Band Alignment in BP/MoS$_2$ heterostructure: Role of Charge Redistribution, Electric Field, Biaxial Strain, and Layer Engineering

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**Abstract:** The objective of this work is to study the effects of charge redistribution, applied layer-normal electric fields, applied strain, and layer engineering on the band alignment of Black Phosphorus (BP)/Molybdenum disulphide (MoS$_2$) heterostructure through Density Functional Theory (DFT) simulations. Black phosphorus works as a $p$-type material with high mobility, mechanical flexibility, and sensitivity to number of layers. Combining it with the more electronegative material, MoS$_2$ results in strong carrier confinement and a Type II heterostructure. Charge redistribution among the layers shifts the band alignment expected from the Electron Affinity Rule. Applied external fields, strain and multiple BP layers provide band-alignment tunability within the Type II range and/or, transition to Type I and Type III heterostructures. The tunability in BP/MoS$_2$ heterostructure may be useful as tunnel field effect transistors, rectifier diodes with tunable barrier height, reconfigurable FETs, and electro-optical modulators. Furthermore, considering heterostructures of monolayer BP with other monolayer Transitional Metal Dichalcogenides (TMD) suggests the ability to achieve different band alignment types. In our simulations, a Type I alignment is found with Tungsten diselenide (WSe$_2$), Molybdenum diselenide (MoSe$_2$), and Tungsten disulphide (WS$_2$), and a Type III for Hafnium disulphide (HfS$_2$) and Hafnium diselenide (HfSe$_2$).
INTRODUCTION

Stacking of individual layers of two-dimensional (2D) materials has been introduced as a means to achieve scalability and band tunability in various devices [1-3]. Monolayers of 2D materials couple to form layered structure via relatively weak van der Waals (vdW) bonds. Such layered structures have demonstrated efficient controllability of band alignments via modification through strain, number of layers, chemical doping, alloying, and externally applied fields [1-7]. They have gained attention due to their ultra-thin bodies that show excellent electrostatic control, high mechanical flexibility, and absence of dangling bonds at the surface, which reduces interface traps and defects [1].

The type of application often depends on the type of band alignment. Heterostructure stacking can result in Type I (straddling), II (staggered) and III (broken) band alignments [2,3]. In vdW materials, a Type I alignment, where the conduction band minimum (CBM) and the valence band maximum (VBM) of the stack occur in the same/narrower bandgap material [3], produces confinement of electron and holes in the same region and thereby enhances radiative recombination and, thus, can be utilized for light emitting applications [3]. A Type II alignment, where the CBM and VBM are located in different materials, is desirable for photovoltaics and photodetectors [3,8]. A Type III alignment, where the CBM of one material overlaps the VBM of the other material, may be utilized for tunnel diodes [3,9].

In this work, we study the impact of strain, electric field, layer, and material engineering on the band properties of heterojunction system, considering a stack of Black Phosphorus (BP) and Molybdenum disulphide (MoS$_2$). BP has potential application in various optoelectronic devices, due to its direct band gap, high mobility, high flexibility, high tunability with number of layers, strain tolerance, and anisotropic physical properties [10-16]. Amongst the Transitional
Metal Dichalcogenide (TMD) family, MoS$_2$ is the most widely studied, and it exhibits many desirable material properties well suited for transistor applications, including relatively good carrier mobility and a sizable band gap [17,18]. BP, MoS$_2$ and their heterostructures have shown potential in a myriad of applications, such as non-volatile memory cells [19], photodetectors [8], rectifier diodes [20], field-effect transistors [18, 21-22]. Expanding the applicability of their heterostructure, however, requires an in-depth analysis of interlayer interactions and the factors that influences the interfaces.

By forming a vertically stacked $pn$ junction, BP/MoS$_2$ heterostructure may be usable for Electron-Hole Bilayer (EHB) Tunnel Field Effect Transistors (TFET), which have been difficult to realize through thin Si-based FETs [23]. Furthermore, a surface-normal electric field can provide electrostatic doping, which can benefit reconfigurable devices [24]. As part of this work, we carefully consider the effects of charge redistribution with the vdW stacks, which can alter the band alignment somewhat from the prediction of the Electron Affinity Rule (Anderson’s Rule) [25] and partially screens externally applied stack-normal electric fields [26].

**COMPUTATIONAL METHOD:**

Our calculations are performed using first-principles Density Functional Theory (DFT) with the projector-augmented wave (PAW) method as implemented using the Vienna Ab initio Simulation Package (VASP) [27]. Exchange-correlation interaction is included with the generalized gradient approximation (GGA) developed by Perdew-Burke-Ernzerhof (PBE) [28]. The optimized monolayer lattice parameters are taken as: 3.18 Å for MoS$_2$, and $a = 3.30$ Å, $b = 4.63$ Å for BP, and their respective calculated bandgaps are 1.68 eV for MoS$_2$ and 0.9 eV for BP. The optimized
lattice parameters of the monolayers of BP [10,13,14], MoS₂, and other TMDs (included at the end of discussion) are consistent with previous literature [3,4].

Creating a 2D vdW heterojunction requires stacking at least two materials, which come with different lattice constants. A challenge is formation of a supercell with both limited lattice strain and computationally tractable number of atoms. We stacked a $1 \times 5\sqrt{3}$ supercell of MoS₂ with a $1 \times 5$ supercell of BP to create a heterostructure of 44 atoms (20 - P atom, 8 - Mo atom and 16 - S atom), as shown in Figure 1a. An anisotropic compressive strain of 1.8% in the zig-zag direction (y-direction) and 3.12% in the armchair direction (x-direction) of BP and a tensile strain of 1.902% in y-direction and 1.891% in x-direction (with four significant digits provided to show that the resulting strain is technically anisotropic as to be expected, but barely so) of MoS₂ is required to form a lattice matched but otherwise relaxed heterostructures with $a = 22.45$ Å, $b = 3.24$ Å.

The van der Waals interactions, modeled using the OptB88 functional method [29], are used to calculate the interfacial distance between the S atom-center to the P atom-center (denoted as “d” in Figure 1a) and binding energy ($E_b$) between the layers. $E_b$ is calculated using, $E_b = E_{BP/MoS₂} - E_{BP} - E_{MoS₂}$, where $E_{BP/MoS₂}$ is the total energy of BP/MoS₂ heterostructure and $E_{BP}$ and $E_{MoS₂}$ are the total energies for isolated monolayers of BP and MoS₂, respectively. The calculation provides a minimum $E_b$ of −85.3 meV/P atom at $d = 3.3$ Å. (The thickness of the remaining vacuum region in the simulation is greater than 15 Å.) The structure was fully relaxed with a force tolerance of 0.01 eV/Å before calculation of the electronic properties of the heterostructure [30]. The energy cutoff was set to 400 eV using a $5 \times 21 \times 1$ Monkhorst–Pack grid for Brillouin zone integration and the break criterion for the electronic self-consistent loop was set to $10^{-5}$ eV.
Figure 1. (a) The crystal structure, (b) projected band structure, (c) side view of differential charge density in the \( x-z \) plane, with an isovalue of \( 1.54 \times 10^{-4} \, e/Å^3 \), (d) the \( x-y \) plane-averaged electron density difference along the \( z \) direction of the BP/MoS\(_2\) heterolayer, and (e) band energy of isolated BP, of isolated MoS\(_2\) and of a BP/MoS\(_2\) heterostructure, with \( E_c \) and \( E_v \) indicating conduction band minima and valence band maxima, respectively. In all cases, the \( z \) direction is taken as normal to the plane of the MoS\(_2\) and BP layers. In (a), (c) BP, Mo, and S atoms are represented in blue, red, and green, respectively. In (b) blue and red dots represent the projection of each energy band onto the BP and MoS\(_2\) layers, respectively, where the size of dots corresponds to the weight of the projections (with the red dots overlaying the blue ones where they overlap). In (c), orange indicates electron gain while green indicates electron loss. All energies are referenced to vacuum level.

RESULTS AND DISCUSSION

The band alignment between layers of the vdW stacks can be altered using different materials and different layer numbers, externally applied electric fields, and strain. Moreover, even with zero applied external field, charge redistribution between the layers can affect band alignment between
layers, which includes band offsets, interlayer band gap, and the Electron Affinity of the heterostructure, all important to device applications.

A. *Zero External Field Band Alignment*

Figure 1b shows the projected band structure of BP/MoS$_2$ heterostructure. It is evident from the figure that the CBM of the heterostructure originates from MoS$_2$, while VBM of the heterostructure originates from BP, indicating a Type II alignment. The BP/MoS$_2$ heterostructure has an indirect band gap with the CBM and the VBM located at different k-points between Y and $\Gamma$ (the latter labeled “G” in Fig 1(b)) and a simulated band gap ($E_g = E_c - E_v$) of 0.407 eV. This value is consistent with previous works [21,30,31].

Notably, the obtained heterostructure bandgap $E_g$ for this strained system under zero applied external field is 32% larger than expected from the Electron Affinity rule (Anderson’s Rule [25]), with $E_{c_{MoS_2}} - E_{v_{BP}} = 0.309$ eV, where $E_{v_{BP}}$ and $E_{c_{MoS_2}}$ are the VBM energy of the BP layer with the MoS$_2$ layer removed and the CBM energy of the MoS$_2$ layer with the BP layer removed, respectively. For the latter purpose, the atomic positions of the atoms within the remaining layer are held fixed to those of the heterostructure to isolate the electronic effects. The bandgap increase, at least in part, is associated with charge redistribution (but not free carrier redistribution in the still gapped and undoped heterostructure) within the heterostructure, as depicted in Figure 1(c). Figure 1(d) shows plot of charge density difference along z, $\Delta \rho (z)$ defined as,

$$\Delta \rho (z) \equiv \int \rho_S (x,y,z)dxdy - \int \rho_{BP} (x,y,z)dxdy - \int \rho_{MoS_2} (x,y,z)dxdy ,$$
where $\rho_s$ is the charge density of the heterostructure stack, and $\rho_{BP}$ and $\rho_{MoS_2}$ are the charge density of the BP layer with the MoS$_2$ layer removed and the charge density of the MoS$_2$ layer with the BP layer removed (each as above), respectively, and the resulting interlayer electric field.

Electrons from the upper portion of the valence band originating from BP evanescently couple into the MoS$_2$, more so than they do into vacuum, skewing these electronic states toward the MoS$_2$, resulting in a net positive (negative) charge on the BP (MoS$_2$) and a corresponding positive electric field directed toward MoS$_2$ from BP. This electric field, in turns, adds to the energy separation between the lower conduction band states still predominantly localized in the MoS$_2$ and the upper valence band states still predominantly localized in the BP, increasing the heterostructure bandgap. Also note that within this simulation of an effectively periodic structure, the charge-induced electric field is split between the physically expected component for an isolated bilayer that passed through the vdW gap between the BP and MoS$_2$ layers and another, smaller, and oppositely directed component that passes through the region outside of the bilayer and the simulation region boundaries, which is an artifact of the finite thickness of the simulation region.

The field splitting artificially reduces the electrostatic bandgap enhancement somewhat in these simulations. (And, by extension, in a multi-layer heterostructure consisting of alternating layers of BP and MoS$_2$, the electrostatic bandgap enhancement can be expected to be further reduced). However, the difference between the results of Figure 1d and the expectations of the electron affinity rule cannot be assumed to be entirely electrostatic in origin. Increased evanescent spreading of the electronic states near the top of the valence band and near the bottom of the conduction band affects the overall confinement energy of these states, which influences the relative and absolute energies with respect to the vacuum of, among others, the VBM and CBM states.
Figure 2 (a) x-y plane-averaged potential as a function of $z$ for electric field magnitudes ($E$) of $-0.3 \, \text{V/Å}$, $0 \, \text{V/Å}$, and $0.3 \, \text{V/Å}$ normal to the stack. (b) Corresponding variation in effective electrostatic potential $V_E - V_{E=0}$ fields at top, $V_{\text{top}}$, and bottom, $V_{\text{bottom}}$, of the simulation region, as indicated in (a). (c) Variation in Bader charge (electron) [32] in the BP layer ($\Delta q_{E}$) with applied electric field in comparison to the case with no applied field ($\Delta q_{E=0}$). Note that the detailed field dependence is nearly but neither entirely linear nor entirely symmetric between positive and negative applied fields.

B. Impact of Applied Electric Field

The impact of an applied stack-normally-oriented electric field is studied through variation in electrostatic potential as a function of normal component of the applied field ($E$), $V_E$ in Figure 2, charge density difference, $\rho_E - \rho_{E=0}$ in Figure 3 and change in the band gap in Figure 4. A positive (negative) field—with the field direction defined as positive from MoS$_2$ to BP—produces a potential variation, as seen in Figures 2a and 2b, and a net electron shift to (from) the MoS$_2$ from (to) BP, as seen in Figure 2c and in Figure 3 in more detail. The charge shift, however, self-consistently partially screens the externally applied field from the interior of the MoS$_2$ and the BP and, somewhat less so, from the vdW gap between the layers. The effective static/low frequency dielectric constant (relative dielectric permittivity [33]) is approximately 7.4, given the not well-defined material edges at this scale. Nevertheless, the vdW stack bandgap still can be adjusted with the externally applied field at reasonable voltages, as shown in Figure 4.

Moreover, although the atom-projected band gaps of individual materials are maintained ($\approx 0.85 \pm 0.03 \, \text{eV}$ for BP and $\approx 1.28 \pm 0.06 \, \text{eV}$ for MoS$_2$), Figure 4 shows that a sufficiently negative
electric field, in the vicinity of $-0.5 \text{ V/Å}$, converts the heterostructure to Type I with the bandgap defined by BP, while a sufficiently positive applied electric field, in the vicinity of 0.7 V/Å, leads to a metallic Type III structure, with the valence band of BP slightly overlapping the conduction band of MoS$_2$. This bandgap tunability within the Type II range through application of an external field offers the possibility of rectifier diodes with tunable barrier height [1], reconfigurable FETs [24], tunnel FETs [22], and electro-optical modulators [34].

**Figure 3** (a) Charge density difference $\rho_E - \rho_{E=0}$ in the x-z plane with an isovalue of $1.54 \times 10^{-4}$ e/Å$^3$ and (b) variation in plane averaged charge density difference along z with negative electric field, and (c) and (d), same for positive applied electric field. The orange region indicates electron accumulation, while green indicates depletion. The arrows point in the direction of increasing electric fields.

**Figure 4** Change in (a) the atom-projected band offsets for CB energies ($\Delta E_{c,\text{BP-MoS2}} = E_{c,\text{BP}} - E_{c,\text{MoS2}}$) and VB energies ($\Delta E_{v,\text{BP-MoS2}} = E_{v,\text{BP}} - E_{v,\text{MoS2}}$) of the BP/MoS$_2$ heterostructure, and (b) the band gap of the BP/MoS$_2$ heterostructure as a function of externally applied electric field. The heterostructure can be tuned from Type I at large negative fields ($< -0.5 \text{ V/Å}$) fields to Type III at large positive fields ($> 0.65 \text{ V/Å}$).
C. Strain Engineering

Strain-dependent modulation of transport properties have been studied and utilized for improving device performance in terms of mobility, tunability and control of magnetic properties [7,11]. Strain applied is defined as the relative change in the lattice constant with respect to the unstrained lattice constant value, i.e., \((a-a_0)/a_0\). Positive valued strain is referred to as tensile strain, and negative valued strain is referred to as compressive. (To achieve compressive strain, the BP-MoS\(_2\) layer-normal (z) displacement would have to be constrained within a larger structure.) Studies have shown that a semiconductor-metal transition in MoS\(_2\) is predicted for a biaxial tensile strain of about 8\% and compressive strain of about 15\% [35], while for BP this transition is observed for compressive strain of about 9\% and tensile strain of ~20\% [36]. (Experimentally, MoS\(_2\) can sustain uniaxial tensile strain greater than 11\% [17], and BP has demonstrated capability to withstand tensile strain up to 30\% in the zigzag direction and 27\% in the armchair direction [11,37]).

![Projected Density of States (DOS) for orbitals in BP/MoS\(_2\) with biaxial strain of −2\%, 0\%, 2\% for: \(d_{z^2}\), \(d_{x^2-y^2}\), \(d_{xy}\) of Mo; \(p\) and \(s\)-orbital of P (blue), and \(p_y\) and \(p_z\) of S; where positive strain values correspond to tensile strain and negative values to compressive strain.](image)

**Figure 5** Projected Density of States (DOS) for orbitals in BP/MoS\(_2\) with biaxial strain of −2\%, 0\%, 2\% for: \(d_{z^2}\), \(d_{x^2-y^2}\), \(d_{xy}\) of Mo; \(p\) and \(s\)-orbital of P (blue), and \(p_y\) and \(p_z\) of S; where positive strain values correspond to tensile strain and negative values to compressive strain.
To understand the impact of biaxial strain on BP/MoS\textsubscript{2} stack and the origin of the energy bands, we projected the Bloch states onto the atomic orbital basis of the constituent atoms as a function of energy, as shown in Figure 5. Considering the apparent bandgaps in Figure 5 as a function of strain and atom-projected Density of States (DOS) in MoS\textsubscript{2} and BP, the visually apparent VBM in MoS\textsubscript{2} is dominated by the $d_{z^2}$ orbital of Mo and, to a lesser degree, the $p_z$ orbital of S \cite{7}. The apparent CBM within MoS\textsubscript{2} is dominated by the $d_{z^2}$ orbitals of Mo. For BP, the apparent VBM is dominated by the $p_z$ orbital. The apparent CBM of BP also is contributed primarily by the $p_z$ orbital, with a significant contribution from $p_x$, $p_y$ and $s$ orbital as well.

Fig. 6(a) shows the change in band offset with applied strain and the projected band gap of BP and MoS\textsubscript{2} is shown in Fig. 6(b). As mentioned previously, the bond length increases with biaxial strain, and the MoS\textsubscript{2} bandgap decreases, consistent with reduced orbital overlap among the atoms. However, the band gap of BP increases with biaxial tensile strain due to decrease in distance between two sub-layers (height of a layer in z-direction) of phosphorus atoms within the puckered BP structure, as has been demonstrated experimentally \cite{11} and explained theoretically \cite{11,16} for isolated BP layer. The bandgap of MoS\textsubscript{2} varies more with tensile strain than compressive, and the opposite is true for BP. For the stacked system, Figure 6(b) shows that as strain varies from $-5\%$ to $5\%$, the band gap of BP/MoS\textsubscript{2} first increases, following the atom projected bandgap of BP in a region of strain where the BP/MoS\textsubscript{2} stack is Type I. Then in the vicinity of and above $-2\%$ strain the BP/MoS\textsubscript{2} bandgap begins to decrease again as the stack becomes Type II with the valence band originating from the BP and the conduction band originating from the MoS\textsubscript{2}. The charge distribution between the monolayers (Figure 6c) shows the electron loss from BP to MoS\textsubscript{2} increases by 0.03 electrons per supercell, from 0.16 to 0.19 for 5\% (tensile) biaxial strain relative to that of the unstrained...
BP/MoS$_2$ stack, while the electron loss decreases by 0.05, from 0.16 to 0.11 for −5% (compressive) strain. Moreover, with tensile strain, the k-space position of the VBM of the BP/MoS$_2$ stack, again originating from the BP, shifts towards the Γ-point, while for compressive strain it shifts towards the Y-point. As for the CBM, while the BP/MoS$_2$ stack remains Type II with strain, the CBM originates from MoS$_2$, and the k-space position located along Γ to Y is essentially independent of strain. However, when the BP/MoS$_2$ stack becomes Type I with compressive strain and the CBM also originates from the BP, the k-space position of the CBM shifts to, and remains at, the Γ-point.

![Figure 6](image)

**Figure 6** Impact of biaxial strain on (a) CB and VB band offsets (as defined in Fig. 4(a)), and (b) band gap of BP, MoS$_2$, and BP/MoS$_2$ in the heterostructure, where positive strain values correspond to tensile strain and negative values to compressive strain. (c) Charge redistribution between BP and MoS$_2$ with the applied strain. Negative Δ$q$ indicates electron redistribution from the BP layer to the MoS$_2$ layer per 2D supercell.

**D. Layer Engineering**

The variation in the band energy and alignment of the heterostructure with the number of BP layers varying from 2 to 4 is shown in Figure 7a-c, respectively. Interlayer coupling between different layers of monolayer BP leads to band splitting, which shifts the CBM and the VBM to lower and higher energies, respectively [6,15]. As a result, the band gap decreases with increased number of BP layers [12,15], varying from 0.4 eV in 1L-BP/MoS$_2$ to 0.03 eV in 4L-BP/MoS$_2$. Table 1 provides the projection of the CBM and VBM onto the individual layers, indicating that
these states are substantially delocalized with respect to BP layers, and, furthermore, the CBM becomes decreasingly localized to the MoS$_2$ layer as the layer-projected CBM of the BP layers approaches that of the MoS$_2$ layer, while the VBM become increasingly localized to the BP layer with increasing number of BP layers.

![Projected band energy of (a) 2L-BP/MoS$_2$, (b) 3L-BP/MoS$_2$, and (c) 4L-BP/MoS$_2$ heterostructure.](image)

Figure 7 Projected band energy of (a) 2L-BP/MoS$_2$, (b) 3L-BP/MoS$_2$, and (c) 4L-BP/MoS$_2$ heterostructure. For 4L-BP/MoS$_2$, (d) side view of the differential charge density in the y-z plane with an isovalue of $1.54 \times 10^{-4}$ e/Å$^3$, and (e) the x-y plane-averaged electron density difference along the $z$ direction of the BP/MoS$_2$ heterolayer. In (d) and (e), the dots represent projected atom positions.

Use of multilayer BP has proven beneficial due to its direct band gap, high mobility, anisotropic electronic properties, and higher sensitivity as compared to other 2D materials including monolayer BP [6,10,12,15]. Few-layered BP can perform better than single-layer BP due to higher carrier density, lighter carrier effective mass and weaker scattering [6,12]. Type III
heterostructures can be obtained by combining layer engineering with an externally applied field, in-plane strain, vertical stress, or plane-normal compression [38]. Multi-layer BP with MoS$_2$ could be useful for low voltage Tunnel FETs. The change in the workfunction of BP, with the stacking of BP layers can possibly be utilized for tuning contact resistance [12,39].

**Table 1.** Contribution of each layer to the CBM and VBM states for $n$-layer-BP/MoS$_2$. These results were obtained through projection of the CBM and VBM wavefunctions onto the atomic orbitals within the individual layers. As shown in Figure 7d, Layer L1 is that closest to the MoS$_2$ layer, L2 the next closest, and so forth. The values are in percentage.

| Stack       | VBM      | CBM      |
|-------------|----------|----------|
|             | MoS$_2$  | L1 | L2 | L3 | L4         | MoS$_2$  | L1 | L2 | L3 | L4         |
| 1L-BP/MoS$_2$ | 16.3     | 83.7 | -  | -  | -          | 91.5     | 8.5 | -  | -  | -          |
| 2L-BP/MoS$_2$ | 5.8      | 48.2 | 46 | -  | -          | 79       | 9   | 12 | -  | -          |
| 3L-BP/MoS$_2$ | 4.1      | 35.2 | 42.2 | 18.5 | -          | 58       | 7   | 16.3 | 18.7 | -          |
| 4L-BP/MoS$_2$ | 2        | 18.2 | 32  | 28.1 | 19.7       | 52.4     | 4.8 | 12.4 | 14.5 | 15.9       |

**E. Material Engineering**

The freedom to combine different materials in vdW heterostructures has led to discoveries potentially useful for various optoelectronic applications. In this work, we replaced MoS$_2$ with MoSe$_2$, WS$_2$, WSe$_2$, HfS$_2$, HfSe$_2$ layers to form a heterostructure with BP. Table 2 provides: the simulated valence and conduction band edge energies for the as-strained TMDs, but with the BP layer removed, and the same for as-strained BP for each heterostructure, but with the TMD layer removed, and the corresponding band edge offsets and band gaps based on the electron affinity rule for comparison; the same obtained from the layer-projected apparent band-edge energies in the heterostructure; and the difference between the calculated bandgap for the heterostructure and that obtained using the electron affinity rule and the band-structure of the strained but isolated layers. As seen, the type of heterostructure formed remains the same by either approach, but the
predicted band edge offsets and bandgap vary significantly, with energy differences varying from a few tens of meV to almost an eV for HfSe₂/BP, depending on the approach used.

**TABLE 2.** Band parameters for as-strained Monolayers of BP and TMDs. $E_c$ and $E_v$ are the conduction band minimum (CBM) energy and valence band maximum (VBM) energy relative to the vacuum, respectively. $\Delta E_c = E_{c,\text{BP}} - E_{c,\text{TMD}}$, $\Delta E_v = E_{v,\text{BP}} - E_{v,\text{TMD}}$ are the band offsets for CB energies and VB energies, respectively. In the simulated heterostructure, BP and the TMD layer-projected band edge energies are used for $E_c$ and $E_v$. $E_{g(\text{HE})}$ is the bandgap obtained from simulation of the heterostructure as a whole, while $E_{g(\text{EAR})}$ is the bandgap of heterostructure obtained from the simulation of the isolated (but identically strained) monolayers using the Electron Affinity Rule (EAR). All energies are in eV. The text highlighted in grey indicates the material and associated band edge energy defining the CBM and VBM of the heterostructure. Again, all band-edge energies are reference to the vacuum level.

| Stack     | Layer | $E_c$  | $E_v$  | $\Delta E_c$ | $\Delta E_v$ | $E_g$ | $E_{c,\text{BP}}$ | $E_{c,\text{TMD}}$ | $E_{v,\text{BP}}$ | $E_{v,\text{TMD}}$ | $\Delta E_c$ | $\Delta E_v$ | $E_{g(\text{HE})}$ | $E_{g(\text{EAR})}$ |
|-----------|-------|--------|--------|--------------|--------------|-------|-------------------|-------------------|-------------------|-------------------|--------------|--------------|-------------------|-------------------|
| MoS₂/BP   | MoS₂  | -4.79  | -6.14  | 0.30         | 1.04         | 0.31  | -5.09            | -6.37             | -4.65            | -5.49             | 0.44         | 0.88         | 0.40              | 0.09              |
| MoS₂/BP   | BP    | -4.49  | -5.1   | -0.17        | 0.36         | 0.92  | -4.17            | -5.61             | -4.26            | -5.25             | -0.08        | 0.36         | 0.99              | 0.07              |
| MoSe₂/BP  | MoSe₂ | -4.16  | -5.60  | -0.17        | 0.92         | 0.36  | -4.41            | 5.95              | -4.36            | 5.24              | -0.03        | 0.84         | 0.67              | 0.06              |
| MoSe₂/BP  | BP    | -4.33  | -5.25  | -0.08        | 0.36         | 0.92  | -4.17            | -5.61             | -4.26            | -5.24             | -0.08        | 0.36         | 0.99              | 0.07              |
| WS₂/BP    | WS₂   | -4.42  | -5.97  | -0.08        | 0.86         | 0.61  | -4.41            | 5.95              | -4.36            | 5.24              | -0.03        | 0.84         | 0.67              | 0.06              |
| WS₂/BP    | BP    | -4.5   | -5.11  | -0.14        | 0.91         | 0.90  | -3.87            | 5.41              | -4.26            | 5.24              | -0.20        | 0.17         | 0.98              | 0.07              |
| WSe₂/BP   | WSe₂  | -3.84  | -5.38  | -0.49        | 0.14         | 0.91  | -3.87            | 5.41              | -4.26            | 5.24              | -0.20        | 0.17         | 0.98              | 0.07              |
| WSe₂/BP   | BP    | -4.33  | -5.24  | -0.08        | 0.86         | 0.61  | -3.87            | 5.41              | -4.26            | 5.24              | -0.20        | 0.17         | 0.98              | 0.07              |
| HfS₂/BP   | HfS₂  | -6.09  | -7.06  | 1.51         | 1.99         | 1.01  | -5.76            | 6.8               | -5.09            | 5.74              | 0.67         | 1.06         | -0.02             | 0.99              |
| HfS₂/BP   | BP    | -4.59  | -5.08  | 1.51         | 1.99         | 1.01  | -5.76            | 6.8               | -5.09            | 5.74              | 0.67         | 1.06         | -0.02             | 0.99              |
| HfSe₂/BP  | HfSe₂ | -5.70  | -6.57  | 1.26         | 1.36         | 0.49  | -5.49            | 6.26              | -4.67            | 5.48              | 0.82         | 0.78         | -0.01             | 0.48              |
| HfSe₂/BP  | BP    | -4.44  | -5.21  | 1.26         | 1.36         | 0.49  | -5.49            | 6.26              | -4.67            | 5.48              | 0.82         | 0.78         | -0.01             | 0.48              |

**CONCLUSION**

This study focused on understanding the impact of charge redistribution, external and internal fields, strain, and material and layer engineering on the band alignment of heterostructure through DFT simulations. Charge density analysis demonstrates electron redistribution from BP to MoS₂ even under no applied bias, which substantially alters that band alignment from the expectations...
of the electron affinity rule, although the alignment type, Type II, remains unchanged in simulation. Biaxial strain affects both the interlayer and intralayer charge distribution and coupling among orbitals due to variation in bond lengths and angles. Moreover, in simulation, a BP/MoS$_2$ heterostructure can be tuned all the way from Type I to Type III with applied strain and/or applied field. Such tunability of the BP/MoS$_2$ band structure offers flexible application to EHB-TFETs, reconfigurable FETs, electro-optical modulators, rectifier diodes, and contacts. The band alignment within other BP/TMD heterostructures also have been evaluated. In our simulations, a Type I alignment is obtained for BP/WSe$_2$, BP/MoSe$_2$, and BP/WS$_2$, and a Type III alignment for Hafnium BP/HfS$_2$ and BP/HfSe$_2$. Again, charge redistribution between layers alters the band alignment from the expectations of the electron affinity rule, while the alignment type remains same.

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