Moiré quantum chemistry: charge transfer in transition metal dichalcogenide superlattices

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Transition metal dichalcogenide (TMD) bilayers have recently emerged as a robust and tunable moiré system for studying and designing correlated electron physics. In this work, we provide an electronic structure theory that maps long-period heterobilayer TMD superlattices to diatomic crystals with cations and anions. We find the interplay between moiré potential and Coulomb interaction leads to filling-dependent charge transfer between AA and AB stacking regions several nanometers apart. We show the insulating state at half filling found in recent experiments on WSe$_2$/WS$_2$ is a charge-transfer insulator rather than a Mott-Hubbard insulator. Our work reveals the richness of simplicity in moiré quantum chemistry.

Following the recent discovery of correlated insulators and unconventional superconductivity in twisted bilayer graphene [1, 2], artificial moiré superlattices have emerged as a new venue for realizing and controlling correlated electron phenomena. The moiré superlattices and natural solids differ greatly in the magnitude of characteristic length and energy. In solids, the average distance between electrons is typically comparable to atomic spacing on the order of Å and their kinetic and interaction energies are typically on the order of eV, while in moiré superlattices a mobile charge is shared by 1000–10000 atoms so that the characteristic length and energy scales are on the order of 10 nm and 10–100 meV respectively. Correspondingly, the quantum chemistry of natural solids involves complex intra-atomic and long-range interactions, while low-energy charge carriers in moiré superlattices only feel a long-period potential and interact with each other predominantly via the long-range Coulomb repulsion. As such, quantum chemistry can be simpler in moiré systems.

In twisted bilayer graphene, the emergence of strong correlation effects requires fine tuning to a magic twist angle, where the moiré energy bands become flattened [3] and sensitive to microscopic details such as lattice relaxation [4, 5] and strain [10]. On the other hand, transition metal dichalcogenide (TMD) bilayers [11–14] have a much simpler moiré band structure. In TMD heterobilayers such as WSe$_2$/WS$_2$, the valence moiré bands are simply formed by holes moving in a periodic moiré potential. As such, TMD superlattices provide a robust platform to study many-body physics with a highly tunable kinetic energy and local interaction strength.

Very recently, a correlated insulating phase has been observed in WSe$_2$/WS$_2$ at half filling [13, 14] of the topmost valence moiré bands with a charge gap around 150K (∼10 meV), and regarded as a canonical Mott-Hubbard insulator [11]. In this scenario, the topmost moiré band is well separated from the rest; its charge distribution is tightly localized near the moiré potential minima, forming a triangular lattice. Strong on-site Coulomb repulsion $U$ suppresses double occupancy and creates an insulating gap at half-filling on the order of $U$.

In this work, we identify a new energy scale associated with charge transfer between regions with different local stacking configurations in the moiré superlattice. When the energy cost of charge transfer $\Delta$ is comparable to or smaller than the local Coulomb repulsion $U$, the Mott-Hubbard description becomes inadequate. Instead, we show that a new type of correlated insulator emerges at half filling, known as the charge-transfer insulator [15]. Using first-principles calculations, we obtain the parameters $U$ and $\Delta$ for various TMD heterobilayers, and find that $\Delta$ in WSe$_2$/WS$_2$ superlattice is comparable to the experimentally observed charge gap [13, 14], whereas $U$ is much larger. We provide a theoretical description of the charge transfer phenomenon by introducing an effective honeycomb lattice model, in which the $A$ and $B$ sublattices correspond to “moiré cations” and “moiré anions” where charges are locally concentrated. We note previous works on twisted bilayer graphene has shown the interaction induced charge redistribution within a local moire region [16, 17, 21]. Here the charge transfer we predict in TMD moiré superlattices takes place on the length scale of the moiré period (∼10 nm) and can be directly observed by scanning tunneling spectroscopy (STS).

Continuum Model—We consider a heterobilayer TMD such as WSe$_2$/WS$_2$, with $a(a')$ as the lattice constant of top (bottom) layer, and $\theta$ as the twist angle. The lattice mismatch leads to a moiré superlattice (see Fig. 1b), with superlattice constant $L_M = a/\sqrt{\delta^2 + \theta^2}$ where $\delta = (a-a')/a'$. As illustrated in Fig. 1, the valence bands of two layers have a large band offset $\Delta E_g$, which is listed for various TMD heterobilayers at zero twist angle in Table. Given $\Delta E_g > 250$meV, the low-energy moiré bands are formed by the holes in one layer moving in the long-period potential provided by both layers. This is captured by the continuum model [11, 18, 19] $H_0 =$

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Angstrom, which has little effect on moiré band structure. Corrections modify the interlayer spacing to 6.57-6.77 Å and relax interlayer distance. We find that the vdW [31]. We assume rigid lattice along in-plane directions.

The interaction between electrons and ionic cores was approximated by the projector augmented wave method, and the exchange-correlation potential was described by the Perdew-Burke-Ernzerhof generalized gradient approximation [30] with the vdW correction incorporated by the vdW-DF (optB86) functionals [31]. We assume rigid lattice along in-plane directions and relax interlayer distance. We find that the vdW corrections modify the interlayer spacing to 6.57-6.77 Å, which has little effect on moiré band structure.

\[
\int \psi^\dagger(r) \hat{H} \psi(r) d^2 r \quad \text{with} \quad \hat{H} = -\frac{\nabla^2}{2m} + V(r),
\]

\[
V(r) = -2V_0 \sum_{i=1}^{3} \cos(G_i \cdot r + \phi),
\]

where \(\psi^\dagger = (\psi^\dagger_x, \psi^\dagger_y)\) denotes the holes and \(m > 0\) is the effective mass. Owing to strong Ising spin-orbit coupling in the valence band, valley indices are locked with spin [20]. Here \(G_i = \frac{4\pi}{\sqrt{3}} L_M^{-1} (\cos \frac{i\pi}{3}, \sin \frac{i\pi}{3})\) are three reciprocal vectors of the moiré superlattice. \(V_0 > 0\) and \(\phi\) are the only parameters associated with the magnitude and overall phase of the three lowest Fourier components of the moiré potential. When the moiré period is large, \(V_0, \phi\) are intrinsic material properties independent of \(L_M\), which we hereafter refer to as moiré potential strength and moiré phase respectively.

To obtain the values of \(V_0, \phi\), we fit the energy dispersion of TMD heterobilayers with continuum model from the density functional theory (DFT) band structures, as shown in Fig. 1 [1]. We calculated the band structure of the heterobilayer lattice structures via DFT as implemented in the Vienna Ab initio Simulation Package [20]. The interaction between electrons and ionic cores was approximated by the projector augmented wave method, and the exchange-correlation potential was described by the Perdew-Burke-Ernzerhof generalized gradient approximation [30] with the vdW correction incorporated by the vdW-DF (optB86) functionals [31]. We assume rigid lattice along in-plane directions and relax interlayer distance. We find that the vdW corrections modify the interlayer spacing to 6.57-6.77 Å, which has little effect on moiré band structure.

From this fitting, we extract \(V_0 = 15\) meV and \(\phi = \frac{1}{3}\pi\) for WSe\(_2\)/WS\(_2\). The values for various TMD heterobilayers are summarized in Table. 1 and Fig. 2. Importantly, the moiré phase \(\phi\) determines the energy landscape of moiré potential. This can be seen from \(V(r)\) at three \(C_3\)-symmetric points (Wyckoﬀ positions) \(r_{AA} = 0\), \(r_{AB} = \frac{1}{4\sqrt{3}} L_M (1, 0)\) and \(r_{BA} = -r_{AB}\) respectively. At the AA spot, a pair of transition metal atoms on top and bottom layers is registered, while at AB (BA) spot,

**TABLE I:** Summary of heterobilayer TMD. Here \(\delta\) is the lattice constant mismatch with respect to the bottom layer, \(\Delta E_g\) is the band offset, \(V_0\) and \(\phi\) are parameters of moiré potential and \(E_{\text{min}}^{\text{opt}} = \delta^2/(2m^2)\) is the moiré kinetic energy at zero twist. All energies are in unit of meV.

| System          | \(\delta\) | \(\Delta E_g\) | \(V_0\) | \(\phi\) | \(E_{\text{min}}^{\text{opt}}\) |
|-----------------|-----------|-------------|--------|--------|------------------|
| WSe\(_2\)/WS\(_2\) | 4%       | 640         | 15     | 45\(^\circ\) | 1.2              |
| WSe\(_2\)/MoS\(_2\) | 4%       | 940         | 11     | 40\(^\circ\) | 1.2              |
| MoSe\(_2\)/MoS\(_2\) | 4%       | 630         | 9      | 42\(^\circ\) | 1.3              |
| MoSe\(_2\)/WS\(_2\)  | 4%       | 270         | 7      | 35\(^\circ\) | 1.3              |
| WSe\(_2\)/MoSe\(_2\) | < 0.1%   | 370         | 8.14   | -4\(^\circ\) | < 10\(^{-3}\)   |
| WS\(_2\)/MoS\(_2\)  | < 0.1%   | 360         | 6.52   | -13\(^\circ\) | < 10\(^{-3}\)   |

**FIG. 1:** (a) Real-space moiré pattern of heterobilayer TMD with \(\delta = 4.0\%\) at \(\theta = 3.1^\circ\), where AA, AB, BA spots within one supercell are labeled. (b) Schematic low-energy band structure from two layers where \(\pm K_{(h)}\) are two valleys of top (bottom) layer. (c) and (d) are continuum model band structures (blue lines) of WSe\(_2\)/WS\(_2\) at \(\theta = 5.684^\circ\) and \(\theta = 0^\circ\) respectively, where open circles in (c) are DFT band structure.

**FIG. 2:** Systems listed in Table. 1 can be described by different limits and tight-binding models for the first and second moiré bands. Each colored line denotes a bilayer TMD, and ends at untwisted limit where \(V_0/E_0\) reaches maximum. Nearly free limit and tight-binding limit are separated by the dashed line where \(W = \Delta\). Within the tight-binding limit, the tight-binding model is a honeycomb lattice formed by AA and AB (open circle) spots with \(s\) orbital on each site above the solid black line, and a triangular lattice formed by AA spots with \(s, (p_x, p_y)\) orbitals on each site below the solid black line.
the chalcogen atom on the top (bottom) layer is registered with the metal atom on the bottom (top) layer. For $0 < \phi < \frac{1}{6} \pi$, within one supercell there are one potential minimum (AA) and two maxima (AB and BA), while for $\frac{1}{6} \pi < \phi < \frac{1}{3} \pi$, there are two minima (AA and AB) and one maximum (BA). In Table. 1 the first four TMD heterobilayers including WSe$_2$/WS$_2$ belong to the parameter range $\frac{1}{6} \pi < \phi < \frac{1}{3} \pi$, where the presence of two potential minima introduces new physics as we shall show below.

In the following sections, we will study interaction effects in TMD heterobilayers in various regimes of $V_0$ and $\phi$. We denote $n_s = 2$ holes per supercell as the full filling and $n = \frac{1}{2} n_s = 1$ hole per supercell as the half filling.

**Charge-Transfer Phenomena**—In this section, we use Hartree approximation to study the effect of Coulomb interaction on the charge distribution in twisted heterobilayer TMD with a relatively large bandwidth, and demonstrate the charge transfer phenomenon.

The Coulomb interaction including background effect is

$$H_C = \int \delta \rho(r) C(r-r') \delta \rho(r') d^2 r d^2 r'$$  \hspace{1cm} (3)

where $\delta \rho \equiv \psi^d \psi - \overline{\rho}$ is the deviation of local hole density from the average $\overline{\rho}$ (which is set by gate voltage), and $C(r) = e^2/(4 \pi \epsilon |r|)$ is the Coulomb potential with dielectric constant $\epsilon$, which controls the interaction strength. We approximate the Coulomb interaction $H_C$ by the mean-field Hatree potential $V_H$ self-consistently

$$V_H(r) = V(r) + \int C(r-r') \langle \delta \rho(r') \rangle d^2 r',$$  \hspace{1cm} (4)

and $\langle \ldots \rangle$ denotes the expectation value in mean-field ground state. As we assume the Hartree potential preserves all symmetries, $V_H$ can be written as Fourier series similar to Eq. (2), and the Coulomb interaction only renormalizes the band structure [21, 22].

In Fig. 3, we plot the renormalized filling factor $n/n_s$ as a function of chemical potential $\mu$ in WSe$_2$/WS$_2$ heterobilayer at twist angle $\theta = 3^\circ$ with different dielectric constants. At low fillings, charge is always localized at AA spots. As we increase the filling, more holes will be accumulated and the repulsive interaction renormalizes the charge distribution to make it more homogeneous. Near half filling $n = \frac{1}{2} n_s$, when interaction is weak, the charge distribution remains at AA spots as shown in Fig. 3b. When the interaction is strong, charge transfer from AA to AB spots occurs and the corresponding charge distribution is shown in Fig. 3c.

In real space, the interaction-induced, filling-dependent charge transfer leads to a significant change of charge distribution on the scale of 10 nm, which can be detected by scanning tunneling spectroscopy (STS).

In energy domain, charge transfer affects band structure on the scale of 10 meV, which may be detected in angle-resolved photoemission spectroscopy and optical measurement of exciton spectrum.

To go beyond the mean-field approximation, in the following we provide a theoretical description of charge transfer physics in TMD heterobilayers with a sufficiently large $L_M$, where the moiré bandwidth $W$ is small compared to the moiré potential $V_0$.

**Tight-Binding Limit**—We first introduce the moiré kinetic energy as $E_0 \equiv (2 m L_M^2)^{-1}$, which increases with the twist angle as $E_0 \propto (\theta^2 + \delta^2)$. When moiré potential is weak compared with kinetic term $V_0 \ll E_0$ (nearly free limit), the first and second bands have a negative indirect gap (e.g. Fig. 1c). When moiré potential is much stronger than kinetic term $V_0/E_0 \gg 1$ (tight-binding limit), moiré bands become flat compared with band gaps $W \ll \Delta$ (e.g. Fig. 1b). All untwisted heterobilayers listed in Table I belong to the tight-binding limit as shown in Fig. 2.

In the tight-binding limit, each potential minimum traps a set of local Wannier orbitals. The lowest-energy one is $s$-orbital, and the next is $(p_x, p_y)$ doublet. The first moiré band is predominantly formed by $s$ orbitals at AA spots, which are global potential minimum in the parameter range of interest $\phi \in (0, \frac{1}{3} \pi)$. The character of the second moiré band depends on $\phi$. For $\phi \in (0, \frac{1}{6} \pi)$, it comes from $p$ orbitals at AA spots. For $\phi \in (\frac{1}{6} \pi, \frac{1}{3} \pi)$ and in a wide range of $V_0$, it comes from $s$-orbitals at AB spots that are local potential minima (see Fig. 2). The energy difference between $s$ orbitals in AB and AA spots defines a charge transfer gap $\Delta_0 = \varepsilon_{AB} - \varepsilon_{AA}$.

By expanding $V(r)$ around a potential minimum, we obtain the characteristic size of $s$-orbitals in AA and AB spots

$$\xi_{AA} = (\cos \phi)^{-1/4} \xi_0, \quad \xi_{AB} = [\sin(\phi - \frac{1}{6} \pi)]^{-1/4} \xi_0$$

$$\xi_0 = (4 \pi^2 m V_0)^{-1/4} \sqrt{L_M}$$  \hspace{1cm} (5)

where $\xi_{AB}$ only applies to $\phi \in (\frac{1}{6} \pi, \frac{1}{3} \pi)$. It is impor-
tant to note that for large $L_M$, $\xi_i \propto \sqrt{L_M}$ is parametrically smaller than the moiré period. Therefore, the local Coulomb repulsion is the largest interaction energy, given by

$$U_i = \frac{e^2}{4\sqrt{2\pi\epsilon\xi_i}} \propto L_{M}^{-1/2}. \quad (6)$$

with $i = AA, AB$. In contrast, the interaction between nearest neighbors $V'$ is proportional to $1/L_M$ and hence parametrically smaller than $U$.

In the Fig. S3 we plot the bandwidth $W$ of the first moiré band and interaction energies $U, V'$ of WSe$_2$/WS$_2$ at different twist angles. While $U, V'$ decrease with $L_M$ in a power-law manner, $W$ is exponentially small in the tight-binding regime. For untwisted WSe$_2$/WS$_2$, we find $L_M = 8.2$ nm, $\xi_{AA} = 2.3$ nm, $\xi_{AB} = 3.0$ nm and $U_{AA} = 764/\epsilon$ meV, $U_{AB} = 594/\epsilon$ meV, $W = 8$ meV, $\Delta = 18$ meV, $V' = 302/\epsilon$ meV.

Depending on the relative strengths of interaction energy, bandwidth and charge transfer gap, we find three phases at half filling as illustrated in Fig. 4.

(I) Metal: $U \ll W$. The system is gapless. Under doping, additional charges are mainly localized at AA spots with s-orbital symmetry.

(II) Mott insulator: $\Delta > U \gg W$. The insulating ground state has one hole per AA spot, and the charge gap is $U$. When doped further, additional charges are mainly localized around AA spots. In this case, the triangular lattice Hubbard model is a good description [11].

(III) Charge-transfer insulator: $U > \Delta \gg W$. The insulating ground state has one hole per AA spot, but the charge gap is $\Delta$. When further doped, additional charges are mainly localized at AB spots, thus resulting in charge transfer on moiré scale as the filling increases.

The insulating gap at half filling inferred from thermal activation of resistivity is only around 10 meV [13, 14], which is significantly smaller than the estimated on-site repulsion $U \approx 64$ meV assuming $\epsilon = 12$. (Note the distance from sample to metallic gates is 20 nm so that screening has little effect on local repulsion $U$). On the other hand, the measured gap is comparable to the charge transfer gap $\Delta \approx 18$ meV. We thus conclude that the insulating phase at half-filling in untwisted WSe$_2$/WS$_2$ is likely a charge transfer insulator, rather than a Mott-Hubbard insulator.

In order to capture the physics of charge transfer between AA and AB spots, we introduce an extended Hubbard model on the honeycomb lattice:

$$H = \Delta \sum_i (-)^i c_i^\dagger c_i - t \sum_{<ij>} (c_i^\dagger c_j + h.c.) + \sum_{ij} V_{ij} n_i n_j,$$

where $c_i = \{c_i^\uparrow, c_i^\downarrow\}^T$ denotes s-orbital holes, $(-)^i = \pm$ for $i = AB$ (AA) spots and $t$ denotes hopping. $V_{ij}$ is the Coulomb repulsion between $s$ orbitals at site $i$ and $j$, which includes both on-site repulsion $U_{AA}, U_{AB}$, nearest-neighbor repulsion $V'$ and etc. When there is strong screening from the metallic gates, interactions decay rapidly with the distance between sites.

![FIG. 4: Schematic phase diagram at half filling. The solid curve illustrates the landscape of moiré potential, filled and open circles denote occupied holes at half filling and additional holes above half filling respectively. In phases (II) and (III), LHB, UHB and AB denote lower Hubbard band, upper Hubbard band and AB anion band respectively, and the density of states at half filling is shown for each phase.]

At temperatures below the charge gap, double occupancy is strongly suppressed by the on-site repulsion $U$. For the triangular lattice Hubbard model, the low-energy physics is described by the $t$-$J$ model [23, 24] with hopping $t$ and antiferromagnetic superexchange interaction $J = 4t^2/U > 0$ between nearest neighbors. Magnetic susceptibility as a function of doping at various temperatures is shown in Supplementary Material. For charge-transfer insulators such WSe$_2$/WS$_2$ described by the honeycomb lattice model [7], their magnetic properties call for future study.

In conclusion, we presented a theory which maps the long period moiré system to an atomic crystal with cation and anion, and studied the correlated insulating behavior. We found that the interplay between moiré potential and interaction strength gives rise to charge transfer insulator and Mott insulator in heterobilayer TMD, and charge transfer phenomenon takes place on moiré superlattice scale.

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Appendix A: Commensurate structure

The lattice constants for MoS₂, MoSe₂, WS₂ and WSe₂ are 3.18818, 3.31579, 3.18719 and 3.31698 Ångstrom respectively[23]. For bilayer with same chalcogen atoms, the lattice mismatch is less than 0.1%. While for bilayer with different chalcogen atoms, the lattice mismatch is around 4%. To build a commensurate structure from two different monolayers with same type Bravais lattices, we consider a bilayer system, whose primitive vectors are denoted by \( \{ a_1, a_2 \} \) and \( \{ a'_1, a'_2 \} \) respectively. When the bilayer system is a commensurate superlattice with primitive vectors \( \{ L_1, L_2 \} \), we have[11]

\[
\begin{align*}
(L_1 \quad L_2) &= M (a_1 \quad a_2) = M' (a'_1 \quad a'_2), \\
M &= (m \quad n \quad p \quad q), \quad M' = (m' \quad n' \quad p' \quad q'),
\end{align*}
\]

where \( m, n, p, q, m', n', p', q' \) are eight integers. These integers are determined by lattice mismatch between two layers (i.e. twist angle and strain) and also information of each layer (such as the anisotropy ratio). The most general way to determine these integers out of lattice information is through enumeration. We search all eight integers in a given range and compute corresponding lattice information for every given set of eight integers. When the calculated lattice information matches with the given one (up to some given precision), we then find the solution. In the following, however, we will discuss two special classes of superlattices where these eight integers have analytical solutions. When the two monolayers with threefold rotations, i.e. they are all triangular lattices, the integer matrices \( M, M' \) have to be conformal (i.e. a scalar times a rotation). Without loss of generality, let us assume \( a_{1,2} = a(1/2, \pm \sqrt{3}/2 \{1/2, \pm \sqrt{3}/2 \} \) with \( a' \geq a \), namely the unprimed layer is not rotated while the primed layer is rotated by angle \( \theta \) along out-of-plane direction. Then the conformal matrices \( M, M' \) will have the following form

\[
M = N \begin{pmatrix} 
\cos \phi - \frac{1}{\sqrt{3}} \sin \phi & -\frac{2}{\sqrt{3}} \sin \phi \\
\frac{2}{\sqrt{3}} \sin \phi & \cos \phi + \frac{1}{\sqrt{3}} \sin \phi
\end{pmatrix}, \quad (S3)
\]

\[
M' = N' \begin{pmatrix} 
\cos \phi' - \frac{1}{\sqrt{3}} \sin \phi' & -\frac{2}{\sqrt{3}} \sin \phi' \\
\frac{2}{\sqrt{3}} \sin \phi' & \cos \phi' + \frac{1}{\sqrt{3}} \sin \phi'
\end{pmatrix}, \quad (S4)
\]

where \( N, N' \) are positive integers and \( \phi, \phi' \) are angles. Since each one of \( M, M' \) is effectively described by two parameters, we can write

\[
M = \begin{pmatrix} m & n \\
-n & m-n
\end{pmatrix}, \quad M' = \begin{pmatrix} m' & n' \\
-n' & m' - n'
\end{pmatrix}. \quad (S5)
\]

Furthermore, we want to consider first-order moiré pattern for simplicity, which is defined in terms of reciprocal vectors. Assume the reciprocal lattice vectors of two layers and the superlattice are \( \{ g_1, g_2 \} \) respectively, then the first-order moiré pattern is defined by the conditions

\[
g_i = G_i - G'_i. \quad (S6)
\]

With this condition, it is found that \( m - m' = n - n' = 1 \), and hence the twist angle and lattice constant ratio between two layers are

\[
\theta = \arctan \left( \frac{\sqrt{3}(m - n)}{2(m^2 + n^2 - mn)} \right), \quad (S7)
\]

\[
r = \frac{a'}{a} = \sqrt{\frac{m^2 + n^2 - mn}{m^2 + n^2 - mn - m - n + 1}} \quad (S8)
\]

and the superlattice vectors are

\[
L_1 = ma_1 + na_2, \quad L_2 = -na_1 + (m - n)a_2, \quad (S9)
\]

\[
L \equiv |L_i| = \frac{a}{\sqrt{1 - 2r \cos \theta + r^2}}. \quad (S10)
\]

Here for TMDs with less than 0.1% lattice mismatch, we construct the commensurate moiré superlattice via twist the top layer with angles \( \theta = 21.78^\circ, 13.1^\circ, 9.43^\circ, 6.58^\circ \) and 5.49°. While for TMDs with lattice mismatch around 4%, the calculated twist angles are \( \theta = 16.31^\circ, 7.31^\circ, 6.39^\circ, 5.68^\circ \) and 4.715°.

Appendix B: Details of the ab-initio calculation

For MoSe₂/WSe₂ and MoS₂/WS₂, we fit the continue model parameters from the energy shift of band maxima from relative shift of monolayer unit cells[11]. For another four systems with lattice mismatch 4%, we fit the parameters of periodic potential and its phase factor directly from DFT band structures at various commensurate structures with different twist angles, a further calculation of charge density distribution is performed to fix sign of the phase factor. We note that bilayer structures with twist angle \( \theta = 5.68^\circ \) fall into the gauge that \( K \) pockets of monolayer unit cell fold to \( \Gamma \) point of mBZ. The band structures of various TMD heterobilayers are summarized in Fig. S1. Note the energy of Gamma pockets is only lower by 120 meV compared with K pockets in MoTe₂, which gives rise to the relatively flat second Moiré band in Fig. S1 (a, b).

Appendix C: Fock term and Details of charge transfer

The full mean-field treatment of the Coulomb interaction also includes Fock decomposition \( \delta \rho (r) \delta \rho (r') \rightarrow \psi(\mathbf{r})\psi(\mathbf{r}') \psi(\mathbf{r})\psi(\mathbf{r}') \), which results in the mean-field Hamiltonian \( H_{MF} = \int \psi(\mathbf{r})g(\mathbf{r})\psi(\mathbf{r}')d^2rd^2r' \) with renormalized propagator \( g(\mathbf{r}) = g_0(\mathbf{r}) + C(\mathbf{r})\psi(\mathbf{0})\psi(\mathbf{r}) \), where \( g_0(\mathbf{r}) \) is the bare propagator. We expect that the moiré potential and hence charge
transfer physics discussed in this work would not be affected by Fock term too much.

We can introduce a dimensionless quantity to describe the charge imbalance between AA and AB spots

\[ P = \frac{n_{AA} - n_{AB}}{n_{AA} + n_{AB}}, \]

and plot it as a function of chemical potential \( \mu \) together with filling factor, as shown in Fig. S2a and b. As we can see, at low filling, charge is mainly concentrated at AA spots \( P > 0 \), when doping increases, AA and AB spots first become balanced in terms of charge distribution \( P \rightarrow 0 \), and then AB spots can have more charges than AA spots \( P < 0 \) since repulsion at AB spots is weaker than AA. As explicit examples, we also plot charge distribution at different fillings \( n = 0.5n_s \) and \( n = 0.1n_s \) in Fig. S2c and d respectively.

**FIG. S1:** Continuum model fitting of DFT band structure of (a)MoSe\(_2\)/MoS\(_2\), (b)MoSe\(_2\)/WS\(_2\), (c)WSe\(_2\)/MoS\(_2\) and (d)WSe\(_2\)/WS\(_2\) at twist angle \( \theta = 5.684^\circ \).

**FIG. S2:** Charge transfer in WSe\(_2\)/WS\(_2\) system at twist angle \( \theta = 3^\circ \) with dielectric constants \( \varepsilon = 12 \). (a) and (b) are filling factor \( n/n_s \) and charge imbalance parameter \( P \) as functions of chemical potential \( \mu \). (c) and (d) are charge distribution at different fillings \( n = 0.5n_s \) and \( n = 0.1n_s \) respectively. Units of colorbars are arbitrary.

**Appendix D: Band structures, Coulomb interactions and tight-binding models**

In Fig. S3 we plot onsite repulsion \( U \), nearest-neighbor repulsion \( V' \) and bandwidth \( W \) of WSe\(_2\)/WS\(_2\) at different twist angles. All three energy scales decrease with decreasing angle \( \theta \) (or equivalently increasing moiré wavelength \( L_M \)), but \( W \) decreases faster than interactions.

As shown in Fig. 2 there are two regimes in the phase space spanned by moiré potential strength \( V_0/E_0 \) and moiré phase \( \phi \), where the second moiré bands are qualitatively different.

Triangular regime where the second and third moiré bands are from \( (p_x, p_y) \) orbitals at AA spots and the corresponding tight-binding model is

\[ H_b = \sum_i c_i^\dagger \tilde{\Delta} c_i - \sum_{\langle ij \rangle} (c_i^\dagger \tilde{T} c_j + h.c.), \]

where \( c = \{ s, p_x, p_y \}^T \) denotes \( s \)- and \( p_x, p_y \)-orbital holes, and \( i \) is AA spot. \( \tilde{\Delta} = \text{diag}(\varepsilon_s, \varepsilon_p, \varepsilon_p) \) denotes onsite energy matrix, where \( \varepsilon_s, \varepsilon_p \) denote the energy of \( s \) and \( (p_x, p_y) \) orbitals at AA spot respectively.

Honeycomb regime where the second moiré band is from \( s \) orbitals at AB spots and the corresponding tight-binding model is

\[ H_O = \frac{\Delta}{2} \sum_i (-i)^i c_i^\dagger c_i - t \sum_{\langle ij \rangle} (c_i^\dagger c_j + h.c.), \]

where \( c_i = \{ c_{i\uparrow}, c_{i\downarrow} \}^T \) denotes \( s \)-orbital holes, \( (-i)^i = \pm \) for \( i = \text{AB (AA)} \) spots and \( t \) denotes hopping. And \( \Delta = \varepsilon_{AB} - \varepsilon_{AA} \) denotes the charge transfer gap from AA to AB spots.

**FIG. S3:** Onsite Coulomb repulsion \( U \), nearest-neighbor repulsion \( V' \) and bandwidth \( W \) of WSe\(_2\)/WS\(_2\) as functions of moiré wavelength \( L_M \) (bottom axis) and twist angle \( \theta \) (top axis) when dielectric constant is chosen as \( \varepsilon = 12 \).
Appendix E: Magnetic Properties

We also study magnetic properties of $t$-$J$ model in the triangular lattice. We performed ED (exact diagonalization) [26] on the triangular lattice $t$ – $J$ model, and calculate temperature and filling dependent spin susceptibility.

From the Curie-Weiss law plot of susceptibilities in Fig. S4 inset, we found that Curie temperature $T_0$ moved towards zero when we increased the filling factor higher than half, indicating that antiferromagnetic correlation is reduced by doping. As shown in Fig. S4 in a wide temperature range, spin susceptibility is a non-monotonic function of filling factor $\nu = n/n_s$ with a maximal peak at optimal filling $\nu(T)$. Among them, at higher temperature $T \gg t$ the peak locates exactly at the half filling $\nu = \frac{1}{2}$, while at lower temperature $T \lesssim t$, the susceptibility peak is shifted to above half filling $\nu > \frac{1}{2}$, in agreement with the result from high-temperature expansion study [27]. These findings are consistent with the spin susceptibility of WSe$_2$/WS$_2$ heterobilayers inferred from optical spectroscopy under the magnetic field [13].

FIG. S4: Uniform spin susceptibility of $t$-$J$ model at $J/t=0.4$ ($U/t = 10$). The peak is around $\nu = n/n_s = \frac{13}{24}$ for $0.5t < T < 1.5t$, but at $\nu = \frac{1}{2}$ for $T > 1.5t$. Here $\chi_0 = t^{-1}$, and $t$ is around 1 meV. Inset: Inverse spin susceptibility as a function of temperature, where dots are numerical results and solid lines are Curie-Weiss fit. The Curie temperature $T_0$ is largest in magnitude at half filling, and gradually moves towards zero as the doping deviates from half filling, indicating the transition from AFM to PM.