strain, MoS2 recovers its semiconducting phase completely.

The change in electronic structure influences the transport and thermoelectric properties significantly. Next, we studied the effect of NC strain on the transport properties of MoS2 with an increase in the number of layers. The calculated
\( \sigma/\tau \) increases with increasing NC strain for both \( p \)- and \( n \)-type carriers. Upon application of NC strain, both conduction and valence bands become more dispersive, giving rise to multcarrier transport, which leads to the increase in conductivity. For the same number of layers, the value of \( \sigma/\tau \) was observed to be higher in the case of \( n \)-type carriers under NC strain. This is expected because conventionally, MoS\(_2\) is an \( n \)-type semiconductor. This observation is in good agreement with previous theoretical studies [38, 39]. The dependence of \( \sigma/\tau \) on strain can be explained from the changes in band dispersion, as shown in figure 2(b) for 3L-MoS\(_2\). Upon application of NC strain, the conduction band is highly affected in comparison to the valence band. CBM becomes more dispersive than VBM, increasing the mobility of \( n \)-type charge carriers and resulting in an enhanced value of conductivity in comparison to \( p \)-type carriers. With the increase in strain, 3L- and 2L-MoS\(_2\) show the highest value of \( \sigma/\tau \) (under both \( p \)- and \( n \)-type doping) due to the contribution from the additional conduction channels, which open upon application of strain. Among all the layers studied here, the factor \( \sigma/\tau \) is maximum for 3L-MoS\(_2\) over the entire range of NC strains. Assuming that the relaxation time \( (\tau) \) is independent of the number of layers, one can conclude that 3L-MoS\(_2\) will show the highest electrical conductivity.

Next, we calculated the thermopower of the unstrained and strained MoS\(_2\) for different layer thicknesses. The average thermopower levels \( (S) \) at 900 K as a function of the NC strain with increasing layer thickness for \( p \)- and \( n \)-type doping are shown in figures 2(d) and (e), respectively. The average thermopower is defined as \( 1/3 \) of the trace of the thermopower tensor \( (S_{xx} + S_{yy} + S_{zz})/3 \). For these calculations, the doping level is fixed at \( 5 \times 10^{19} \) cm\(^{-3} \), which is the optimized value for all the layers. The thermoelectric performance peaks at 900 K, and therefore all the results are presented at this temperature.

With an increase in the number of layers, the thermopower rises due to an increase in charge carrier pockets, as seen in figure 2(b). Under applied NC strain, the changes in the thermopower show the same trend for different layer thicknesses, except for 2L- and 3L-MoS\(_2\) at lower strains, where the thermopower first increases and then decreases, with peaks at -0.04 and -0.09 for \( p \)- and \( n \)-type carriers, respectively. The absence of such peaks for four and higher numbers of layers indicates the advent of bulk-like behaviour. With the application of strain, the band gap starts to decrease, which leads to a slight decrease in thermopower. However, under the strain range studied here, the value of thermopower still remains high, lying between 250–380 and 390–440 \( \mu \)V/K for \( p \)- and \( n \)-type doping, respectively. Such high thermopower values are comparable to the best known thermoelectric materials, such as PbTe [40] and Bi\(_2\)Te\(_3\) [37]. These high thermopower values can be explained by analyzing the

Figure 2. (a) The variation of band gap under NC strain plotted for various multilayers. The variation of \( \epsilon_{th} \) with the inverse of layer thickness \( (d) \) is shown in the inset. (b) Band structure of 3L-MoS\(_2\) with increasing NC strain. (c) Calculated \( \sigma/\tau \) ratio for MoS\(_2\) as a function of NC strain for different layer thicknesses. Solid and dotted lines correspond to \( p \)- and \( n \)-type doping, respectively. Thermopower \((S)\) for MoS\(_2\) as a function of strain at different layer thickness for (d) \( p \)-type and (e) \( n \)-type doping. Calculated power factors with respect to relaxation time \( (\sigma_0/\tau) \) in the unit of W/mK\(^2\)s for MoS\(_2\) as a function of strain for different layer thicknesses for (f) \( p \)-type and (g) \( n \)-type doping. In the above transport calculations, the doping level and temperature are fixed at \( 5 \times 10^{19} \) cm\(^{-3} \) and 900 K, respectively.
band structure, as mentioned previously. Upon application of strain, the bands move close to the Fermi level, giving rise to more electron and hole pockets, which lead to high thermoelectric performance.

In order to quantify the effect of strain on thermoelectric performance (\(ZT = S^2\sigma/\kappa_{\text{total}}\), where \(\kappa_{\text{total}}\) is the total thermal conductivity), we calculate power factor (\(S^2\sigma/\tau\)), which is the most dominant term in \(ZT\). The power factor represents the ability of a material to produce useful electrical power at a given temperature gradient. The large power factor is indicative of better thermoelectric performance. As a first approximation for power factor (\(S^2\sigma/\tau\)), the quantity \(S^2\sigma/\tau\) is calculated at 900 K for different layer thicknesses as a function of applied NC strain, and is shown in figures 2(f) and (g) for \(p\)- and \(n\)-type doping, respectively. 3L-MoS\(_2\) gives the highest value of \(S^2\sigma/\tau\) due to its highest conductivity and large thermopower for all the NC strain ranges. For 2L- and 3L-MoS\(_2\), the power factor peaks at \(-0.04\) and \(-0.09\) strain for \(p\)- and \(n\)-type doping, respectively. With the applied NC strain, the power factor slightly increases for \(p\)-type doping. However, for \(n\)-type doping, the power factor increases by nearly two times in comparison to the unstrained case, attaining a maxima near \(-0.09\) strain. Therefore, NC strain has emerged as an effective way to tune both electronic and thermoelectric properties.

3.2. Biaxial compressive strain

We further study the effect of BC strain on the electronic structure and thermoelectric properties of few-layered MoS\(_2\). The calculated band gap as a function of BC strain is plotted in figure 3(a) for an increasing number of layers. For BC strain, the band gap increases first and then decreases all the way to zero, as shown in figure 3(a). The change in band structure is also observed to be very different for BC strain compared to NC strain. The nature of the dispersion changes near the Fermi level with the increase in strain, as shown in figure 3(b) for 2L-MoS\(_2\). The position of VBM and CBM changes, as we move toward higher strain. With the change in the combination of the positions of VBM and CBM, the slope of the band gap versus the strain plot changes, as seen in figure 3(a). Five different slopes were seen in the band gap versus the strain plot (figure 3(a)). Initially, the position of CBM and VBM are at the high-symmetric K- and \(\Gamma\)-points, respectively, until a strain of \(-0.02\) is reached. During this interval of strain, the band gap increases, as shown in figure 3(a) (region of first slope). The position of CBM then changes from the K-point to in between the K-point and the \(\Gamma\)-point, while VBM remains at the \(\Gamma\)-point until a strain of \(-0.04\) is reached (region of second slope). Beyond this strain, the band gap begins to decrease as VBM changes to the K-point, while CBM remains in between the K- and \(\Gamma\)-points (region of third slope). At a strain of \(-0.12\), the VBM changes from the K- to M-point, while the CBM remains unchanged. At this point, the dispersion of the band becomes flat near the VBM (region of fourth slope). The position of VBM shifts slightly from the M-point toward the \(\Gamma\)-point, after a strain of \(-0.13\) (region of fifth slope). Finally, the CBM crosses the Fermi level at a strain of \(\epsilon_{th} = -0.15\) to give S-M transition. The magnitude of \(\epsilon_{th}\) decreases with an increasing number of layers, as shown in figure 3(a) inset. Overall, both CBM and VBM move toward the Fermi level. Unlike NC strain, CBM crosses the Fermi level first. The nature of change in the band structure remains the same for all multilayers under BC strain.

Similarly to the band gap, the transport and thermoelectric properties also show different behaviour under BC strain. The plot of \(\sigma/\tau\) as a function of BC strain, as shown in figure 3(c), shows an opposite trend for both types of charge carriers. \(\sigma/\tau\) first decreases with increasing strain and subsequently increases for both types of carriers. This effect can, once again, be explained on the basis of the band structure. As shown in figure 3(a), the band gap first increases for lower strain values, which leads to an initial decrease in conductivity. With a further increase in strain, the value of \(\sigma/\tau\) increases for all the multilayers. The rate of change of conductivity is higher for \(n\)-type than it is for \(p\)-type, because the conduction band becomes more dispersive (figure 3(b)) under increasing BC strain, giving rise to enhancement in \(\sigma/\tau\). However, the bands close to VBM become less dispersive (heavy), as seen in figure 3(b), which reduces the mobility of holes, and hence, \(\sigma/\tau\). Under BC strain, 2L-MoS\(_2\) shows the highest value of \(\sigma/\tau\) for both \(p\)- and \(n\)-type doping.

Next, we study the effect of BC strain on thermopower, as shown in figures 3(d) and (e) for \(p\)- and \(n\)-type doping, respectively. The thermopower decreases with an increase in strain, and saturates at higher strains for \(n\)-type doping. However, for \(p\)-type doping, there is an initial decrease with a gradual increase in thermopower, which finally saturates. This difference in trend of the thermopower for \(n\)- and \(p\)-type of carriers can also be attributed to the band structure, as shown in figure 3(b). Under strain, the conduction band becomes more dispersive. However, some of the valence bands become heavy (e.g., the band along M-\(\Gamma\)). The presence of these heavy bands increases the thermopower with increasing strain for \(p\)-type doping. A similar trend is also observed for all the multilayers. Furthermore, the power factor increases and attains a maxima around the \(-0.05\) and \(-0.075\) BC strain for \(p\)- and \(n\)-type doping. The highest power factor achieved is for 2L- and 5L-MoS\(_2\) under \(p\)- and \(n\)-type doping. In particular, under \(n\)-type doping, the factor \(S^2\sigma/\tau\) gets enhanced 4.5 times. Interestingly, these layers also possess the highest electrical conductivity, implying that by tuning the electrical conductivity using BC strain, one can enhance the thermoelectric performance considerably.

3.3. Biaxial tensile strain

We investigate the effect of BT strain on the electronic structure and transport properties of MoS\(_2\). For all the multilayers, the band gap reduces smoothly with an increase in BT strain and becomes zero after a threshold strain, \(\epsilon_{th}\), exhibiting S-M transition (figure 4(a)). Similar to the BC strain, the magnitude of \(\epsilon_{th}\) decreases with an increasing number of layers, as shown in the inset of figure 4(a). The nature of the dispersion does not change, as shown in figure 4(b) for 2L-MoS\(_2\). The VBM and CBM remain at the
K- and Γ-points, respectively, throughout the applied strain range. No significant splitting of bands was observed for this type of strain. The CBM and the VBM move toward the Fermi level, as shown in the band structure plots. Similar to the case of NC strain, VBM crosses the Fermi level at Γ point at the S-M transition. However, the nature of the change in the band gap versus strain plot is different in BT strain (figure 4(a)) than it is in the NC and BC strains.

The calculated σ/τ for BT strain is shown in figure 4(c). σ/τ ratio increases with increasing strain for both types of carriers. This is similar to the NC strain. However, the rate of increase in conductivity is more in the case of n-type carriers than in p-type carriers. Under strain, CBM becomes more dispersive than VBM, thereby increasing the mobility of charge carriers and leading to enhanced value of conductivity in comparison to the p-type carriers. More importantly, the factor σ/τ attains a high order of magnitude under strain when compared to NC strain, indicating better tuning of transport properties. We next calculate the thermopower under BT strain, as shown in figures 4(d) and (e) for p- and n-type doping. The thermopower with BT strain shows similar behaviour as that in the case of NC strain. For biaxial strains, as suggested by high conductivity values, the quantity $S^2\sigma/\tau$ becomes maximum for tensile strain. The highest power factor achieved under BT strain is for 2L–MoS$_2$, which is nearly 1.5 and 4 times higher in comparison with the unstrained case for p- and n-type doping, as shown in figures 4(f) and (g), respectively. The figure of merit, ZT, closely follows the overall change in the $S^2\sigma/\tau$, and hence it can also be enhanced by the same factor.

All the results presented here are calculated at the constant relaxation time ($\tau$) approximation, which may not be valid because of the dependence of $\tau$ on strain. Therefore, to get a rough estimation of $\tau$ as a function of strain, we calculated the relaxation time from the experimental data of Nayak et al [30]. $\tau$ was estimated by comparing theoretical $\sigma/\tau$ with the experimentally reported $\sigma$ at 300 K for bulk MoS$_2$. $\tau$ varies from $7.5 \times 10^{-14}$ s at 0% strain to $8.1 \times 10^{-15}$ s at 12.2% strain. This similar range can also be expected for multilayered MoS$_2$. As presented in figure 4(c), the factor $\sigma/\tau$ increases by more than two orders of magnitude under strain, whereas $\tau$ decreases only by one order of magnitude. At the same time, the decrease in band gap will compensate for this reduction in $\tau$. Therefore, the change in $\sigma/\tau$ will more or less be same.

### 3.4. Mechanism of S-M transition

In order to compare the sensitivity in terms of the change in band gap under the application of the NC, BC, and BT strains, the percentage reduction in band gap was calculated for all the
multilayers considered in this work. The plots of band gap reduction as a function of strain are shown in figures 5(a), (b), and (c) for NC, BC, and BT strains, respectively. The curves are almost linear for both the NC and BT strains. The curves are non-linear in the case of BC strain, showing a combination of different slopes corresponding to the different regions, as seen in the figure 3(a). From the plots, one can see that the BT strain leads to the fastest S-M transition when compared to other strains. Increase in the number of layers increases the sensitivity for this kind of strain. Though the threshold strain ($\varepsilon_{th}$) is the lowest for BT strain, the application of NC strain is still more practically feasible than the application of biaxial strains. This is due to the fact that intralayer covalent bonding between Mo and S is much more stronger than interlayer vdW bonding. Although the strain required is small in the case of BT strain, in comparison to NC strain, more energy, and hence pressure, will be required to obtain S-M transition as compared to the later case.

To understand the mechanism for this S-M transition under NC, BC, and BT strains, we analyze the contribution from different molecular orbitals by performing LDOS and band-decomposed charge density calculations. This is shown in figure 6 for 3L-MoS$_2$ under NC strain and in figure 7 for 2L-MoS$_2$ under biaxial strain. For all unstrained MoS$_2$ multilayers, the Mo-$d$ and S-$p$ orbitals have the highest contribution to both the VB and CB, as shown in figures 6(a) and 7(a) for 3L- and 2L-MoS$_2$, respectively. Both VB and CB are mainly composed of Mo-$d_{xz,zy}^2$ and $d_z^2$. However, in the case of VB, there is some additional contribution from the S-$p_z$ orbital. This is clearly seen in the band-decomposed charge density (figure 6(a)), where CBM and VBM mainly originate from around Mo-$d_{xz,zy}^2$ (in-plane lobes) and $d_z^2$ (out-of-plane lobes). The contribution of the S-$p_z$ orbital to the VBM is also indicated by the out-of-plane lobes in the band-decomposed charge density. With the application of NC strain, the LDOS corresponding to VB and CB move towards the Fermi level, resulting in a reduction in band gap. All the orbitals of Mo and S atoms contribute to the shift in CB, while in the case of VB, the movement towards the Fermi level occurs mainly due to the contribution from Mo-$d_z^2$ and S-$p_z$ orbitals. The most dominant interaction happens between the Mo-$d_z^2$ orbital of one layer and the S-$p_z$ orbital of another layer. Similar changes were observed for other layers and bulk MoS$_2$. Based on the LDOS and band-decomposed charge density analysis, one can conclude that the strong interlayer interaction between Mo-$d_z^2$ and S-$p_z$ is the main cause for S-M transition under NC strain.

The change in LDOS is completely different in the case of BC strain. The tail in the LDOS of Mo-$d_z^2$, forming the VBM and CBM, moves away from the Fermi level as the in-plane interaction increases because of reduction in Mo-S bond lengths. Due to this movement of Mo-$d_z^2$ and S-$p_z$ orbitals, initially the band gap increases for lower strain values. With a further increase in strain, the LDOS of Mo-$d_z^2$ crosses the tail of the...
LDOS of Mo-$d_{x^2}$, which now consists of both CBM and VBM. The in-plane orbitals begin to interact strongly, causing the shift in the position of VBM from $\Gamma$ to $K$, while the CBM moves from $K$ to in between $K$ and $\Gamma$. This can also be seen in the band-decomposed charge density plots where the VBM changes to completely planar, while CBM has a slight out-of-plane contribution from the Mo-$d_{x^2}$ orbital (figures 7(b) and (c)). With a further increase in in-plane interaction, the Mo-$d_{x^2}$ and S-$p_z$ orbitals hybridize strongly within the layer, as seen in figure 7(d). This strong intra layer hybridization leads to the closing of the gap. This phenomenon can be seen in the band-decomposed charge density shown in figure 7(d), where the VBM and CBM show strong in-plane characteristics near the S-M transition.

In the case of BT strain, the VBM and the CBM have maximum contributions from Mo-$d_z^2$ orbitals (figure 7(e)). With the increase in BT strain, the Mo-$d_z^2$ and S-$p_z$ orbitals start to hybridize strongly within the same layer. This strong hybridization further leads to S-M transition, as shown in figure 7(f). In the case of both NC and BT strains, the S-M

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**Figure 5.** Percentage change in band gap with strain for (a) NC, (b) BC, and (c) BT strain types.

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**Figure 6.** LDOS of Mo and S and corresponding isosurfaces (value of 0.09 e/Å$^3$) of the band-decomposed charge density (VBM and CBM) for 3L-MoS$_2$ under NC strains of (a) 0.00, (b) −0.06, and (c) −0.12, respectively. The Fermi level is shown by red dotted lines.
transition is dominated by Mo-$d^2_\sigma$ and S-$p_z$, but in the case of NC strain the interaction happens between Mo and S atoms from different layers. However, for the BT strain, this interaction is within the same layer.

Having discussed the mechanism of S-M transition under various strains, at last it is worth mentioning that due to the presence of artificial self-interaction [59] and the absence of derivative discontinuity in the exchange-correlation potential, DFT in the local-density approximation and GGA suffers from an underestimation of the band gap. As shown in our previous work [22], bilayer MoS$_2$ and other semiconducting transition metal dichalcogenides (TMDs) also suffer from the band gap problem. Although some of the improved methods within DFT, such as hybrid Heyd-Scuseria-Ernzerhof (HSE) functional [60] and GW approximations [61], tend to produce accurate band gap values, these methods are computationally very expensive and beyond the scope of our study. Also, as shown in our previous work for bilayer MoS$_2$ [22], the nature of both the band dispersion and the S-M transition remain independent of the method used. Since the band gap obtained from HSE/GW calculations will be greater than those with the GGA (i.e., for bilayer MoS$_2$, the PBE band gap was 20% underestimated [22], which leads to $\sim20\%$ increase in threshold strain) an increase in the value of threshold strain.

Figure 7. LDOS of Mo and S and corresponding isosurface (value of 0.09 e/Å$^3$) of band-decomposed charge density (VBM and CBM) for 2L-MoS$_2$ under BC and BT strains. (a) For unstrained case. (b)-(d) Under $-0.04$, $-0.07$, and $-0.15$ BC strains, respectively. (e)-(f) Under 0.03 and 0.06 BT strains. The Fermi level is shown by red dotted lines.
(pressure) is expected. On the other hand, an accurate estimation of the band gap will improve the thermoelectric performance. Therefore, GGA results reported in the manuscript serve as a lower limit for both the thermoelectric performance and threshold strain for the S-M transition.

4. Conclusion

In conclusion, we show the tuning of the band gap in multilayer MoS2 under the application of normal and biaxial strains. A reversible S-M transition is obtained by applying NC, BC, and BT strains. The nature of the transition, in terms of the electronic structure, is different for each kind of strain. For a particular strain, the reduction in the band gap remains unchanged for different numbers of layers. However, the threshold strain at which the transition occurs increases (decreases) with an increase in number of layers for normal (biaxial) strain. Threshold strain is the least in the case of the BT strain, and is the maximum in the case of the BC strain. The mechanism behind the S-M transition is also investigated in terms of angular momentum resolved density of states and band-decomposed charge density. We demonstrate that interlayer interaction between Mo-d\textit{dz}^2 and S-p\textit{z} causes the S-M transition under NC strain. However, the S-M transitions under BC and BT strains are caused by the strong hybridization of the intraplane Mo-d\textit{dz}^2 and S-p\textit{z} orbitals and Mo-d\textit{dz}^2 and S-p\textit{z} orbitals, respectively. The change in the transport properties of multilayers of MoS2 were also investigated under the application of NC, BC, and BT strains for different layer thicknesses. The strain modifies the dispersion of bands, which improves the thermoelectric performance of the material significantly. The thermopower results suggest that under NC strain, the efficient thermoelectric performance can be achieved at -0.04 and -0.09 strain for \( p \)- and \( n \)-type doping, respectively. The 3L-MoS\textsubscript{2} shows a maximum power factor under NC strain, while for biaxial strain, the enhanced performance could be achieved under 0.05 compressive/tensile strain for 2L-MoS\textsubscript{2}. The possibility of tuning the band gap by applying strain provides potential application of MoS\textsubscript{2} multilayers not only in thermoelectric devices, but also in sensors and other electromechanical devices. Moreover, the value of the threshold strain provides a means for determining the number of layers in an experimentally grown, multilayer MoS\textsubscript{2}. Our results indicate that the maximum thermoelectric performance can be achieved under biaxial strain, which is achievable in experiments. Recently, it has been shown that strain on Mo\textsubscript{S2} can be applied by growing thin films on elastomeric [62–64] or lattice mismatched [65] substrates. Therefore, the complete potential of tuning electronic and thermoelectric properties of this wonderful material can be realized experimentally. Owing to the similar crystal structure and electronic properties, the proposed S-M transition mechanism for few-layered MoS\textsubscript{2} can be extended to all other semiconducting TMDs under various types of strains.

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