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Electric Field Tuning of Band Offsets in Transition Metal Dichalcogenides

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We use first-principles calculations to investigate the band structure evolution of WX\(_2\)/MoX\(_2\) (X = S, Se) heterobilayers under a perpendicular electric field. We characterize the extent to which the type-II band alignment in these compounds can be tuned or inverted electrostatically. Our results demonstrate two effects of stacking configuration. First, different stackings produce different net dipole moments, resulting in band offset variations that are larger than 0.1 eV. Second, based on symmetry constraints that depend on stacking, a perpendicular electric field may hybridize WX\(_2\) and MoX\(_2\) bands that cross at the Brillouin Zone corner \(K\). Our results suggest that external electric fields can be used to tune the physics of intralayer and interlayer excitons in heterobilayers of transition metal dichalcogenides.

The richness of properties of the layered compounds known as transition metal dichalcogenides (TMDCs) and the ability to stack individual monolayers, either by mechanical transfer or chemical vapor deposition (CVD), afford several degrees of freedom with which to engineer desired functionalities [1] for a wide range of applications. Single-atomic layers of TMDCs possess a direct band gap in the visible spectrum [2, 3] and continue to show promise for many applications that involve electronic excitations, including optoelectronic devices [4]. Of particular interest are heterobilayers of the form WX\(_2\)/MoX\(_2\) (X, Y = S, Se), which have staggered, type-II band alignment. In most cases, states at the valence and conduction band extrema are localized on the WX\(_2\) and MoY\(_2\) layers, respectively. Photoexcitation can therefore drive charge separation, wherein hot electrons (holes) migrate to the MoY\(_2\) (WX\(_2\)) layer [Fig. 1(e)]. Experimentally, ultrafast charge transfer has been observed as a quenching of photoluminescence (PL) signals [5–9] or broadening of reflectance signals [10] from intralayer excitons, signaling the dissociation of electron-hole pairs confined to a single layer. Such separation of charge is fundamental to photovoltaic devices [5, 11]. In many cases, however, the photoexcited electron and hole on the different layers remained bound as an interlayer exciton, giving rise to a new PL signal [12–18]. Although the detailed properties of interlayer excitons have varied with substrate or annealing conditions [8, 14, 19], the spatial separation of their charges endows them with intrinsic advantages over intralayer excitons. The interlayer excitons have longer radiative [15] and valley [17] lifetimes, such that their diffusion dynamics can be observed. In addition, the interlayer excitons carry an out-of-plane dipole moment that can be coupled to an external electric field [15].

Rivera \textit{et al.} [15] demonstrated that the binding energy of interlayer excitons, as measured by PL, undergoes redshifts or blueshifts depending on the direction of an applied electric field. Within back-gated devices of WSe\(_2\)/MoSe\(_2\) and MoSe\(_2\)/WSe\(_2\) on SiO\(_2\)/Si substrate, they observed shifts up to 0.06 eV. To first order, they attributed this phenomenon to the electrostatic tuning of band offsets. As a caveat, they noted that with a single gate, they could not independently adjust electric field and carrier density, the latter also having an effect through screening [20]. Notwithstanding the interpretation of experimental results, it remains crucial to verify theoretically the extent to which an electric field oriented perpendicular to the heterobilayers can modify their band structure features and to elucidate the physics of the induced changes from the fundamental features of the constituents. Such investigations can also provide practical pathways towards realizing excitonic condensates in gate-tunable, double quantum wells of TMDCs [21].

In this work, we use density functional theory (DFT) to examine how the band structure of WX\(_2\)/MoX\(_2\) heterobilayers can be tuned by a perpendicular electric field. Previous theoretical studies of electric field effects have focused on TMDC homostructures [22–29] and/or band-gap variations [30, 31]; here, we focus on band offsets at the Brillouin Zone (BZ) corner \(K\), where direct optical transitions and valley effects prevail. By constructing different stacking registries, we observe variations in the zero-field band offsets larger than 0.1 eV. Our electric field calculations also reveal stacking-dependent hybridization of WX\(_2\) and MoX\(_2\) bands that cross at \(K\), which we explain on the basis of wave function symmetries. We discuss potential implications of all these effects on the physics of intralayer and interlayer excitons as probed by PL experiments.

DFT calculations were performed using the Vienna \textit{ab-initio} simulation package (\textit{VASP}) [32, 33], which implements the projector augmented-wave method [34, 35]. The valence states are 4s4p5s4d for Mo, 5s5p6s5d for W, 3s3p for S, and 4s4p for Se. We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [36]. To simulate a perpendicular electric field, \textit{VASP} introduces dipole sheets in the middle of the vacuum re-
gious [37, 38], which we took to be larger than 20 Å to avoid interactions between periodic images, making sure that this vacuum size gives well converged energetics and electronic structure features (for details see Supplemental Material). For each heterobilayer and for each value of electric field, we performed an ionic relaxation within the supercell. To obtain accurate interlayer distances, we included van der Waals corrections using rescaled $C_6$ coefficients according to the scheme of Tkatchenko and Scheffler [39], with an energy cutoff of 800 eV. Previous calculations of bulk MoS$_2$ with the Tkatchenko-Scheffler correction produced interlayer distances within 2% of the experimental value [40]. Due to the small dispersion energy, low force tolerances ($<0.2$ meV/Å) were required for convergence. Following the ionic relaxation, we calculated the non-spin-polarized charge density on a dense grid ($43 \times 43 \times 1$) of the BZ, then used it to obtain the wave function with spin-orbit coupling included.

We considered WS$_2$/MoS$_2$ and WSe$_2$/MoSe$_2$ in three stacking configurations, motivated by experimental and theoretical considerations, labeled $AA'$ (180°), $AB$ (0°), and $BA$ (0°), Figs. 1(a)-(c), following the convention of Ref. [41]: specifically, $AA'$ is fully eclipsed; $AB$ is staggered with W atoms aligned with X atoms of the other layer; $BA$ is staggered with Mo atoms aligned with X atoms of the other layer [dashed lines in Figs. 1(a)-(c)]. Although arbitrary twist angles can be achieved by mechanical transfer, interlayer excitons generated at the $K/K'$ valleys are direct for small angles around 0° and 180°, resulting in brighter PL [42]. Furthermore, CVD growth of WS$_2$ on MoS$_2$ resulted in $AA'$ stacking [8, 14], while similar growth of WSe$_2$ on MoSe$_2$ resulted in $AA'$ and $AB$ stackings [16, 18]. We restricted ourselves to pure chalcogenide compounds ($X = Y$ in WX$_2$/MoY$_2$) in order to minimize strain within a commensurate, $1 \times 1$ cell. When optimized, the lattice constants $(a)$ of the heterobilayers deviate at most by 0.3% from the lattice constants of their constituent layers in homobilayer form. Similarly, the interlayer distances $(d)$ of $AA'$-WX$_2$/MoX$_2$ lie within 0.2% of the average between $AA'$-bilayer WX$_2$ and $AA'$-bilayer MoX$_2$. At the largest electric field considered (5 V/nm), $d$ values change by less than 0.4% of their zero-field values.

Figures 2(a)-(e) display the band structure evolution of an example heterobilayer, $AA'$-WS$_2$/MoS$_2$, under a perpendicular electric field. High-symmetry points in the BZ are defined in Fig. 1(d). At zero field, $AA'$-WS$_2$/MoS$_2$ exhibits an indirect gap of 1.21 eV. The conduction band minimum at $K$ originates from MoS$_2$, whereas the valence band maximum at $\Gamma$ has sizeable contributions from WS$_2$ and MoS$_2$. However, the valence band at $K$ originates from WS$_2$, resulting in a type-II band alignment at $K$ with a direct gap of 1.35 eV. We compare these results with experimental data acquired by scanning tunneling spectroscopy (STS), which probes the single-particle spectrum without excitonic effects [43]. In a recent measurement of WS$_2$/MoS$_2$ and MoS$_2$/WS$_2$ transferred onto fused quartz, the single-particle gap observed was 1.45 eV [44]. The MoS$_2$ conduction band minimum was found to lie at $K$, whereas it was experimentally uncertain whether the WS$_2$ valence band maximum resided at $K$ or $\Gamma$. Previous theoretical works on $AA'$-WS$_2$/MoS$_2$, using hybrid functionals [45] or single-shot $G_0W_0$ [46], predicted gap values of 1.60 eV (direct) and 1.96 eV (indirect) respectively (none of these calculations included substrate effects, which are known to be present in the STS measurements). We note that the order of band alignments predicted by PBE and $G_0W_0$ agree with each other [47].

As the electric field increases [in the direction shown in Fig. 1(a)], there are various non-rigid transformations in the band structure, such as the shifting of the conduction band minimum from $K$ to a midway point along $\Gamma - K$. The primary feature of interest for our purposes is the band alignment at $K$, which becomes inverted beyond 4 V/nm [Fig. 2(e)], as well as the possible hybridization of bands at these crossings. We hereafter focus on the $K$ point, where direct transitions result in bright PL signals [42] and interlayer excitons exhibit valley-polarized dynamics [17].

Figure 3 shows the evolution of valence and conduction bands at $K$ across a range of positive and negative electric fields, for all six heterobilayers considered. Away from crossings, the energies of WX$_2$-derived bands decrease linearly with electric field, while the energies of MoX$_2$-derived bands increase linearly with electric field. These results show clearly several important trends: (i) Electrostatic inversion of the type-II band alignment...
FIG. 2. (a)-(e) Evolution of the band structure of $AA'$-WS$_2$/MoS$_2$ under a perpendicular electric field. The positive direction of the field points from the WS$_2$ to MoS$_2$ layer [Fig. 1(a)]. The zero energy is referenced to the valence band maximum at zero field. The bands are colored based on the projection of their wave functions onto the WS$_2$ and MoS$_2$ layers.

is possible, but requires large fields. The $AB$-stacked heterolayers have the smallest critical fields, which are 3.0 V/nm for WS$_2$/MoS$_2$ and 3.1 V/nm for WSe$_2$/MoSe$_2$, based on linear fits to the spin-up bands.

(ii) The magnitudes of the slopes of the band energies versus field decrease in the order of WS$_2$-, MoS$_2$-, WSe$_2$-, and MoSe$_2$-derived bands. This trend is partly due to the greater polarizability of Se over S.

(iii) The distinction between $AB$ and $BA$ stacking being whether the W or Mo atoms are aligned with the X atoms of the opposite layer, these two registries produce net dipole moments at zero field pointing in opposite directions. Thus, to first order, the $BA$ plots are horizontal shifts of the $AB$ plots by 1.7 V/nm for WS$_2$/MoS$_2$ and 1.4 V/nm for WSe$_2$/MoSe$_2$.

(iv) Away from crossings, the spin splittings remain relatively constant, and are larger in magnitude for heavier elements.

(v) There is a sizeable hybridization between valence bands of same spin in the $AA'$ heterolayers. Smaller hybridizations can also occur when opposite-spin bands cross [for example, in Figs. 3(b) and (f)], but they are more difficult to observe due to our discrete sampling of electric field values.

To elucidate the origin of these effects, we consider the wave functions in the monolayer limit. Figures 4(a) and (b) show the charge density isosurfaces of the valence and conduction band states at $K$ in a monolayer of MoS$_2$. Near the S atom, the valence band state has lobes directed along the bonds, whereas the conduction band state has lobes directed between the bonds. Based on Wannier transformations of DFT calculations [48], the state at the valence band maximum can be decomposed into $(d_{x^2-y^2} + i d_{xy})$-like orbitals on the Mo atom and $(p_x + ip_y)$-like orbitals on the S atoms. Similarly, the state at the conduction band minimum can be decomposed into $d_{x^2}-$like orbitals on the Mo atom and $(p_x - ip_y)$-like orbitals on the S atoms. These states at $K$ have $R_3$ symmetry (threefold rotation); under a counterclockwise rotation of 120° about the S atom, they acquire phase factors of $\exp(-i2\pi\mu/3)$, where $\mu = \pm 1$ for the valence and conduction bands, respectively.

Generalizing to heterolayers, we note that for $AA'$, $AB$, and $BA$ stacking configurations, $R_3$ crystalline symmetry is maintained about each atomic site, and is un-
affected by a perpendicular electric field. Thus, for states located on opposite layers to hybridize, their wave functions must transform with the same phase factor under threelfold rotation. For a given state, counterclockwise rotation of 120° about a fixed atomic site engenders a phase factor of \( \exp(i\phi) \), where

\[
\phi = -K \cdot \delta r - \frac{2\pi \tau \mu}{3} - \frac{2\pi \tau s_z}{3}.
\]

The first term represents a Bloch phase, where \( K = \frac{4\pi}{a} \hat{a} \) and \( \delta r \) is a displacement vector of the \( X \) atom that may arise from rotation. The second term, which was introduced in the previous paragraph, is generated by orbital angular momentum, with \( \tau = \pm 1 \) being the valley index. We note that \( \tau = -1 \) for the 180°-oriented \( WX_2 \) layer in the \( AA' \) heterobilayers, and +1 otherwise. The third term is due to spin, with \( s_z = \pm \frac{1}{2} \) for spins pointing in the positive/negative \( c \) direction. Using Eq. 1, we derive a set of hybridizations permitted by symmetry, shown in Table 1. The actual strength of hybridization depends on matrix elements of the electric field operator, and appears to be greatest in the valence bands of \( AA' \) heterobilayers. The stronger hybridization of these states could be due to a greater overlap of the charge densities near the \( X \) atoms facing the interlayer cavity [Figs. 4(c)-(f)].

In what concerns direct excitons at \( K \), our results imply that in the 0°-stacked heterobilayers, the offset between the spin-up conduction bands defines an upper bound on the binding energy of interlayer excitons relative to that of the intralayer, \( WX_2 \ A \) exciton [15] [see Fig. 3(e)]. The actual binding energy of interlayer excitons is reduced due to the weaker Coulomb interaction between their spatially-separated charges, and vary depending on fabrication details [8, 14, 19]. Our results suggest that these energies can be tuned in two ways: First, by shifting the stacking registry from \( AB \) to \( BA \), the spin-up, conduction band offset increases from 0.27 eV to 0.41 eV in \( WS_2/MoS_2 \) and from 0.23 eV to 0.34 eV in \( WSe_2/MoSe_2 \) (DFT total energies for the \( AB \) and \( BA \) stackings are degenerate within 1 meV, suggesting that the configurations are equally stable). Second, by applying electric fields up to \( \pm 1 \text{ V/m} \), which are attainable in experiments involving dual-gated devices [49], the spin-up, conduction band offsets vary on average by \( \pm 0.09 \) eV in \( WS_2/MoS_2 \) and \( \pm 0.08 \) eV in \( WSe_2/MoSe_2 \).

In the 180°-stacked heterobilayers, the large hybridization of valence bands at \( K \) should in principle affect the intralayer, \( WX_2 \ B \) exciton and the intralayer, \( MoX_2 \ A \) exciton [see Fig. 3(d)]. At zero field, the \( WX_2 \ B \) exciton can dissociate due to charge transfer from the spin-up \( WX_2 \) bands to the spin-up \( MoX_2 \) bands, so its PL signal may already be quenched. However, the \( MoX_2 \ A \) exciton cannot dissociate by hole transfer onto \( WX_2 \) without a spin flip, which is expected to occur rarely [17]; thus, its PL signal should be observable. As the system is tuned towards the hybridization point (near \(-1 \text{ V/m} \) for \( WS_2/MoS_2 \)), we expect the recombination rate of the \( MoX_2 \ A \) exciton to drop. This is due to the hole sector of the excitonic wave function becoming spread over both layers, reducing its overlap with the electron sector that is confined to the \( MoX_2 \) layer [49]. Thus, valence band hybridization should lead to an observable darkening of the \( MoX_2 \ A \) exciton.

In summary, we report two effects of the stacking configuration that have impact on optoelectronic properties of \( WX_2/MoX_2 \) TMDC heterobilayers: First, relative shifts in the stacking registry can induce different net dipole moments, leading to band offset variations that affect the binding energy of interlayer excitons. Second, depending on the stacking configuration, a perpendicular electric field may hybridize \( WX_2 \) and \( MoX_2 \) bands that cross at \( K \), darkening the intralayer excitons associated with these bands. We expect that these stacking effects may be enriched upon introduction of small twist angles.

![Fig. 4. (a), (b) Charge density isosurfaces of the valence and conduction band states at \( K \) in a monolayer of MoS2. Side and top views are presented for each state. (c)-(f) Schematic depictions of possible interlayer hybridization of \( K \) states in \( AA' \) and \( AB \)-stacked \( WS_2/MoS_2 \). Only the \( S \) atoms and their charge densities are shown for clarity (1 = MoS2 layer, 2 = WS2 layer). Interlayer hybridization is allowed when the wave functions on both layers transform identically under threelfold rotation. The overlap appears largest in (e), where the lobes of charge density are directed towards each other.](image)

**Table 1.** Symmetry-allowed hybridizations of valence (\( V \)) and conduction (\( C \)) bands that cross at \( K \). The requisite spin characters from each layer are denoted by the arrows.
about 0° or 180°.

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