Ultraflat bands and shear solitons in Moiré patterns of twisted bilayer transition metal dichalcogenides.

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Ultraflat bands in twisted bilayers of two-dimensional materials have potential to host strong correlations, including the Mott-insulating phase at half-filling of the band. Using first principles density functional theory calculations, we show the emergence of ultraflat bands at the valence band edge in twisted bilayer MoS$_2$, a prototypical transition metal dichalcogenide. The computed band widths, 5 meV and 23 meV for 56.5$^\circ$ and 3.5$^\circ$ twist angles respectively, are comparable to that of twisted bilayer graphene near ‘magic’ angles. Large structural transformations in the Moiré patterns lead to formation of shear solitons at stacking boundaries and strongly influence the electronic structure. We extend our analysis for twisted bilayer MoS$_2$ to show that flat bands can occur at the valence band edge of twisted bilayer WS$_2$, MoSe$_2$ and WSe$_2$ as well.

Combining bilayers of two-dimensional materials with a small-angle twist between the layers or combining two dissimilar 2D materials with a small lattice mismatch leads to the formation of Moiré superlattices (MSL) with periodicity in the order of nanometers [1–5]. MSL in twisted bilayer graphene (tBLG) host a plethora of fascinating physics at the structural [1,4,5] and electronic level [6,11]. Rearrangement of atoms in the MSL leads to the formation of shear solitons and topological point defects [1,5,12,13]. The electronic structure of these MSLs can be different from that of the constituent layers, like formation of flat bands and localization of states close to the Fermi level [12,13,17]. Probing flat bands in tBLG has recently led to the discovery of unconventional superconductivity close to a ‘magic’ angle [10,19].

MoS$_2$, a 2D transition metal dichalcogenide (TMD), is arguably the most popular 2D material after graphene [20,22]. Due to its semiconducting nature extensive applications in electronics and optoelectronics have been explored [21,23]. However, in contrast to tBLG, MSL in twisted bilayer MoS$_2$ (tBLM) have not received as much attention [24–30]. In this letter, we use first-principles density functional theory (DFT) calculations to study the electronic and structural transformations in the MSLs of tBLM. We show a large structural reconstruction in the Moiré pattern, leading to the formation of shear solitons and ultraflat bands at the valence band edge of tBLM. These flat bands have band widths comparable to those observed in tBLG close to ‘magic’ angles [10,17]. Our calculations show that in-plane relaxations of the layers drive the out-of-plane relaxations, which in turn lead to localization of the VBM. We show that the spatial localization of the flat band significantly changes if the bilayers are rigidly twisted, and relaxations ignored. Localization of the flat band can influence exciton dynamics and binding energy in the Moiré pattern. The ratio of on-site Coulomb interaction to band width of the flat band is found to be large, indicating the possibility of a Mott-insulating phase at half-filling of the band.

tBLM forms two distinguishable MSLs for small twist angles close to 0$^\circ$ and close to 60$^\circ$. For tBLG, these are equivalent. Fig. 1 (a) and (c) show the MSLs formed for twist angle 3.5$^\circ$ (M$^{3.5}$) and 56.5$^\circ$ (M$^{56.5}$), respectively. These superlattices are composed of various high-symmetry stackings. We define B$^{X/Y}$ as being a bernal-like stacking of the two layers with X atom in the top layer directly above the Y atom in the bottom layer. M$^{3.5}$ consists of the AA stacking, B$^{S/Mo}$ and B$^{Mo/S}$ (Fig. 1). M$^{56.5}$ similarly consists of the B$^{S/8}$, B$^{Mo/Mo}$ and AB (Fig. 1) stackings. We note that no simple translation transforms the AA stacking to AB stacking. We define an order-parameter, $\vec{u}$ [1,12], for twist angles close to 0$^\circ$ as the shortest displacement vector that takes any given stacking to the highest energy stacking in the corresponding Moiré pattern; AA stacking in this case. For twist angle close to 60$^\circ$, we define $\vec{u}$, as the shortest displacement vector that takes any given stacking to the highest energy stacking, B$^{S/8}$.

All the DFT calculations are performed using the pseudopotential plane-wave package, Quantum Espresso [32]. We simulate the following angles in this study: 3.5$^\circ$, 5.1$^\circ$, 7.3$^\circ$, 56.5$^\circ$, 54.9$^\circ$ and 52.7$^\circ$ [33,34]. The code Twister [35] is used to generate the atom positions for these structures. M$^{3.5}$ and M$^{56.5}$ are the largest systems in our calculation, containing 1626 atoms. In all MSL calculations, the Brillouin zone is sampled at the $\Gamma$ point to obtain the self-consistent charge density. The Hamiltonian is subsequently constructed and diagonalized at other k-points in the Brillouin zone to obtain the band structure. (see Supplementary Materials (SM) for more details [36]).

To understand the relaxation in the MSL, we study the relative energies of the stackings keeping the interlayer spacing (ILS) fixed at 5.9 Å. The relative total energy per unit MoS$_2$ along the line traversing high-symmetry stackings (defined in Fig. 1 (a) and (e)) in M$^{3.5}$ and M$^{56.5}$ is shown in Fig. 2 (a). The AA (O point) and B$^{3/S}$ (B’ point) stackings have S atoms of the top layer
The electronic structure of the MSLs can be understood in terms of the constituent high-symmetry stackings. The band structure of BLM is sensitive to stacking and ILS. Fig. 3 shows the band structure of the five high-symmetry stackings. The VBM in all BLM stackings is at the Γ point, unlike BLG where it is at the K point. The band structure close to the Fermi level, for all stackings, shows large band splittings at the Γ point and relatively small splittings at the K point. This is indicative of the strength of hybridization between the two layers at these points. The K and Γ point wavefunctions close to the Fermi level in monolayer MoS$_2$ have small and large spreads in the out-of-plane direction, respectively. This spread determines the hybridization, leading to the different splittings.

Among the band structures of stackings shown in Fig. 3 (a), (b) and (c); AA and B$^{S/S}$ show the largest splittings at the Γ point VBM (Fig. 3 (a)). This is due to the close proximity of the S atoms in these stackings. Note that the ILS is fixed at 5.9 Å for these band structures, same as that for rigidly tBLM. The effect of these large splittings is that the VBM (with respect to the vacuum level) of the AA and B$^{S/S}$ stackings is higher (~4.8 eV) than for rigidly tBLM.
FIG. 2. (a) The relative energy and ILS of the stackings along a line in the MSL. The blue (green) lines correspond to the path in M$^{3.5}$ (M$^{56.5}$). The solid (dashed) lines represent the relative total energy (ILS) along the path. (b) Maximum (squares) and minimum (circles) ILS in the MSL as a function of twist angle. The green and blue lines correspond to angles approaching 60° and 0°, respectively. The dashed lines represent the maximum and minimum equilibrium ILS of the corresponding isolated stackings. (c) and (d) ((d) and (f)) show the distribution of $|\vec{u}|$ and $|\vec{v}|$ in the unrelaxed (relaxed) MSLs. The dashed lines denote stacking boundaries. The arrows in (d) and (f) denote the direction of order parameters. (g) and (h) Show the structure, order parameter (red arrows) and the change in order parameter across a stacking boundary.

FIG. 3. (a), (b) and (c) Band structures of the isolated high-symmetry stackings with interlayer spacing fixed at 5.9Å. AA and B$^{S/S}$ are shown in (a) with black solid line and green dashed line, respectively. AB is shown in (b) with black solid line. B$^{Mo/S}$ and B$^{Mo/Mo}$ are shown in (c) with black solid line and orange dashed line, respectively. In the same order and colors, (d), (e) and (f) show the band structures at their equilibrium ILS. The blue or red shaded region marks the difference in VBM energy between B$^{Mo/S}$ and AA stackings. These splittings are now smaller than the other stackings (Fig. 3 (e) and (f)). As a result, the VBM of the AA and B$^{S/S}$ stackings is now lower than the rest of the stackings. The VBM in relaxed M$^{3.5}$ is then expected to originate from the local B$^{S/Mo}$ and B$^{Mo/S}$ regions. Fig. 4 (b) shows the VBM wavefunction in M$^{3.5}$, which is indeed localized at these regions, forming a hexagonal network. The localization pattern is significantly different from the rigidly twisted case, demonstrating the important role of atomic relaxations. The VBMs of AB and B$^{Mo/Mo}$ stackings are close to each other (within $\sim$0.1 eV). Based on the band structures, the wavefunction is expected to lie at the B$^{Mo/Mo}$ region in the MSL, since this stacking has a higher VBM level than AB. But the opposite localization is found in M$^{56.5}$, shown in Fig. 4 (d), where the VBM is restricted to the AB (O’ point) stacked regions. This is due to small tensile and compressive strains in the local B$^{Mo/Mo}$ and AB regions, respectively. On taking this strain ($\sim$0.3%) into account, the order of the VBM with respect to the vacuum level is reversed (see SM). The VBM thus localizes completely to the AB stacked regions (Fig. 4 (d)). Furthermore, the CBM with respect to the vacuum level lines up among the stackings in Fig. 3 (d), (e) and (f). Hence, no localization is found close to the CBM for M$^{3.5}$ and M$^{56.5}$.

The localization of the VBM in the MSL is accompa-
the localized state and in-plane dielectric constant, $\epsilon = 3$ (see SM). A large ratio for $U/W$ suggests the possibility of a Mott insulator phase at half-filling of the band [17]. As discussed above, the conduction bands show no localization close to the Fermi level. The CBM is two-fold degenerate and delocalized in the MSL with weak interlayer hybridization. Hence, an external electric field in the out-of-plane direction can easily split these bands (see SM) and localize the CBM onto one of the layers [38].

We find that the band width, localization of the flat band and atomic relaxations do not change if a different exchange-correlation functional is used in the DFT calculations (see SM). We also find that the relative ordering of the VBM among the stackings which determines the localization remains the same in GW calculations. [39, 40] (see SM) Furthermore, we show that this feature is generic to other TMDs (MX$_2$) by computing the VBM with respect to the vacuum level for the five high-symmetry stackings at the DFT level. The results are shown in Table I (see SM for band structures) for the equilibrium ILS. For all TMDs, the AA and B$_X$/X stackings have VBM levels about $\sim 0.3$ eV below the VBMs of other stackings. The CBMs, on the other hand, line up among the stackings. We do not expect spin-orbit coupling to significantly alter our conclusions (see SM).

Hence we posit that a similar localization should occur at the valence band edge of these TMDs, in close resemblance to what we have shown for MoS$_2$.

In conclusion, we show the formation of ultraflat electronic bands close to the valence band edge in MSLs of tBLM. Our analysis of the origin of the flat band indicates that twisted bilayers of other TMDs must also show a flat band at the valence band edge. The spatial-localization of electrons at the valence band edge will influence the binding energy and dynamics of excitons. The spatially varying band gap could lead to the formation of exciton funnels [41]. Doping the flat band with holes could lead to spin-liquid states, quantum anomalous Hall insulators, Mott-insulating phases, etc. at special filling factors [42]. Furthermore, the localization pattern of the flat band can be tuned with twist angle, and is determined by atomic relaxations in the Moiré pattern. The solitons can be probed through scanning tunnelling microscopy and transport measurements, and could host

| MX$_2$ | AA | B$_X$/X | AB | B$_M$/X | B$_M$/M |
|-------|----|---------|----|---------|---------|
| MoSe$_2$ | -5.06 | -5.07 | -4.70 | -4.68 | -4.73 |
| WS$_2$  | -5.34 | -5.34 | -4.93 | -4.90 | -4.87 |
| WSe$_2$ | -5.02 | -5.04 | -4.67 | -4.73 | -4.62 |

TABLE I. VBM (in eV), with respect to the vacuum level, for the five stackings in other transition metal dichalcogenides: MoSe$_2$, WS$_2$ and WSe$_2$. M stands for the transition metal and X for the chalcogen.
topological edge states at small twist angles [43–45].

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