The role of Anderson’s rule in determining electronic, optical and transport properties of transition metal dichalcogenide heterostructures†

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Two-dimensional (2D) transition metal dichalcogenides (TMDs) MX2 (M = Mo, W; X = S, Se, Te) possess unique properties and novel applications in optoelectronics, valleytronics and quantum computation. In this work, we performed first-principles calculations to investigate the electronic, optical and transport properties of the van der Waals (vdW) stacked MX2 heterostructures formed by two individual MX2 monolayers. We found that the so-called Anderson’s rule can effectively classify the band structures of heterostructures into three types: straddling, staggered and broken gap. The broken gap is gapless, while the other two types possess direct (straddling, staggered) or indirect (staggered) band gaps. The indirect band gaps are formed by the relatively higher energy level of Te-d orbitals or the interlayer couplings of M or X atoms. For a large part of the formed MX2 heterostructures, the conduction band maximum (CBM) and valence band minimum (VBM) reside in two separate monolayers, thus the electron–hole pairs are spatially separated, which may lead to bound excitons with extended lifetimes. The carrier mobilities, which depend on three competitive factors, i.e. elastic modulus, effective mass and deformation potential constant, show larger values for electrons of MX2 heterostructures compared to their constituent monolayers. Finally, the calculated optical properties reveal strong absorption in the ultraviolet region.

1 Introduction

The family of two-dimensional (2D) materials has grown rapidly due to their unique properties, different from their 3D counterparts. A wide range of 2D materials, e.g. graphene,1,2 BN,3,4 transition metal dichalcogenides (TMDs),5,6 black phosphorus,7–9 etc., have been proposed and are under intense investigations. Among these, transition metal dichalcogenides, with the formula MX2 (where M is a transition metal and X is a chalcogen), are prominent due to their finite direct band gaps with strong optoelectronic responses,10 large on–off ratios and high carrier mobilities.11,12 Furthermore, a spin–orbit driven splitting of the valence band was found in 2H monolayer TMDs due to the lack of inversion symmetry, which ultimately allows for valley-selective excitation of carriers.13–15 In addition, the electronic properties of TMDs can be tuned by strain,16 multilayers,17 nanostructuring18 and electrostatic gating,19 or by combining individual 2D monolayers into van der Waals (vdW) stacked heterostructures.20 The vdW heterostructures can be obtained by transfer or direct epitaxial growth.21,22 The interface of the heterostructures is atomically sharp, with a two-atom thick junction region,21 and the interlayer coupling intensity can be further tuned. Thus, vdW heterostructures open up many possibilities for creating new TMD material systems with rich functionalities and novel physical properties.23 When two different atomically thin layers are stacked and bound by van der Waals forces to form MX2 heterostructures, the electronic properties of the formed vdW MX2 heterostructures will be significantly affected by the band alignment of the monolayer MX2, forming various band structures different from the monolayer counterpart, which can be direct- or indirect-band gap, or metallic materials.24

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8cp05522j
Moreover, as we show here, a large proportion of vdW MX\textsubscript{2} heterostructures possess the band structures with the conduction band maximum (CBM) and valence band minimum (VBM) residing in different monolayers. Due to the separate spatial locations of the CBM and VBM, the photon-generated electron-hole pairs are therefore spatially separated, resulting in much longer exciton lifetimes and the possible existence of interlayer exciton condensation,\textsuperscript{25} which might help develop two-dimensional lasers, light-emitting diodes and photovoltaic devices.\textsuperscript{26,27} The strong interlayer coupling between the two individual MX\textsubscript{2} monolayers in a MoS\textsubscript{2}–WSe\textsubscript{2} hetero-bilayer was shown to lead to a new photoluminescence (PL) mode.\textsuperscript{28} Hong et al. have also investigated the ultrafast charge transfer in a MoS\textsubscript{2}–WS\textsubscript{2} heterostructure\textsuperscript{29} and found the charge-transfer time is on the femtosecond scale, much smaller than that in monolayer MoS\textsubscript{2} or WS\textsubscript{2}. Furthermore, the recombination times of interlayer charge transition are tunable for different stacking orders of MoS\textsubscript{2}–WS\textsubscript{2} heterostructures, being 39 ps for the one obtained by vertical epitaxial growth and 1.5 ns for the randomly-stacked bilayer.\textsuperscript{30} Finally, tunneling transistors\textsuperscript{31} and photovoltaic detectors\textsuperscript{32} based on a MoS\textsubscript{2}/MoTe\textsubscript{2} heterostructure show excellent performance.

Until now, most researches on MX\textsubscript{2} heterostructures focus on S and Se systems. For example, the indirect-to-direct band gap transition and semiconductor-to-metal transition in MoS\textsubscript{2}/MX\textsubscript{2}(M = Mo, Cr, W, Fe, V; X = S, Se) heterobilayers can be realized by tensile strain or an external electrical field.\textsuperscript{33} Hetero-layered TMDs (MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2} and WSe\textsubscript{2}) with different stacking modes exhibit tunable direct band gaps.\textsuperscript{24} Furthermore, Kang et al. calculated the band offsets of MX\textsubscript{2} heterostructures and found that the MoX\textsubscript{2}/WX\textsubscript{2} (X = S, Se) heterostructures have type-II band alignment.\textsuperscript{34} However, a systematic study on vdW MX\textsubscript{2} heterostructures including a Te system is still lacking. In this paper, using first-principles calculations, we theoretically investigate the electronic, mechanical, transport and optical properties of vdW MX\textsubscript{2} (M = Mo, W; X = S, Se, Te) heterostructures with different stacking modes. The band alignment and interlayer coupling can result in much smaller band gaps of MX\textsubscript{2} heterostructures compared to those of the constituent MX\textsubscript{2} monolayers, and a direct to indirect band gap transition may occur. The excellent mechanical properties show the structural stability of the optimized vdW MX\textsubscript{2} heterostructures. The theoretical values for the transport properties are predicted based on deformation-potential theory. Furthermore, to demonstrate the contribution from monolayer MX\textsubscript{2}, the relative relationship between MX\textsubscript{2} heterostructures and the constituent monolayers with respect to the elastic modulus, deformation-potential constants and effective masses is studied in detail. Finally, we also point out the strong optical absorption of the vdW MX\textsubscript{2} heterostructures in the ultraviolet region.

## 2 Methodology

All calculations are performed using the Vienna ab initio simulation package (VASP) based on density functional theory (DFT).\textsuperscript{15} The exchange–correlation energy is described by the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) parameterization. We choose the DFT-D2/D3 approach to involve the long-distance van der Waals (vdW) interactions.\textsuperscript{36–39} The calculation is carried out using the projector-augmented-wave (PAW) pseudopotential method with a plane-wave basis set and a kinetic energy cutoff of 600 eV. A 15 × 15 × 1 \Gamma-centered k-mesh is used during structural relaxation for the unit cell until the energy differences converge to within 10\textsuperscript{-6} eV, with a Hellman–Feynman force convergence threshold of 10\textsuperscript{-4} eV Å\textsuperscript{-1}. The vacuum size is larger than 25 Å between two adjacent atomic layers to eliminate artificial interactions between them. The electronic band structures of the vdW layered heterostructures are further verified by calculations using a hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional,\textsuperscript{40,41} which improves the precision of band structures by reducing the localization and delocalization errors of PBE and Hartree–Fock (HF) functionals. Here, the mixing ratio is 25% for the short-range HF exchange. The screening parameter is 0.2 Å\textsuperscript{-1}.

As we know, electron–phonon scatterings play an important role in determining the intrinsic carrier mobility \( \mu \) of 2D vdW MX\textsubscript{2} heterostructures, in which the scattering intensities by acoustic phonons are much stronger than those by optic phonons in two-dimensional materials.\textsuperscript{42} Therefore, the deformation-potential theory for semiconductors, which considers only longitudinal acoustic phonon scattering processes in the long-wavelength limit\textsuperscript{43–46} and was originally proposed by Bardeen and Shockley,\textsuperscript{47} can be used to calculate the intrinsic carrier mobility of 2D materials. In the long-wavelength limit, the carrier mobility of 2D semiconductor can be written as:\textsuperscript{46,48,49}

\[
\mu = \frac{2e\hbar^2C}{3k_B T |m^*| D^5},
\]

where \( e \) is the electron charge, \( \hbar \) is the reduced Planck's constant and \( T \) is the temperature (equal to 300 K throughout the paper). \( C \) is the elastic modulus of a uniformly deformed crystal by strain and derived from \( C = [\varepsilon^2 E/\partial^2(\Delta l/l_0)/S_{0}], \) in which \( E \) is the total energy, \( \Delta l \) represents the change of lattice constant \( l_0 \) along the strain direction and \( S_{0} \) is the lattice area at equilibrium for a 2D system. \( m^* \) is the effective mass given by \( m^* = h^2[C^2(E(k)/\partial k^2)^{-1} \) (k is wave-vector, and \( E(k) \) is the energy). The spacing of the k-mesh we used to calculate the effective masses is 0.02 Å\textsuperscript{-1}. In addition, \( D_{1} \) is the deformation potential (DP) constant defined by \( D_{1}(b) = \Delta E^{\text{BMVM}}/(\Delta l/l_0), \) where \( \Delta E^{\text{BMVM}} \) is the energy shift of the band edge with respect to the vacuum level under a small dilation \( \Delta l \) of the lattice constant \( l_0 \).

## 3 Results and discussion

### 3.1 Geometric structures of hetero-bilayer MX\textsubscript{2}

Generally, MX\textsubscript{2} crystals have four stable lattice structures, i.e., 2H, 1T, 1T’ and 3R,\textsuperscript{59} with the first being the dominant one in nature at room temperature. Most MX\textsubscript{2} crystals, like MoS\textsubscript{2} and WSe\textsubscript{2} with a stable 2H phase (1H for monolayer),...
have been studied widely.\textsuperscript{51} For 2H-phase MX\textsubscript{2} crystals, the M atoms and X atoms are located in different layers, which can be described by the point group $D\textsubscript{3h}$. While for the 3R-phase unit cell shown as Fig. 1(b and d), one M atom is eclipsed by the X atoms above and the other one is located in the hexagonal center, leading to the AB Bernal stacking. In fact, the electronic structure of the MX\textsubscript{2} heterostructure is sensitive to the stacking modes, due to the different interlayer interactions. AA and AB stacking structures possess the weakest and strongest interlayer electronic coupling, respectively.\textsuperscript{52} For simplicity, we only consider these two stacking modes. However, some interesting properties, e.g. the relatively constant change in both electronic and mechanical couplings at twist angles between $0^\circ$ (AA stacking) and $60^\circ$ (AB stacking) found in twisted MoS\textsubscript{2} bilayers\textsuperscript{53} and so on, may not be captured by these two modes and are beyond the scope of our work. One stacking type can be geometrically transformed to the other by horizontal sliding or by rotation around the vertical axis. For MX\textsubscript{2} heterstructures with two different constituent monolayer MX\textsubscript{2} crystals, both AA and AB stacking crystals possess a lower symmetry of $C\textsubscript{3v}$ point group, with the symmetry operations of $C\textsubscript{3}$ and vertical mirror reflection $\sigma\textsubscript{v}$,\textsuperscript{54} rather than the mirror reflection operation $\sigma\textsubscript{h}$ in the horizontal plane.

To determine the energetically stable structure before geometry optimization, an interlayer-distance optimization algorithm is implemented to reach an optimized $d_1$ (defined in Fig. 1(a)) using the universal binding energy relation (UBER) method, which provides a simple universal form for the relationship between binding energy and atomic separation.\textsuperscript{55,56} The optimized interlayer distance is predicted from a series of relaxed models with different values of $d_1$ (from 5 to 8 Å). We then calculate the surface adhesion energy $W\textsubscript{ad}$ for all 30 types of 2D vdW MX\textsubscript{2} heterostructure under investigation here (e.g. MoS\textsubscript{2}/WSe\textsubscript{2} hetero-bilayer),

$$W\textsubscript{ad} = \frac{E\textsubscript{MoS\textsubscript{2}} + E\textsubscript{WSe\textsubscript{2}} - E\textsubscript{MoS\textsubscript{2}/WSe\textsubscript{2}}}{A},$$

where $A$ is the interface area and $E\textsubscript{MoS\textsubscript{2}}$, $E\textsubscript{WSe\textsubscript{2}}$, and $E\textsubscript{MoS\textsubscript{2}/WSe\textsubscript{2}}$ are the total energies of the monolayer MoS\textsubscript{2} and WSe\textsubscript{2} and the MoS\textsubscript{2}/WSe\textsubscript{2} heterostructure, respectively. The optimal interlayer distances $d_1$ can be obtained by maximizing the value of $W\textsubscript{ad}$. Then, further structure optimizations are implemented without any external constraints. Furthermore, the formation energies $E \ (E = E\textsubscript{AB} - E\textsubscript{A} - E\textsubscript{B})$ are listed in Table S2 (ESI\textsuperscript{†}). The negative values for the formation energies also confirm the stability of our structures and, for most MX\textsubscript{2} heterostructures, AA stacking is more energetically favorable.

The calculated lattice constants $a$ and interlayer distances $d$ for the above-mentioned 30 types of 2D MX\textsubscript{2} heterostructure are summarized in Table 1 and are in good agreement with previous theoretical and experimental results.\textsuperscript{57–60} As shown in Table 1, the optimized interlayer distances of AA stacking structures are larger than those of the corresponding AB
stacking structures. This is due to the fact that, in AB structures, the X atoms are not aligned along the vertical axis and a shorter interlayer distance leads to a smaller total energy. Furthermore, the change of stacking type of the heterostructures will affect the interlayer interactions of M or X atoms.

3.2 Electronic band structure of hetero-bilayer MX₂

Previous studies have revealed that monolayer MX₂ possesses a direct band gap and both the CBM and VBM are located at the K point in the first Brillouin zone. Owing to the lack of inversion symmetry and the strong spin–orbit coupling (SOC), the valence bands possess a significant spin–orbit splitting at the K valleys. The band alignment for MX₂ shows the following trends (see Fig. 2(b)): (1) for common-X systems, the band gaps of MoX₂ are larger than that of WX₂, and the CBM and VBM of WX₂ are higher than those of MoX₂; (2) for common-M systems, an increase in the atomic number of X results in a shallower anion p orbital and thus a shift of the VBM to higher

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<th>System (Anderson)</th>
<th>Stacking type</th>
<th>a (Å)</th>
<th>d₁ (Å)</th>
<th>d₂ (Å)</th>
<th>Band type</th>
<th>E_{PB} (eV)</th>
<th>E_{HSE} (eV)</th>
<th>E_{SOC} (eV)</th>
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<td>MoS₂–WSe₂(II)</td>
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<td>3.215</td>
<td>6.164</td>
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<td>0.75/1.33/0.53</td>
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Fig. 2 (a) Various possible band-edge lineups in semiconductors A and B. (b) Band alignment for monolayer MX₂. The vacuum level is taken as 0 reference.
energy levels, finally leading to decreased band gaps.\textsuperscript{66} To understand these two trends in band alignment, the atomic orbital composition of the states should be taken into consideration. Taking MoS\textsubscript{2} as an example, the CBM of MoS\textsubscript{2} is mainly composed of the d\textsubscript{z\textsuperscript{2}} orbital of Mo and the p\textsubscript{x} and p\textsubscript{y} orbitals of S, whereas the VBM mostly consists of the d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} and d\textsubscript{xy} orbitals of Mo.

For the hetero-bilayer MX\textsubscript{2} crystals constructed from two MX\textsubscript{2} monolayers, the formation of their band structures can be understood by the so-called Anderson’s rule, which provides a scheme for the construction of energy band diagrams for heterostructures consisting of two semiconductor materials.\textsuperscript{67} According to Anderson’s rule, the vacuum energy levels of the two constituent semiconductors on either side of the heterostructure should be aligned at the same energy,\textsuperscript{68} and there are three types of possible band-edge lineups: straddling, staggered and broken gap, as shown in Fig. 2(a). For type I heterostructures, the CBM and VBM mainly consist of the orbitals of semiconductor B, which possesses a smaller band gap compared to semiconductor A. Thus, the band type of the heterostructure is consistent with the smaller-gap material. For type II heterostructures, the VBM and CBM around the Fermi

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**Fig. 3** Band structures of the AA and AB stacking vdW MX\textsubscript{2} heterostructures and atomic orbital weights in the energy bands. The blue and orange circles represent d orbitals of the cations. The green and red circles represent p\textsubscript{x} + p\textsubscript{y} and p\textsubscript{z} orbitals of the anions, respectively. The size of each circle is proportional to the weight of the atomic orbital. (a and b) Type I band alignment system: WTe\textsubscript{2}–WSe\textsubscript{2} and MoTe\textsubscript{2}–WSe\textsubscript{2} hetero-bilayer. (c and d) Type II band alignment system: MoS\textsubscript{2}–WSe\textsubscript{2} and MoSe\textsubscript{2}–WSe\textsubscript{2} hetero-bilayer. (e and f) Type III band alignment system: WTe\textsubscript{2}–MoS\textsubscript{2} and WTe\textsubscript{2}–WS\textsubscript{2} hetero-bilayer.
level reside in two separate semiconductors, and the formed heterostructure still possesses a small direct or indirect band gap. As for type III heterostructures, the locations of the CBM and VBM are similar to those of type II heterostructures, but band gap does not exist, and the formed heterostructure is a semi-metal. It should be noted that, for type II and type III heterostructures, since the CBM and VBM may locate in different semiconductors, the photon-generated excitons are thus spatially separated, which will suppress the recombination of electron–hole pairs and extend the exciton lifetime compared with the corresponding individual semiconductors.

The band structures for the vdW MX₂ heterostructures are calculated using the PBE and HSE06 method and the results, i.e., band types and band gaps, are shown in Table 1. The direct band gap at the K point for monolayer MX₂ is transformed into three types of band gap when a hetero-bilayer MX₂ crystal is formed, i.e., direct, indirect (M–K, Γ–K, K–Q) and zero band gap or overlapping bands, according to the calculated results shown in Table 1 and the above-mentioned analyses based on Anderson’s rule. The formation types of band gap for the vdW MX₂ heterostructures categorized according to Anderson’s rule are also shown in Table 1. The classification of the band types according to Anderson’s rule is called as Anderson band type hereafter. It is shown in Table 1 that the Anderson band types for the vdW MX₂ are determined by the constituent monolayer MX₂ irrespective of the stacking manner. This is probably due to the fact that the VBM/CBM of the hetero-bilayer structure is attributed to the d/p-orbitals of M/X atoms, and the weak vdW interactions will not change the charge distribution of the constituent monolayers significantly, thus the relative CBM/VBM energies of the constituent monolayers will not change.

For simplicity, we first consider the Anderson band type I heterostructure, e.g. band structures for WTe₂–WSe₂ and MoTe₂–WSe₂ hetero-bilayers, shown in Fig. 3(a and b). Generally, as we mentioned above, two monolayer MX₂ crystals with identical M atoms but different X atoms possess different CBM/VBM energy levels, and the crystal with the X atoms with the larger atomic number has a higher energy level CBM or VBM. However, as shown in Fig. 2(b), the CBM energy level of WTe₂ is lower than that of WSe₂, although the atomic number of Te is larger than Se. Such a deviation can be understood by the fact that the bond length d₀,W–Te of WTe₂ is the largest one among those of the monolayer MX₂ crystals, which leads to a small overlap integral V between the d orbitals of the M atoms and the p orbitals of the X atoms for the formation of the CBM due to $V \propto \frac{1}{d_{W–Te}}$, and thus counteracts the increase of the CBM energy level from Se with smaller p orbitals compared to Te. The smaller CBM energy level of WTe₂ ultimately results in the Anderson band type-I alignment of band edges in the WTe₂–WSe₂ hetero-bilayer, leading to a direct band gap at the K point for both AA and AB stacking manners, as shown in Fig. 3(a).

According to Table 1, most of the hetero-bilayer MX₂ crystals are Anderson band type II heterostructures, e.g., hetero-bilayer MoS₂–WSe₂ and MoTe₂–WTe₂. Fig. 3(c) shows the energy band structures of the AA and AB stacking MoS₂–WSe₂ hetero-bilayers, exhibiting direct band gaps of 0.60 eV and 0.75 eV for the AA and AB stacking types, respectively, which are consistent with the previous results. The CBM locates in the MoS₂ layer and the VBM locates in the WSe₂ layer, resulting in the formation of spatially separated electron–hole pairs. Experiments on hetero-bilayer MoS₂–WSe₂ revealed the dramatic quenching of the photoluminescence (PL) intensities and the extended exciton lifetime.
As for the formation of indirect band gaps for type-II heterostructures, there are three types of such indirect band gap, i.e. $M-K$, $\Gamma-K$ and $K-Q$, resulting from the relatively higher energy level of the Te-5p orbital, the relatively stronger $p_z-p_z$ bonds of X atoms in different monolayers and the hybridization of $M-d$ and $X-p$ orbitals, respectively.

As shown in Fig. 3, the valence band at the $M$ point is attributed to the $p_z$ and $p_y$ orbitals of X atoms, and the corresponding energy level for hetero-bilayer MX$_2$ crystals containing Te atoms is larger than those only containing Se or S atoms, since the atomic number of Te is the largest one. Therefore, for hetero-bilayer MTe$_2$-MX$_2$, the valence band energies at the $M$ point significantly increase compared with the hetero-bilayer MS$_2$-MX$_2$ (X $\neq$ Te) or MS$_2$-MX$_2$ (X $\neq$ Te), which subsequently leads to the formation of the $M-K$ indirect band gap, e.g. hetero-bilayer MoTe$_2$-WSe$_2$, as shown in Fig. 3(b).

The valence band at the $Q$ point can be attributed to the inter-layer overlap integral of $p_z$ orbitals of X atoms belonging to different monolayers at the $Q$ point, as shown in Fig. 3. For hetero-bilayer MX$_2$ considered here, the distance between X atoms in different monolayers for the AB stacking hetero-bilayer, i.e. $d_z$ shown in Fig. 1(a and b), is smaller than the corresponding AA stacking hetero-bilayer, as shown in Table 1, thus the energy level of the valence band at the $Q$ point for the former is the higher one, due to $V_{p_z-p_z} \propto 1/d_z^2$. The increase of the energy level of the valence band at $Q$ points sometimes leads to the formation of $\Gamma-K$ indirect band gaps with AB stacking, e.g. AB-stacking MoTe$_2$-WTe$_2$ as shown in Fig. 3(d).

Another indirect band gap ($K-Q$), e.g. MoSe$_2$-WSe$_2$ shown in Fig. S2 (ESI†), is formed by the VBM located at the $K$ point and the CBM located at the $Q$ point between $\Gamma$ and $K$. According to the analysis on the atomic orbitals, the energy level of the valence band at the $Q$ point is formed by the strong hybridization between the Mo-$d$ orbitals and W-$d$ orbitals, which lowers the energy level at the $Q$ point and ultimately leads to the shift of the CBM from the $K$ to $Q$ point. However, the CBM and VBM at $K$ are insignificantly hybridized, due to the higher symmetry and a larger bond length $d_{Mo-W}$ compared to those at the $Q$ point, thus the VBM is fixed at the $K$ point.

The extreme state of staggering is the formation of broken bond gaps, which is also known as the Anderson band type III alignment, as shown in Fig. 2(a). For example, the CBMs of MoS$_2$ and WS$_2$ are much lower than those of other MX$_2$ monolayers and WTe$_2$ possesses the highest VBM, as shown in Fig. 2(b). The band alignment in hetero-bilayer WTe$_2$-MoS$_2$ and WTe$_2$-WS$_2$ thus can be approximately considered as the Anderson band type III alignment, as shown in Fig. 3(e and f). The band overlaps at the $K$ point, changing the heterostructures into metallic phase.

The band gaps of the hetero-bilayer MX$_2$ crystals based on the HSE06 and SOC calculations are also provided in Table 1 and Fig. 4. The negative SOC effects decrease the band gap and the HSE calculations increase the band gap by 0.4–0.6 eV, compared to the PBE calculations. It should be noted that the metallic phases of the hetero-bilayer MX$_2$ crystals, i.e. the Anderson band type III heterostructures, e.g. hetero-bilayer WTe$_2$-MoS$_2$ and WTe$_2$-WS$_2$ crystals as shown in Fig. 3(e and f), are replaced by direct band gaps based on HSE calculations, which means that the hetero-bilayer MX$_2$ crystals considered here do not possess Anderson band type III alignment.

In summary, the CBM state at the $K$ point is weakly localized and not usually affected by the stacking types. The VBM may shift from the $K$ to $\Gamma$ point in regard to different stacking types due to the inter-layer electronic coupling. Kang et al. have stated that the inter-layer coupling strength of the $\alpha$ configuration at the $\Gamma$ point is the strongest among the heterostructures with arbitrary in-plane angular rotations to push the band energy at the $\Gamma$ point up to a highest level. In contrast, the inter-layer coupling strength of AA configuration (0 degree) is the weakest. This argument can be proved by the Moiré pattern of these heterostructures to demonstrate that the pattern becomes smaller and more complex with the rotation angle $\theta$ increasing. Moreover, this Moiré pattern-induced wave function localization of the VBM will significantly affect the carrier mobilities of MX$_2$ heterostructures and will be discussed in the next section.

3.3 Mechanical properties and transport properties of hetero-bilayer MX$_2$

Since the MX$_2$ heterostructures under consideration here possess $C_{3v}$ symmetry, the number of independent second-order elastic coefficients $c_{ij}$ is five and $c_{11} = c_{22}$. The calculated elastic coefficients of all MX$_2$ heterostructures are shown in Table S2 (ESI†) and all the vdW MX$_2$ heterostructures are mechanically stable, according to the Born criteria: $C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0, C_{44} > 0$  (3)

The 2D Young’s moduli of all MX$_2$ heterostructures, given by $Y_{2D} = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}}$, are listed in Table 2. The 2D Young’s modulus for monolayer MX$_2$ crystals decreases from MS$_2$ to MSe$_2$ to MTe$_2$, which is due to the fact that the strength of $d_{x^2-y^2}-p$ orbital coupling, which forms M-X bonding, becomes weaker with an increase of the atomic number of chalcogen. The calculated 2D Young’s moduli for monolayer MX$_2$ crystals are shown in Table S1 (ESI†). The contributions to the mechanical properties of MX$_2$ heterostructures can be roughly considered from constituent monolayer MX$_2$ crystals and the weak interlayer bonding.

The Young’s moduli of the MTe$_2$-MX$_2$ heterostructures are lower than others due to the weakest $Y_{2D}$ of monolayer MTe$_2$ among the monolayer MX$_2$ crystals considered here. Meanwhile, the Young’s moduli of the MX$_2$ heterostructures are a little lower than the sum of those of the constituent monolayer MX$_2$ crystals, which means that the contribution from the interlayer bonding to the total Young’s modulus is negative. The Poisson’s ratio is given by $\nu_{2D} = \frac{c_{12}}{c_{22}}$, which describes the lateral deformation when applying uniaxial strains, is calculated and shown in Table 2. Generally materials with a high Poisson’s ratio possess good plasticity. The Poisson’s ratios for the MX$_2$ heterostructures are numerically close to each other except WTe$_2$-MX$_2$, with the lowest Poisson’s ratio
of 0.20 of monolayer WTe₂ crystal among the monolayer MX₂ crystals (see Table S1, ESI†).

The effective masses for electrons \( m_e^* \) and holes \( m_h^* \) of vdW MX₂ heterostructures along armchair and zigzag directions are calculated, and the results along the armchair direction are shown in Table 2. The values of \( m_e^* \) for AA-stacking MX₂ heterostructures are close to those of the corresponding AB-stacking ones, however, the values of \( m_h^* \) for AA-stacking heterostructures are obviously deviated from those of AB-stacking ones, e.g. MoS₂–WS₂ and MoTe₂–WTe₂ heterostructures, especially when the band types for AA and AB stackings are different (direct vs. indirect), as shown in Tables 1 and 2. Such phenomena can be understood by the fixed CBM (electrons) at the \( K \) or \( \Gamma \) point for all the MX₂ heterostructures, and the transition of the VBM (holes) from the \( K \) point to the \( M \) or \( \Gamma \) point for MX₂ heterostructures with an indirect band gap.

As mentioned above, the band structures of MX₂ heterostructures can be roughly decomposed into those of the constituent monolayer MX₂ crystals, according to Anderson’s rule, which also leads to the formation of the effective masses of electrons and holes for MX₂ heterostructures. Fig. 5 shows the effective masses of electrons and holes for MX₂ heterostructures and the corresponding constituent monolayer MX₂ crystals along all directions, taking WTe₂–WS₂ and MoS₂–WS₂ hetero-bilayer as examples without loss of generality.

The WTe₂–WS₂ hetero-bilayer belongs to Anderson band type I and the CBM and VBM are attributed to those of the monolayer WTe₂ crystal. It is shown in Fig. 5(a and b) that the effective masses of electrons and holes for the WTe₂–WS₂ hetero-bilayer are close to those of monolayer WTe₂ crystals. However, for MoS₂–WS₂ hetero-bilayers (Anderson band type II), since the CBM is attributed to that of monolayer MoS₂ crystals and the VBM is attributed to that of monolayer WS₂ crystals, the \( m_e^* \) value for the MoS₂–WS₂ hetero-bilayer is similar to that of monolayer MoS₂ and the \( m_h^* \) value is similar to that of monolayer WS₂, as shown in Fig. 5(c and d).

According to eqn (1), the third factor determining carrier mobilities \( \mu \) is the deformation potential constant, \( D_{el} \), which describes the scatterings of electrons/holes by longitudinal acoustic phonons. The calculated \( D_{el} \) values for MX₂ heterostructures and monolayer MX₂ crystals are shown in Table 2 and Table S1 (ESI†), respectively. By comparison, it is found that the deformation potential constants of MX₂ heterostructures are larger overall than those of the constituent monolayer MX₂, which means that the formation of the vdW MX₂ heterostructures increases the electron–acoustic phonon coupling, leading to the increase of deformation potential constant \( D_0 \) especially for MoS₂–WS₂ heterostructures.

Since the CBM and VBM of the MX₂ heterostructures can be attributed to the respective band structures of the constituent monolayer MX₂ according to the Anderson rule, the shift of the VBM from the \( K \) point to the \( \Gamma/M \) point will result in a dramatic change of the deformation potential constants and hole effective masses for MX₂ heterostructures with indirect band gaps, e.g. MoTe₂–WTe₂.
In order to figure out the exact contributions from the three factors, i.e. effective masses $m_{e,h*}$, deformation potential constants $D_{e,h}\ell$, and elastic modulus $C$, to the carrier mobilities compared to the constituent monolayer $\text{MX}_2$ crystals, we plot the values of the three factors for constituent monolayer crystals and hetero-bilayer structures in Fig. S4 (ESI†). It is clear that the elastic modulus of hetero-bilayer structures is nearly twice that of the constituent monolayer $\text{MX}_2$ crystals, while the deformation potential constants of hetero-bilayer structures are larger overall or close to the constituent monolayer $\text{MX}_2$ crystals. Moreover, the effective masses of hetero-bilayer structures, mostly determined by the constituent monolayer crystals, are close to those of the constituent monolayer crystals, except some hetero-bilayer structures with VBM points shifted from K to Γ/M, e.g. $\text{MoTe}_2$–$\text{WTe}_2$. Finally, the carrier mobility of electrons and holes along armchair and zigzag directions for the $\text{MX}_2$ hetero-bilayer can be calculated according to eqn (1), as shown in Fig. 6. Fig. 6(a, b) and (c, d) show electron/hole mobilities along the armchair and zigzag directions, respectively. The mobilities for monolayer $\text{MX}_2$ as a contrast are shown as color blocks in the diagonal direction and the color blocks in the lower/upper triangular part correspond to the cases of AA/AB-stacking types. For example, the red block of the 1st row and 4th column in Fig. 6(a) corresponds to the electron mobility along the armchair direction of the AB-stacking $\text{MoS}_2$–$\text{WSe}_2$ heterostructure, i.e. $\mu = 573 \text{ cm}^2 (\text{V s})^{-1}$. The electron mobilities of hetero-bilayer structures are larger overall than those of constituent monolayer $\text{MX}_2$ crystals, and the same situation takes place for the hole mobilities of hetero-bilayer structures with the VBM located at the K point. However, the hole mobilities of hetero-bilayer structures with the VBM located at the Γ/M point are smaller than those of constituent monolayer $\text{MX}_2$ crystals.

The AA stacked $\text{MoTe}_2$–$\text{MoSe}_2$ heterostructure possesses the highest electron mobility along the zigzag direction, i.e. $3658 \text{ cm}^2 (\text{V s})^{-1}$, and the AA stacked $\text{MoSe}_2$–$\text{WSe}_2$ heterostructure possesses the highest hole mobility along the armchair direction, i.e. $3752 \text{ cm}^2 (\text{V s})^{-1}$.

### 3.4 Optical properties of hetero-bilayer $\text{MX}_2$

The optical properties of the vdW MX$_2$ heterostructures are described by the complex dielectric function, i.e. $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric tensor $\varepsilon_2(\omega)$ is determined by a summation over empty band states as follows:

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{k,v,z} \delta(E^z_k - E^v_k - \hbar\omega) \left| \langle \Psi_k^v | \mathbf{u} \cdot \mathbf{r} | \Psi_k^z \rangle \right|^2,$$

(4)

where $\Omega$ is the crystal volume, $\varepsilon_0$ is the vacuum dielectric constant, $\hbar\omega$ represents the photon energy, $v$ and $c$ mean the valence and conduction bands respectively, $\mathbf{u}$ is the polarization vector in the incident electric field, $\mathbf{r}$ is the momentum operator and $\Psi_k$ is the wave function at the $k$ point. The real
part of the dielectric tensor $\varepsilon_1(\omega)$ is obtained by the well-known Kramers–Kronig relation:\cite{83}

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(\omega')\omega'}{\omega^2 - \omega'^2 + i\eta} d\omega',$$

where $P$ denotes the principle value. Based on the complex dielectric function, the absorption coefficient $\alpha(\omega)$ is given by:\cite{84, 85}

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \left\{ \left[ \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right]^{1/2} - \varepsilon_1(\omega) \right\}^{1/2}. \tag{6}$$

In 2D semiconductor materials, the band gap obtained by HSE06 is usually close to the real optical band gap due to the underestimation of the band gap by neglecting excitonic effects.\cite{86} Thus, we only performed HSE06 calculations to obtain

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Fig. 6 The calculated carrier mobilities for the vdW MX$_2$ heterostructures, with the AA stackings in the lower left corner and AB stackings in the upper right corner. The values along the diagonal are the mobilities for monolayer MX$_2$. (a and b) The electron mobilities of the vdW MX$_2$ heterostructures along armchair and zigzag directions, respectively; (c and d) The hole mobilities of the vdW MX$_2$ heterostructures along armchair and zigzag directions, respectively.

Fig. 7 HSE06 calculations of (a) the real part of the dielectric function, (b) the imaginary part of the dielectric function and (c) refractive and (d) optical absorption spectra of AA and AB stacking hetero-bilayer WTe$_2$–WSe$_2$, MoS$_2$–WSe$_2$ and WTe$_2$–MoS$_2$ for incident light with polarization along $a$. 

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optical properties for the hetero-bilayer MX$_2$ under consideration here, which show that all of them are semiconductors with a finite band gap, as shown in Table 1. All the optical constants are calculated for incident radiations with the electric field vector E polarized along the a and b directions, as shown in Fig. 1(c).

Due to the $C_3$ symmetry of the hexagonal structure of the hetero-bilayer MX$_2$, the dielectric function $\varepsilon(\omega)$ possesses the same results along the a and b directions. The $\varepsilon(\omega)$ results for AA and AB stacking types are also close to each other, as shown in Fig. 7(a and b) and Fig. S4 (ESI†), irrespective of the corresponding Anderson band type. The similarity in $\varepsilon(\omega)$ results between AA and AB stacking hetero-bilayer MX$_2$ can be understood by the fact that the band structure of the hetero-bilayer MX$_2$ can be roughly decomposed into the respective band structures of the constituent monolayer MX$_2$ according to Anderson’s rule. Thus, the contribution to the total optical response, i.e. $\varepsilon_2(\omega)$, from absorption of an incident photon $\hbar\omega$ and then transition from $\Psi_+^a$ to $\Psi_+^b$, can be traced back to the behaviors of electrons located within the constituent monolayer MX$_2$. Therefore, the $\varepsilon_2(\omega)$ results for AA and AB stacking hetero-bilayer MX$_2$ probably are similar since they contain identical constituent monolayer MX$_2$ according to eqn (4).

The optical properties of hetero-bilayer MX$_2$, e.g. WTe$_2$–WSe$_2$, MoS$_2$–WSe$_2$ and WTe$_2$–MoS$_2$, are shown in Fig. 7. The main absorption peaks of these three hetero-bilayer MX$_2$ locate in the range of 3.0 to 5.0 eV, i.e. the ultraviolet region, with a refractive range from 2.80 to 4.27 in this region.

4 Conclusion

In this work, we have investigated the structure and electronic, mechanical, transport and optical properties of the vdW MX$_2$ heterostructures using first-principles calculations. The AA and AB stacked hetero-bilayer MX$_2$ exhibit three types of band alignment according to Anderson’s rule, with a wide band gap range between 0 and 2 eV. The main differences between AA and AB stacked hetero-bilayer MX$_2$ lie in the band structure and mechanical properties due to the interlayer coupling, such as the indirect $\Gamma$–K band gap. The band structure of MT$_2$–MX$_2$ will possess a higher valence band at the M point due to the high band energy of the 5p$_\sigma$ orbitals of Te. The type II band alignment of the vdW hetero-bilayer MX$_2$ makes interlayer transitions possible, leading to spatially separated excitons. The transport properties of the vdW MX$_2$ heterostructures are consistent with the symmetry of the geometric structures. It should be noted that the carrier mobilities of the hetero-bilayer MX$_2$ are often higher than those of monolayer MX$_2$, attributed to the higher elastic modulus for the hetero-bilayer MX$_2$, while the hetero-bilayer MX$_2$ with an indirect band gap possesses much lower hole mobilities due to the increased effective masses and deformation potential constants. Furthermore, the calculated optical properties show strong optical absorption for vdW MX$_2$ heterostructures, enabling novel applications in optoelectronics from the visible to ultraviolet regions, such as photodetectors, light-emitting diodes and photovoltaics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China under grant nos. 11374063 and 11404348, the National Basic Research Program of China (973 Program) under grant no. 2013CBA01505 and FDUROP (Fudan’s Undergraduate Research Opportunities Program) under no. 16066. Work at Ames Laboratory is partially supported by the US Department of Energy, Office of Basic Energy Science, Division of Materials Science and Engineering (Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract no. DE-AC02-07CH11358). The European Research Council under ERC Advanced grant no. 320081 (PHOTOMETA) supports work at FORTH.

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