Band Alignment in Black Phosphorus/Transition Metal Dichalcogenide Heterolayers: Impact of Charge Redistribution, Electric Field, Strain, and Layer Engineering

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Abstract
In this work, the energy band alignments of heterostructures of 2D materials are studied, where these are crucial for various device applications. Using density functional theory (DFT), we consider heterostructures of black phosphorus (BP) with transition metal dichalcogenides [MX2, where M = molybdenum (Mo), tungsten (W), or hafnium (Hf), and X = sulfide (S) or selenide (Se)] and, specifically, the effects of charge redistribution and associated electrostatic fields on the band alignments beyond the electron affinity rule, as well as band tunability via applied layer-normal electric fields, applied strain, and layer engineering in BP/MoS2. BP is a material with high mobility and mechanical flexibility, and is also sensitive to the number of BP layers. Absent such tuning, calculations for BP combined with the more electronegative materials result in a staggered (type II) alignment for MoS2, and a broken gap (type III) alignment for HfSe2 and HfS2. Calculation for BP with less electronegative materials, WSe2, MoSe2, and WS2 materials, results in straddling (type I) alignment, with a direct gap for WSe2 and MoSe2, and an indirect gap for WS2. The amount of charge redistribution between layers and associated variations from the electron affinity rule increase going from type I to type II to type III, where the band alignment becomes significantly pinned in the latter case by the creation of mobile charge carriers. With such tuning, these band alignments can then be altered quantitatively and qualitatively.

Keywords Heterostructure · band alignment · electron affinity · biaxial strain · black phosphorus · molybdenum disulfide · charge redistribution · 2D monolayers · dielectric · TMD

Introduction
Stacking of individual layers of two-dimensional (2D) materials has been introduced to achieve scalability and band tunability in various devices.1–3 Monolayers of 2D materials couple to form a layered structure via relatively weak van der Waals (vdW) bonds. Such layered structures have demonstrated controllability of band alignment 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 electrons and holes in the same region and thereby enhances radiative recombination; thus, it can be utilized for light-emitting applications.7 A type II alignment, where the CBM and VBM are 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

Black phosphorus (BP) has potential applications in various optoelectronic devices because of its direct bandgap, high mobility, flexibility, and tunability with number
of layers, strain tolerance, and anisotropic physical properties. Transition metal dichalcogenides (TMDs) have a sizable bandgap, unlike graphene, and have demonstrated potential applications in optoelectronic and nanoelectronic devices. Among the TMD family, molybdenum disulfide (MoS2) is the most widely studied, and it exhibits many desirable material properties well suited for transistor applications, including relatively good carrier mobility. BP, MoS2, and their heterostructures have shown potential in myriad applications including nonvolatile memory, photodetectors, rectifier diodes, and field-effect transistors (FETs). A vertically stacked pn junction formed with BP and MoS2, hafnium disulfide (HfS2), or hafnium diselenide (HfSe2) may be usable for electron–hole bilayer (EHB) tunnel field-effect transistors (TFETs), which have been difficult to realize using silicon (Si). Stacked BP and tungsten disulfide (WS2), and stacked BP and molybdenum diselenide (MoSe2) can also be tuned to operate as a pn junction, while stacked BP and tungsten diselenide (WSe2) is well suited to function as a p/p or an n/n heterojunction. Furthermore, a surface-normal electric field can provide electrostatic doping of these 2D materials while also allowing for reconfigurable devices.

The impact of applied electric field on the band offsets of BP/MoS2 has been studied and has shown the possibility of using the heterostructure for various applications, thus warranting further exploration. Strain engineering provides the flexibility to modulate the bandgap and carrier effective mass. Experimentally, MoS2 can sustain uniaxial tensile strain greater than 11%, and BP has demonstrated capability to withstand tensile strain up to 30% in the zigzag direction and 27% in the armchair direction. It has been suggested that strain engineering the MoS2 could be used to create tunable photonic devices and solar cells and even to control the magnetic properties of MoS2. The effect of uniaxial strain and surface-normal compressive strain on the heterojunction of BP/MoS2 has been studied. Previous works show promising application with few-layer BP for high-performance devices because of its higher carrier density, lighter carrier effective mass, and weaker scattering compared with single-layer BP. Improving and expanding the applicability of these heterostructures requires an in-depth understanding of interlayer interactions and the factors that influence the interfaces, including material and layer engineering, strain, applied normal fields, and the environment of surrounding materials.

In this work, using density functional theory (DFT), we study heterostructures of BP with the MoS2, MoSe2, WS2, WSe2, HfS2, and HfSe2. We demonstrate how charge redistribution among layers and associated electrostatic fields alter the band alignments from the expectations of the electron affinity rule (Anderson’s rule). We show, specifically, that interlayer charge transfer has a near-linear dependence on the difference in the workfunctions of the isolated materials and, by the example of BP/MoS2, that vdW stack bandgaps can be adjusted not only quantitatively but also qualitatively among bandgap types with reasonable applied electric fields. We study the impact of biaxial strain on the origin of the band structure in real space and among orbitals. The results show that the bilayer can be tuned between a type I and type II within a limited range of ±5% strain. Implementing a multilayer BP with a MoS2 leads to band splitting, which shifts the CBM and the VBM to lower and higher energy, respectively, and eventually changes the heterostructure alignment from type II to type I with four layers of BP.

**Computational Method**

Our calculations are performed using first-principles DFT with the projector-augmented wave (PAW) method as implemented using the Vienna Ab initio Simulation Package (VASP). The exchange–correlation interaction is included within the generalized gradient approximation (GGA) developed by Perdew–Burke–Ernzerhof (PBE). The optimized lattice parameters of monolayers of BP and TMDs are consistent with published literature and are provided (see supplementary Table S1). Creating a 2D vdW heterojunction requires stacking at least two materials. The challenge for simulation is the formation of supercells with both limited lattice strain and computationally tractable numbers of atoms. We combined 1 × 4√3 supercells of MoS2, MoSe2, WS2, and WSe2 with a 1 × 5 supercell of BP to create a heterostructure of 44 atoms (20 P atoms, 8 M atoms, and 16 X atoms), while 5 × √3 supercells of HfS2 and HfSe2 are combined with a 4 × 2 BP to create a heterostructure of 62 atoms (32 P, 10 Hf, 20 S/Se) (Fig. 1a). That said, the strain required to realize practical unit cell sizes can quantitatively affect the band structures of the considered materials. Therefore, while we necessarily provide specific values for various quantities below, our focus is on qualitative effects.

Van der Waals interactions, modeled using the OptB88 functional method, are used to calculate the interfacial distance from the X atom-center to the P atom-center (denoted as “d” in Fig. 1a) and binding energy (E_b) between the layers. E_b is calculated as E_b = E_{BP/TMD} − E_{BP} − E_{TMD}, where E_{BP/TMD} is the total energy of the BP/TMD heterostructure, and E_{BP} and E_{TMD} are the total energy for isolated monolayers of BP and TMDs, respectively. The thickness of the remaining vacuum region outside the heterostructure 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. The energy cutoff was set to 400 eV, and the Brillouin zone was sampled using Monkhorst–Pack grids of 5 × 21 × 1 for bilayers composed of BP with MoS2, MoSe2, WS2, or WSe2.
and $6 \times 11 \times 1$ for bilayers of BP with HfS$_2$ or HfSe$_2$. The break criterion for the electronic self-consistent loop was set to $10^{-5}$ eV. The resulting heterostructure lattices and their binding energy values are included (see supplementary Table S2).

**Results and Discussion**

The band alignment between layers of the vdW stacks can be altered using different materials, 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 and the interlayer bandgap, and the electron affinity of the heterostructure, all important to device and material applications.

**Heterostructure Band Alignment (Zero External Field)**

Figure 1 shows the BP/MoS$_2$ heterostructure with its projected band structure. It is evident from the figure that the CBM of the heterostructure originates from MoS$_2$, while the VBM of the heterostructure originates from BP, indicating a type II alignment. The BP/MoS$_2$ heterostructure has an indirect bandgap, with the CBM and the VBM located between Y and $\Gamma$ (the latter labeled “G”) but at different $k$-points and a simulated bandgap, $E_g = E_c - E_v$, of 0.407 eV. This value is comparable to those of previous works. 21,40,41

The band structure of the other heterostructures is shown in the supplementary data (see Figure S1), while the band alignments of the stacked system are included in Table I and shown in Fig. 2a.

BP/WSe$_2$ and BP/MoSe$_2$ show type I heterostructure band alignments with direct bandgaps of 0.98 eV and 0.99 eV, respectively, located at $\Gamma$. BP/WS$_2$ also shows a type I heterostructure but has an indirect bandgap of 0.67 eV with the CBM at $\Gamma$ and the VBM located at a $k$-point between Y and $\Gamma$. BP/HfSe$_2$ and BP/HfS$_2$ form a type III heterostructure with an overlap of 0.01 and 0.11 eV, respectively, between $E_c$ and $E_v$ with CBM and VBM located at different $k$-points between Y and $\Gamma$.

For each heterostructure, Table I shows the simulated valence and conduction band edge energy values for electronically isolated (but still strained, consistent with the heterostructure) BP and TMD materials, and the corresponding band edge offsets and heterostructure bandgaps to be expected from the electron affinity rule for reference; the same obtained from the calculated layer-projected apparent band edge energy in the heterostructure; and the difference between these two bandgap calculations for each heterostructure. As can be seen, the type of heterostructure formed remains the same by either approach, but the predicted band edge offsets and bandgaps vary significantly, with energy differences varying from a few tens of meV to almost an eV for HfS$_2$/BP.

These differences between the expectations of the electron affinity rule and the as-calculated heterostructure band structures can be attributed significantly to charge redistribution—but not free carrier transfer in the still gapped type I and II undoped systems at 0 K—within and between the layers resulting from heterostructure formation, as shown in Fig. 2b and c, although distortion of he orbitals may make
Table I  Band parameters for strained monolayers of BP and TMDs. $\Delta E_c=E_{c_{BP}}-E_{c_{TMD}}$, $\Delta E_v=E_{v_{BP}}-E_{v_{TMD}}$ are the band offsets for CB and VB energies, respectively

| Stack        | Layer | $E_c$  | $E_v$  | $\Delta E_c$ | $\Delta E_v$ | $E_g$  | $E_g$(Het)–$E_g$(EAR) |
|--------------|-------|--------|--------|--------------|--------------|--------|------------------------|
| MoS$_2$/BP   | MoS$_2$| −4.79  | −6.14  | 0.30         | 1.04         | 0.31   | −4.74                |
|              | BP     | −4.49  | −5.1   | 0.30         | 1.04         | 0.31   | −4.74                |
| MoSe$_2$/BP  | MoSe$_2$| −4.16  | −5.60  | 0.17         | 0.36         | 0.92   | −4.17                |
|              | BP     | −4.33  | −5.248 | 0.17         | 0.36         | 0.92   | −4.17                |
| WS$_2$/BP    | WS$_2$ | −4.43  | −5.97  | −0.08        | 0.86         | 0.61   | −4.41                |
|              | BP     | −4.5   | −5.111 | 0.08         | 0.86         | 0.61   | −4.41                |
| WSe$_2$/BP   | WSe$_2$| −3.84  | −5.38  | −0.49        | 0.14         | 0.91   | −3.87                |
|              | BP     | −4.33  | −5.238 | 0.49         | 0.14         | 0.91   | −3.87                |
| HfS$_2$/BP   | HfS$_2$| −6.09  | −7.06  | 1.51         | 1.99         | −1.01  | −5.78                |
|              | BP     | −4.59  | −5.08  | 1.51         | 1.99         | −1.01  | −5.78                |
| HfSe$_2$/BP  | HfSe$_2$| −5.70  | −6.57  | 1.26         | 1.36         | −0.49  | −5.49                |
|              | BP     | −4.44  | −5.21  | 1.26         | 1.36         | −0.49  | −5.49                |

In the simulated heterostructure, BP and the TMD layer-projected band edge energy values are used for $E_c$ and $E_v$. $E_g$(Het) is the bandgap obtained from simulation of the heterostructure as a whole, while $E_g$(EAR) is the bandgap of the heterostructure obtained from the simulation of the isolated (but identically strained) monolayers using the electron affinity rule (EAR). The text highlighted in gray indicates the material and associated band edge energy defining the CBM and VBM of the heterostructure. All energy values are in eV, and band edge energy values are referenced to the vacuum level.

Fig. 2  (a) DFT-calculated band alignment of BP/TMD heterostructures relative to the vacuum level, along with schematic illustration of the migration of photogenerated electrons and holes (such as in photodiodes) in type I and II heterostructures, and of tunneling in type III heterostructures. (b) Variation in the charge redistribution (in units of electron charge magnitude) between layers ($\Delta q$) as a function of the workfunction difference between the TMD monolayer ($\phi_{TMD}$) and the BP monolayer ($\phi_{BP}$). Positive $\Delta q$ indicates electron redistribution from the BP to the TMD. (c) The $x$–$y$ plane-averaged electron density difference along the $z$ direction of the BP/TMD heterolayer. The shaded region in (c) represent the interlayer spacing ($d$)
a quantitative contribution to the band structure changes as well, and the effects cannot be entirely decoupled. The work function for each isolated but strained monolayer is evaluated as in\textsuperscript{5}. Figure 2c illustrates the charge density difference along \( z \), \( \Delta \rho (z) \), defined as,

\[
\Delta \rho (z) \equiv \int \rho _{S} (x, y, z) dx dy - \int \rho _{BP} (x, y, z) dx dy - \int \rho _{TMD} (x, y, z) dx dy,
\]

where \( \rho _{S} \), the density of the heterostructure stack, and \( \rho _{BP} \) and \( \rho _{TMD} \) are the densities of the isolated BP and TMD layers, respectively. The net charge transfer between layers of Fig. 2b is calculated using Bader charge analysis included with VASP. Bader charge analysis approximates the charge associated with an atom according to Bader partitioning, where the surfaces between atoms are defined as the surfaces along which the gradient of the charge density vanishes.

Note, however, that unlike the case for an interface between two semi-infinite pieces of three-dimensional materials, it cannot be assumed that the band alignment between these 2D materials is independent of their environment of surrounding materials. For example, for a test heterostructure of MoS\textsubscript{2}-BP-MoS\textsubscript{2}, the heterostructure bandgap is increased by 55 meV in these simulations (qualitatively opposite what would be expected from any state splitting due to coupling between the electronic states of the MoS\textsubscript{2} layers through the BP), still further from the electron affinity rule. Put another way, changing the environment on one side of the BP from vacuum to MoS\textsubscript{2} has a significant impact on the band alignment on the other side. However, when we considered a test heterostructure of BP-MoS\textsubscript{2}-BP, the calculated band alignments were almost same. Similar conclusions can be derived by considering a freestanding BP, BP-MoS\textsubscript{2}, and MoS\textsubscript{2}-BP-MoS\textsubscript{2}, and a freestanding MoS\textsubscript{2}, MoS\textsubscript{2}-BP, and BP-MoS\textsubscript{2}-BP, where the projected bandgap of BP changes in each case by approximately 200 meV with the change in environment, while for MoS\textsubscript{2}, the projected bandgap is altered by 20 meV. To understand this relative insensitivity in the latter case, note that the charge redistribution of Fig. 2c occurs primarily between and about the most proximate atoms of the two intrinsic material layers, which are the chalcogenide atoms in the case of MoS\textsubscript{2}, as can be seen in Fig. 2b, while the near-band-edge band structure of TMDs is dominated by the central transition metal atoms.\textsuperscript{7} These findings are consistent with the results of prior works\textsuperscript{6} and suggest that TMDs may be unique in offering such strong isolation between the opposite sides of 2D materials.

### Impact of Applied Electric Field

The impact of an applied electric field oriented normal to the layer stack, \( E \), on the electrostatic potential and the bandgap of the heterostructure, \( E _{g} \), is now addressed. A positive (negative) applied field—with the field direction defined as positive from BP to MoS\textsubscript{2}—produces a potential variation, as seen in Fig. 3a, and a net electron shift to (from) the BP from (to) MoS\textsubscript{2}. The applied field is significantly screened within the bilayer, and even more so within the individual MoS\textsubscript{2} and the BP material layers. The effective static/low frequency dielectric constant for the bilayer (defined here considering the thickness of the bilayer as that of two material layers as well as the vdW gap between the layers and one-half that vdW gap on each side of the bilayer system) is approximately 4.5 and varies slightly with applied normal electric field (Fig. 3b). We note that when we allow the atomic structure to relax with the applied electric field, we didn’t find a significant change in the dielectric constant within the margin of error of the simulations. Despite this dielectric screening, the vdW stack bandgap can be adjusted quantitatively and qualitatively among bandgap types with reasonable applied fields, as shown in Fig. 3c.

A positive electric field of approximately 0.15 V/Å converts the heterostructure to type I with the bandgap defined by BP, while a negative applied electric field of approximately \( \leq -0.13 \) V/Å, leads to a metallic type III structure, with the valence band of BP slightly overlapping the conduction band of MoS\textsubscript{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,\textsuperscript{4} reconfigurable FETs,\textsuperscript{29} TFETs,\textsuperscript{22} and electro-optical modulators.\textsuperscript{43}

### 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.\textsuperscript{7,11} Here, tensile (positive) and compressive (negative) strain, \((a-a_0)/a_0\), are considered. (To achieve compressive strain in practice, 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\%\textsuperscript{45}, while for BP this transition is observed for compressive strain of about 9\% and tensile strain of \(\sim 20\%\textsuperscript{46}\). (Experimentally, MoS\(_2\) can sustain uniaxial tensile strain greater than 11\%,\textsuperscript{17} and BP has demonstrated capability to withstand tensile strain up to 30\% in the zigzag direction and 27\% in the armchair direction\textsuperscript{11,31}).

To understand the impact of biaxial strain on BP/MoS\(_2\) 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 Fig. 4. Considering the apparent bandgaps in Fig. 5 as a function of strain and atom-projected density of states (DOS) in MoS\(_2\) and BP, the visually apparent VBM in MoS\(_2\) is dominated by the \(d_{z^2}\) orbital of Mo and, to a lesser degree, the \(p_z\) orbital of S.\textsuperscript{7} The apparent CBM within MoS\(_2\) 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 the \(p_{x}, p_{y}\), and \(s\) orbitals as well.

Figure 5a shows the change in band offset with applied strain, and the projected bandgap of BP and MoS\(_2\) is shown in Fig. 5b. As mentioned previously, the bond length increases with biaxial strain, and the MoS\(_2\) bandgap

![Fig. 3](image-url) **Fig. 3** (a) \(x-y\) plane-averaged potential and electric field as a function of position \(z\) for an applied electric field \((E)\) of 0.15 V/A normal to the stack, where the pink shaded region corresponds to the regions of the MoS\(_2\) layer as defined in the text, (b) Relative dielectric constant \((\varepsilon)\) of the heterostructure as a function of applied electric field obtained from \(\varepsilon_\text{rel} = \varepsilon_\text{ext} / \varepsilon_\text{int}\)\textsuperscript{44}, where \(\varepsilon_\text{ext} = -\partial V_{\text{ext}} / \partial z\) and \(\varepsilon_\text{int} = -\partial V_{\text{int}} / \partial z\) are the average values of the MoS\(_2\) external and internal fields, respectively, as illustrated in (a) via the dashed lines superimposed on the \(x-y\) plane-averaged potential. (c) The bandgap and type of the BP/MoS\(_2\) heterostructure as a function of a normal electric field. The heterostructure can be tuned from type III at negative fields (approximately \(\sim 0.13\) V/A) to type I at positive fields (approximately \(\sim 0.15\) V/A). In (b) and (c), “relaxed” and “unrelaxed” refer to allowing the atomic structure to relax under the applied electric field or not, respectively. (Note that for the results of this figure (only), slightly altered DFT mixing parameters were used to achieve converge under all considered applied fields.)

![Fig. 4](image-url) **Fig. 4** Projected density of states (DOS) for orbitals in BP/MoS\(_2\) with biaxial strain of \(-2\%\), \(0\%\), and \(2\%\) for \(d_{z^2}\), \(d_{x^2-y^2}\), and \(d_{xy}\) of Mo; \(p\) and \(s\) orbitals 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 (Color figure online)
decreases, consistent with reduced orbital overlap among the atoms. However, the bandgap of BP increases with biaxial tensile strain due to the decrease in the 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\textsuperscript{11} and explained theoretically\textsuperscript{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, Fig. 5b shows that as strain varies from $-5\%$ to $5\%$, the bandgap 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 (Fig. 5c) 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\textsubscript{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\textsubscript{2} stack, again originating from the BP, shifts towards the $\Gamma$-point, while for compressive strain it shifts towards the Y-point. As for the CBM, while the BP/MoS\textsubscript{2} stack remains type II with strain, the CBM originates from MoS\textsubscript{2}, and the k-space position located along $\Gamma$ to Y is essentially independent of strain. However, when the BP/MoS\textsubscript{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 $\Gamma$-point.

Layer Engineering

Use of multilayer BP has proven beneficial due to its direct bandgap, high mobility, anisotropic electronic properties, and higher sensitivity as compared with other 2D materials including monolayer BP.\textsuperscript{6,10,12,15} Few-layer BP can perform better than single-layer BP because of its higher carrier density, lighter carrier effective mass, and weaker scattering.\textsuperscript{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.\textsuperscript{35} Multilayer BP with MoS\textsubscript{2} could be useful for low-voltage TFETs. Multilayer BP with WSe\textsubscript{2}/MoS\textsubscript{2} have shown applicability for MIR light-emission applications.\textsuperscript{27} The change in the workfunction of BP with the stacking of BP layers possibly could be utilized for tuning contact resistance.\textsuperscript{12,47}

The variation in the band energy and alignment of the heterostructure with the number of BP layers varying from two to four is shown in Fig. 6a, b, and 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 energy, respectively.\textsuperscript{6,15} As a result, the bandgap decreases with increased number of BP layers,\textsuperscript{12,15} varying from 0.4 eV in one layer (1L) BP/MoS\textsubscript{2} to only 0.03 eV in four-layer (4L) BP/MoS\textsubscript{2}. Table II provides the projection of the CBM and VBM onto the individual layers, showing a type II to type I transition from 3L-BP/MoS\textsubscript{2} to 4L-BP/MoS\textsubscript{2} and substantial delocalization of the VBM and—for the type I alignment at least—CBM states among the BP layers.

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 heterostructures through DFT simulations. Charge density analysis demonstrates electron redistribution between BP and the TMD layers, from BP to the TMD except in the case of WSe\textsubscript{2} where the redistribution is in the opposite direction, under no applied bias due to workfunction difference between the materials. This redistribution substantially alters the band alignment quantitatively from the expectations of the electron affinity rule, although the alignment type remains the...
same. By either approach, a type I alignment is obtained for BP/WSe$_2$, BP/MoSe$_2$, and BP/WS$_2$, type II alignment is obtained for BP/MoS$_2$, and a type III alignment for BP/HfS$_2$ and BP/HfSe$_2$ under our simulation conditions. Adding biaxial strain affects both the interlayer and intralayer charge distribution and coupling among orbitals due to variation in bond lengths and angles. Moreover, simulation of BP/MoS$_2$ heterostructures suggests that band alignment can be tuned among all types, I, II and III, via an applied layer-normal electric field, and that it can be varied widely with strain or by increasing the number of BP layers. Such tunability offers flexible application to electron–hole bilayer-TFETs, reconfigurable FETs, electro-optical modulators, rectifier diodes, contacts, photoconductors, and light-emitting devices.

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Conflict of interest The authors declare that they have no conflict of interest.

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