Moiré lattice-induced formation and tuning of hybrid dipolar excitons in twisted WS$_2$/MoSe$_2$ heterobilayers

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Abstract

Moiré superlattices formed in van der Waals bilayers have enabled the creation and manipulation of new quantum states, as is exemplified by the discovery of superconducting and correlated insulating states in twisted bilayer graphene near the magic angle. Twisted bilayer semiconductors may lead to tunable exciton lattices and topological states, yet signatures of moiré excitons have been reported only in closely angularly-aligned bilayers. Here we report tuning of moiré lattice in WS$_2$/MoSe$_2$ bilayers over a wide range of twist angles, leading to the continuous tuning of moiré-lattice induced interlayer excitons and their hybridization with optically bright intralayer excitons. A pronounced revival of the hybrid excitons takes place near commensurate twist angles, 21.8° and 38.2°, due to interlayer tunneling between states connected by a moiré reciprocal lattice vector. From the angle dependence, we obtain the effective mass of the interlayer excitons and the electron inter-layer tunneling strength. These findings pave the way for understanding and engineering rich moiré-lattice induced phenomena in angle-twisted semiconductor van der Waals heterostructures.

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The ability to create atomically thin heterostructures by stacking van der Waals materials marks a new frontier in materials science and condensed matter physics [1–3]. When two monolayer crystals of the same lattice symmetries overlay on each other, a moiré superlattice may form due to a small mismatch in their lattice constants or angular alignment [4, 5]. The latter – the twist angle between the two layers – provides a unique tuning knob for engineering the electronic properties of the heterostructure. Seminal results have been obtained in twisted bilayer graphene, where superconducting and correlated insulating states are created by fine control of the twist angle [6–9]. In semiconductors, such as transition metal dichalcogenides heterobilayers, a wide variety of phenomena become possible and tunable with angle in moiré lattices, ranging from single exciton arrays to topological bands, to strongly correlated states [10–13]. Localized excitons, exciton minibands, and correlated states in moiré superlattices have been reported in TMD bilayers with very small twist angles [14–20]. Increasing the twist angle, however, has led to suppression of measurable effects of moiré superlattices. Hybrid exciton resonances formed by coupling between inter- and intra-layer excitons have also been reported in angularly-aligned WS₂/MoSe₂ heterobilayers and it was suggested that the moiré lattice may enhance interlayer coupling; yet only a single resonance was resolved as the twist angle deviates from 0° or 60° [21].

In this work, we demonstrate twist-angle tuning of moiré lattices in WS₂/MoSe₂ bilayers and show how the moiré lattices drastically change the properties of excitons. Due to band folding in the moiré reciprocal lattice and electron tunneling in the moiré lattice, new, momentum-direct interlayer exciton states are formed which can hybridize with nearly-resonant intralayer excitons, leading to two bright hybrid moiré exciton states over a wide range of twist angles θ. The role of the moiré lattice is corroborated by revival of strong inter-layer tunneling when θ is near 21.8° and 38.2°. At these angles, moiré-lattices are formed commensurate with the monolayer lattices, bringing angularly shifted valleys of the two monolayers into equivalent momentum in the moiré Brillouin zone, thereby enabling strong inter-layer tunneling. The resulting hybrid exciton states resemble the features in hetero-bilayers with θ = 60° and 0°, respectively. The observation of these new moiré states in the twisted bilayers directly demonstrates the discrete translational symmetry, or periodicity, of the moiré pattern — the defining feature of a lattice.

We furthermore measure continuous tuning of the energy and spectral weight of the hybrid excitons in the moiré lattice by the twist angle. The results agree very well with an analytical theory model that takes into account the interplay between spin-orbit splitting of the conduction
band, valley selection rules, atomic stacking orders and the lattice symmetries. By comparing with
the model, we obtain from the angle dependence the effective mass of the interlayer excitons and
the inter-layer electron tunnelling strength. Lastly, by comparison of hybrid states formed from
different intra-layer exciton states, we find that the binding energies of the uncoupled inter-layer
and intra-layer exciton states differ by merely 10-16 meV, as opposed to ∼100 meV based on
first-principle calculations when interlayer tunneling is neglected [22].

The devices used in this work are WS₂/MoSe₂ heterobilayers with different twist angles θ,
encapsulated by few-layer hexagonal boron nitride (hBN) (see Methods for details). Figure 1a
shows an example of the optical microscope image of an encapsulated heterobilayer, where the
sharp edges of two monolayers are aligned. The twist angle is measured to be θ = 59.8° ± 0.3°
by comparing the angle-dependence of second harmonic generation from each monolayer and from
the bilayer (see Supplementary Information SI figure2 for details). The hole band offset is large
but the conduction band offset is small between WS₂ and MoSe₂. Therefore inter-layer electron
tunneling is expected between states of the same spin and valley, which leads to hybridization
between the corresponding intra- and inter-layer exciton transitions that share the same hole state,
as illustrated in the inset of Figure 1a.

We first characterize exciton hybridization in closely aligned hetero-bilayers, with θ ∼ 0° or
60°. In such bilayers, the Brillouin zones of the two layers closely overlap in momentum space to
form nearly direct bandgaps for both the inter- and intra-layer transitions (Figure 1b), and thereby
inter- and intra-layer excitons can hybridize [23].

To identify optically bright resonances, we measure the reflectance contrast (RC) spectrum,
\( \frac{R_{\text{sample}} - R_{\text{substrate}}}{R_{\text{substrate}}} \) (see Methods for details). Interlayer exciton has an oscillator strength two orders
of magnitude weaker than that of the intra-layer exciton, due to separation of the electron and
hole wavefunction, so it is typically too weak to be measurable in absorption or RC spectroscopy.
However, when interlayer excitons hybridize with intra-layer ones via electron or hole tunneling, the
hybrid states acquire an oscillator strength through the intra-layer exciton component. Therefore,
we can identify the hybrid excitons via their spectral weight in the absorption spectra of the
heterobilayer in comparison to those of the monolayer.

As shown in fig. 1c, the MoSe₂ monolayer region of the device (as marked on fig. 1a) shows
a strong intralayer MoSe₂ A exciton resonance near 1.65 eV, while the WS₂ monolayer has no
exciton resonances nearby. In the bilayer, stacking of the WS₂ layer is expected to lead to a red
shift of the MoSe$_2$ A exciton resonance$^{[21]}$ while also introducing an interlayer exciton transition, between an electron in WS$_2$ and a hole in MoSe$_2$, that is close in energy. The interlayer exciton has a negligible oscillator strength due to electron-hole separation. However, two clearly-resolved resonances appear in our bilayer, both with significant spectral weight (top spectrum in fig. 1c). The same two resonances are also measured in photoluminescence (See supplementary material SI figure 3). We therefore identify them as the inter- and intra-layer hybrid states, both of which inherit an oscillator strength from their intra-layer component$^{[21]}$. There are multiple pairs of intra- and inter-layer excitons that can hybridize. We focus on the transition region of MoSe$_2$ A exciton first and label these states as MoA excitons, of which the hole is always in the highest MoSe$_2$ valence band. Other pairs will be analyzed later.

The relative spectral weight of the lower (LHX) and upper hybrid excitons (UHX) corresponds to the ratio of their oscillator strengths $f_{LHX}/f_{UHX}$. It is controlled by their intra-layer exciton fractions, which in turns is controlled by the energy detuning $\delta = E_{IX} - E_X$ between the uncoupled inter-layer ($E_{IX}$) and intra-layer ($E_X$) resonances. Therefore $f_{LHX}/f_{UHX}$ greater or less than one corresponds to positive or negative detuning $\delta$.

As clearly seen in the spectra (fig. 1c), in the R-stacking bilayers ($\theta = 2.1^\circ$), the LHX has a larger spectral weight than the UHX, suggesting the uncoupled interlayer state lies above the intralayer one, or $\delta_R > 0$, as illustrated in fig. 1b. In contrast, in the H-stacking bilayer ($\theta = 59.8^\circ$), the UHX has a larger spectral weight, suggesting $\delta_H < 0$. These results are consistent with the spin selection rules of the excitonic transitions (see more detailed illustration in Fig. 1b)$^{[23]}$. The difference in the detuning between R- and H-stacking bilayers correspond to the spin-orbit splitting of WS$_2$ conduction band (see illustration in fig. 1b).

To analyze the results quantitatively, we first obtain the energies, $E_{LHX}$ and $E_{UHX}$, and oscillator strengths of the hybrid states by fitting the RC spectra using the transfer matrix method, where the hybrid excitons are modeled as Lorentz oscillators (See supplementary information SI figure1 for details)$^{[23][24]}$. The fitted spectrum agrees well with the data, as shown in fig. 1c. Describing the hybrid modes with the coupled oscillator model, we have $E_{LHX} - E_{UHX} = -\sqrt{J^2 + \delta^2}$, and $f_{LHX}/f_{UHX} = \frac{\sqrt{\delta^2 + 4J^2} + \delta}{\sqrt{\delta^2 + 4J^2} - \delta}$ (see Methods for details). Thereby using the fitted $E_{LHX,UHX}$ and $f_{LHX,UHX}$, we can obtain $\delta$ and $J$. The results are summarized in fig. 1d. The coupling strength is found to be around 20 meV for both R- and H-stacking. The detuning of the R- and H-stacked bilayers differ by $25.9 \pm 0.5$ meV$^{[25]}$, consistent with the spin-orbit splitting of WS$_2$ from theory calculation.
confirming the hybrid states are formed by spin-conserved electron tunneling between the two layers.

To study tuning of the hybrid excitons by the moiré lattice, we perform the same measurements and analysis as discussed above on 30 samples with different twist angles, and obtain how the exciton energies, oscillator strengths and inter-layer tunneling vary with the changing moiré lattice. We define $\theta_0 < 30^\circ$ as the angular deviation from aligned bilayers of R- or H-stacking. $\theta_0 = |\theta|$ for R-stacking and $\theta_0 = |60^\circ - \theta|$ for H-stacking.

As shown in fig. 2, the MoA hybrid exciton doublets are clearly resolved for $\theta_0$ up to 6°, which would correspond to a tuning of the moiré lattice constant by nearly three-fold [27]. The spectral weights of the doublets evolve continuously with the twist angle, reflecting continuous increase of $f_{LHX}/f_{UHX}$ and $\delta$ with $\theta_0$ (middle panel of fig. 2). At the same time, the inter-layer tunneling $J$ decreases continuously (bottom panel of fig. 2). These observations show clearly moiré lattice induced hybridization and tuning of intra-layer and inter-layer excitons, as we explain below.

We illustrate in fig. 2b the MoA exciton bands at different twist angles, corresponding to the six samples shown in fig. 2a. The intra-layer MoSe$_2$ A exciton transition (red band) remains direct, with the band minimum at zero center-of-mass momentum $q_X \sim 0$, irrespective of the twist angle. It is close in energy with the inter-layer exciton formed by a hole from the same MoSe$_2$ valence band but an electron from a WS$_2$ conduction band. This inter-layer exciton band has the band minimum also at zero center of mass momentum: $q_{IX} \sim 0$, when $\theta \sim 0^\circ$ ($\theta_1$ in fig. 2a-b) or 60° ($\theta_6$ in fig. 2a-b), neglecting the small lattice constant mismatch. This is the situation discussed in fig. 1.

As the two lattices rotate relative to each other by $\theta$ ($\theta_2$ to $\theta_5$ in fig. 2a-b), the Brillouin zones of MoSe$_2$ and WS$_2$ also rotate by $\theta$. The inter-layer exciton band minimum shifts away from the intra-layer exciton band minimum by momentum $K_W - K_M$ for R stacking, where $K_M$ and $K_W$ are respectively the Brillouin zone corners for MoSe$_2$ and WS$_2$ layers. Due to this momentum mismatch, hybridization between intra-layer MoSe$_2$ A excitons and the interlayer state at the band minimum is not allowed.

However, interlayer electron tunneling in the moiré lattice can lead to the formation of new moiré miniband states to hybridize with the optically bright intralayer excitons. As illustrated in fig. 2b and fig. 3c, three interlayer excitons $|q_i\rangle_{IX}$ overlap with the optically bright intralayer exciton, where the center of mass momentum $q_i$, measured relative to the band minimum of interlayer
exciton, correspond to $q_1 = K_M - K_W$ for R-stacking, with $q_{2,3}$ connected to $q_1$ by $2\pi/3$ and $4\pi/3$ rotations, respectively, via moiré reciprocal lattice vectors. These three inter-layer states are offset from their band minimum by the kinetic energy $\hbar^2 q_i^2 / (2M_{\text{IX}})$, for $i = 1, 2, 3$ and $M_{\text{IX}}$ the total mass of inter-layer exciton. These three states can couple due to the moiré lattice and therefore, superpose to form moiré miniband states, of which one interlayer exciton state shares the same angular momentum as the intra-layer MoSe$_2$ A exciton at $q_X \sim 0$, giving rise to the hybrid doublet we observe in angularly misaligned bilayers (see Methods for details).

When $\theta$ deviates more from $0^\circ$ or $60^\circ$, the interlayer exciton formed in the moiré lattice continuously blueshifts because of the increasing kinetic energy, which explains the measured continuous blueshift of the LHX and UHX resonances, and the continuous increase of the spectral weight of LHX compared to UHX.

To analyze our results more quantitatively, we develop an analytical microscopic theory based on the above understanding (see Methods for details). Comparing it with the measured twist-angle dependence of the hybrid states, we obtain the key band parameters of the bilayer, including the interlayer exciton effective mass and interlayer coupling strength.

We first compare the measured detuning $\delta$ vs. $\theta_0$ and the interlayer exciton kinetic energy. As discussed above, $\delta$ is given by:

$$\delta = \delta_0 + \frac{\hbar^2 q_1^2}{2M_{\text{IX}}}$$

(1)

where $\delta_0$ is the detuning at $\theta = 0^\circ$ or $60^\circ$ for bilayers close to R- and H-stacking, respectively. $q_1$ is equal to $4\pi/(3a_M)$, and $a_M$ is the moiré period approximated by $a_0/\sqrt{\theta_0^2 + \epsilon^2}$, for $a_0$ the monolayer lattice constant and $\epsilon$ the lattice constant mismatch $|a_0 - a_0'|/a_0$ between the two layers.

Equation (1) shows that $\delta$ increases quadratically with $\theta_0$. As $\theta_0$ increases from $0^\circ$ to $6^\circ$, $a_M$ changes by nearly three fold, and $\delta - \delta_0$ changes by seven-fold [27]. Fitting the measured $\delta$ vs. $\theta_0$ with Equation (1), we find the inter-layer exciton total mass $M_{\text{IX}}$ to be $(6.9 \pm 3.2)m_0$ and $(1.41 \pm 0.28)m_0$ for R- and H-stacking heterobilayers, respectively, for $m_0$ the electron free mass.

From our microscopic theory, we can also estimate the conduction-band interlayer tunneling parameter $w$ from the coupling strength $J$ through the relation

$$J = \frac{\sqrt{3}w}{A} \sum_k \phi_k^* \frac{m_{h,iX}}{m_{\text{IX}}} \psi_k,$$

(2)

where $\phi_k$ and $\psi_k$ are respectively the relative-motion wave function for interlayer and intralayer excitons with the normalizations $(1/A) \sum_k |\psi_k|^2 = 1$ and $(1/A) \sum_k |\phi_k|^2 = 1$. Here $A$ is the
system area and \( m_{h,IX} \) is the hole mass for the interlayer exciton. Because of the momentum shift \((m_{h,IX}/M_{IX})q_1\) in the integral of Eq. (2), \( J \) decreases with increasing \( \theta_0 \), which agrees with the experimentally observed angle dependence of \( J \). At small \( \theta_0 \), \( J \) can be approximated by \( \sqrt{3}w \). Using our experimentally measured value of \( J \) at \( \theta_0 \sim 0 \), we estimate the interlayer tunneling \( w \) to be about 14 meV for both R- and H-stacking bilayers.

When the twist angle \( \theta_0 \) is greater than \( 6^\circ \), the hybrid exciton doublets become hard to be resolved, likely because there is a large blue detuning and the UHX has a vanishing oscillator strength (See supplementary material SI figure 4 for details).

Remarkably, pronounced and well-resolved doublets re-appear in hetero-bilayers with \( \theta = 20.1^\circ \pm 0.3 \) and \( 40.3^\circ \pm 0.3 \), as shown in Fig. 3. In the bilayer with \( 20.1^\circ \) twist angle, the LHX has a smaller spectral weight than UHX has, corresponding to a negative detuning (\( \delta = -5.6 \) meV), which is similar to H-stacking bilayers formed at \( \theta \sim 60^\circ \). In contrast, in the bilayer with \( 40.3^\circ \) twist angle, the LHX has a larger spectral weight than UHX has, corresponding to a positive detuning (\( \delta = 11.8 \) meV), which is similar to R-stacking bilayers formed at \( \theta \sim 0^\circ \). In both devices, the coupling strength \( J \sim 8 \) meV is weaker than but of the same order of magnitude as aligned bilayers with \( \theta \) close to \( 0^\circ \) or \( 60^\circ \).

The revival of hybrid excitons in these two bilayers can be understood as a direct result of interlayer tunneling induced by a moiré lattice that is nearly commensurate with the monolayer lattices. The two twist angles are close to the commensurate angles \( 21.8^\circ \) and \( 38.2^\circ \), respectively. At the commensurate angles, the moiré reciprocal lattice constant is \( 1/\sqrt{7} \) of the monolayer reciprocal lattice constant, and corners of the Brillouin zones of the two monolayers become connected by moiré reciprocal lattice vectors, as illustrated in Figs. 3(d) and 3(e). That is, the MoSe\(_2\) and WS\(_2\) band minima overlap again in the moiré reciprocal lattice, allowing strong nearly-resonant tunneling between the intra- and inter-layer states. Specifically, when \( \theta \approx 21.8^\circ \), \( K\)-valley of MoSe\(_2\) and \( K'\)-valley of WS\(_2\) are connected by moiré reciprocal lattice vectors and are folded into equivalent momentum in the moiré Brillouin zone (Figs. 3(d)). The corresponding hybridized excitons have the same valley configuration as those in bilayers with \( \theta \sim 60^\circ \), which is consistent with the observed negative detuning in both cases. When \( \theta \approx 38.2^\circ \), \( K\)-valley of MoSe\(_2\) and \( K\)-valley of WS\(_2\) are folded into equivalent momentum in the moiré Brillouin zone (Figs. 3(e)), and the corresponding hybridized excitons have the same valley configuration as those in bilayers with \( \theta \sim 0^\circ \), consistent with the observed positive detuning in both cases. Moreover, since interlayer
tunneling only needs one Umklapp scattering by a moiré reciprocal lattice vector, the tunneling strength remains of the same order of magnitude as in angularly aligned bilayers. Therefore, the strong revival of the hybrid excitons and their similarities with the angularly-aligned bilayers show again the critical role of moiré lattice in interlayer tunneling.

In the above discussion, we have focused on hybrid states formed with the MoSe$_2$ A excitons, which feature large spectral weight, relatively narrow linewidths, and well-resolved doublets at small detunings. Hybrid states can also form with higher-energy bands, including the MoSe$_2$ B, WS$_2$ A and WS$_2$ B excitons. The B excitons have broader linewidths than the A excitons; as a result the doublets are not well resolved in most samples. The WS$_2$ A excitons have a broader linewidth than MoSe$_2$ A excitons and generally a larger detuning. We observe well-resolved WA doublets only in bilayers with $\theta \sim 0^\circ$, corresponding to hybrid excitons formed by a hole in the WS$_2$ valence band and an electron tunneling between the MoSe$_2$ and WS$_2$ conduction bands (fig. 4).

It is interesting to compare the detuning for MoA and WA states for $\theta \sim 0^\circ$, which we label as $\delta_{MoA}$ and $\delta_{WA}$, respectively. As shown in the schematic electronic band diagram in fig. 4a, neglecting exciton binding energies, the detuning of the inter-layer transition from the intra-layer one is the same magnitude but opposite signs between the MoA and WA states. The sum of the two detuning should be zero. However, this is different from our observation that both the LHX states have larger spectral weight for both MoA and WA states. This can be understood as due to the weaker binding energy of interlayer excitons compared to intra-layer ones, resulting from electron-hole separation. The difference in intra- and inter-layer exciton binding energies, $\Delta E^R_B = E_{BX} - E_{BIX}$, adds to both $\delta_{MoA}$ and $\delta_{WA}$. Assuming $\Delta E^R_B$ is approximately the same for the MoA and WA state, the sum of $\delta_{MoA}$ and $\delta_{WA}$ becomes twice of $\Delta E_B$, or, $\Delta E^R_B = 1/2(\delta_{MoA} + \delta_{WA})$. From our measurements of MoA and WA states in bilayers with $\theta < 1^\circ$, we estimate $\Delta E^R_B$ of 10 to 16 meV (fig. 4b). The value is significantly lower than predictions based on first principle calculations when interlayer tunneling is neglected [22].

In summary, we demonstrate continuous tuning of hybrid moiré excitons that are formed by coupling between intralayer excitons and moiré lattice induced interlayer excitons. The twist-angle dependent hybridization of the excitons and their revival at the commensurate angles are direct manifestations of the discrete translational symmetry of the underlying moiré superlattice, which enables transitions that otherwise would not conserve momentum. The freedom to tune the excitonic properties by tuning the moiré lattice provides a new venue to uncover fundamental
properties of the system that are difficult to access otherwise, and may enable tuning and control of exotic states of matter with novel applications in nanophotonics and quantum information science [10–13, 18–20].

**METHODS**

**Sample fabrication.** Monolayer MoSe$_2$, WS$_2$ and few layer hexagonal boron nitride (hBN) flakes are obtained by mechanical exfoliation from bulk crystals. A PET stamp was used to pick up the top hBN, WS$_2$ monolayer, MoSe$_2$ monolayer, and the bottom hBN under microscope. After picking up all the layers, PET stamp was then stamped onto sapphire substrate, and the PET was dissolved in dichloromethane for six hours at room temperature.

**Optical measurements.** For low temperature measurements, the sample is kept in a 4 K cryostat (Montana Instrument). The excitation and collection are carried out with a home-built confocal microscope with an objective lens with numerical aperture (NA) of 0.42. For reflection contrast measurement, white light from a tungsten halogen lamp is focused on the sample with a beam size of 10 $\mu$m in diameter. The spatial resolution is improved to be 2 $\mu$m by using pinhole combined with confocal lenses. The signal is detected using a Princeton Instruments spectrometer with a cooled charge-coupled camera.

**Coupled oscillator model on hybrid excitons.** To extract the coupling strength $J$ and detuning $\delta$ of intralayer and interlayer excitons, we use the coupled oscillator model to describe the exciton hybridization, and write the Hamiltonian as:

$$H = \begin{bmatrix} E_{IX} & J \\ J & E_X \end{bmatrix}$$

where $E_{IX}$ and $E_X$ represent the energies of uncoupled interlayer exciton and intralayer exciton, and $J$ is the tunneling strength of conduction bands electrons. By diagonalizing the matrix, the eigen energies can be extracted, and difference of the two eigen states is $\Delta E = \sqrt{4J^2 + \delta^2}$, where $\delta = E_{IX} - E_X$. Since the oscillator strength of uncoupled interlayer exciton state is negligibly small compared with the intralayer exciton state, we set it as 0 in the calculation. The ratio of the oscillator strength between the hybrid excitons is

$$\frac{\text{I}_L}{\text{I}_U} = \frac{\sqrt{\Delta^2 + 4J^2 + \delta}}{\sqrt{\Delta^2 + 4J^2 - \delta}}.$$

**Theory for hybrid moiré excitons.** We present a microscopic theory to account for our experimentally observed phenomena of hybrid moiré excitons. For definiteness, here we focus on
R-stacking bilayers with a small twist angle $\theta$ near 0°, and the hybrid MoA states at $K$ valley. The corresponding intralayer $A$ exciton state of MoSe$_2$ can be represented as

$$|X\rangle = \frac{1}{\sqrt{\mathcal{A}}} \sum_k \psi_k a_{c,M,(K_M+k)}^{\dagger} a_{v,M,(K_M+k)} |G\rangle,$$

where $|G\rangle$ represents the ground state of the system with fully filled valence bands, and $a_{c,M,(K_M+k)}^{\dagger} a_{v,M,(K_M+k)}$ creates a particle-hole excitation at valley $K$ in MoSe$_2$ layer, and $\psi_k$ is the relative-motion wave function. In Eq. (3), $\mathcal{A}$ is the system area, $k$ is the relative momentum between electron and holes, and $K_M$ is the momentum of the $K$ point in the Brillouin zone of monolayer MoSe$_2$. The exciton state $|X\rangle$ in Eq. (3) has a zero center-of-mass momentum, and therefore, can couple directly to the light and lead to optical absorption.

For interlayer excitons, we consider states with a generic finite center-of-mass momentum $Q$

$$|Q\rangle_{IX} = \frac{1}{\sqrt{\mathcal{A}}} \sum_k \phi_k a_{c,W,(K_W+k+q_n Q)^{\dagger}} a_{v,M,(K_M+k-q_n M_{IX}^{-1} Q)} |G\rangle,$$

where $a_{v,M,(K_M+k+p)}$ and $a_{c,W,(K_W+k+p)}^{\dagger}$ respectively create a hole in MoSe$_2$ valence band and an electron in WS$_2$ conduction band. $\phi_k$ is the corresponding wave function, and $k$ is the relative momentum. $m_{e,IX}$ and $m_{h,IX}$ are respectively electron and hole mass in the interlayer exciton, and $M_{IX} = m_{e,IX} + m_{h,IX}$ is the exciton total mass. The interlayer exciton state $|Q\rangle_{IX}$ has an energy $\hbar \omega_0 + \hbar^2 Q^2/(2M_{IX})$, which includes an energy constant $\hbar \omega_0$ and a kinetic energy of the center-of-mass motion. In Eq. (4), $K_W$ is the momentum of the $K$ point in the Brillouin zone of monolayer WS$_2$, and differs from $K_M$ due to lattice constant mismatch and misalignment.

The hybridization between intralayer and interlayer excitons is due to interlayer conduction-band tunneling [10] in the moiré pattern, which is given in $+K$-valley by:

$$H_T = w \sum_k \sum_{n=1,2,3} a_{c,W,(K_W+k+q_n a_M)}^{\dagger} a_{c,M,(K_M+k)} + \text{H.c.},$$

where $w$ is a tunneling parameter. In Eq. (5), $q_1$, $q_2$ and $q_3$ are momenta that compensates the momentum shift between $K_W$ and $K_M$ and are connected by the moiré reciprocal lattice vectors. $q_1$ is equal to $K_M - K_W$, while $q_2$ and $q_3$ are respectively related to $q_1$ by $2\pi/3$ and $4\pi/3$ rotations. $|q_1|$ is given by $4\pi/(3a_M)$, and $a_M$ is the moiré period approximated by $a_0/\sqrt{\theta^2 + \epsilon^2}$, where $a_0$ is the monolayer lattice constant, and $\epsilon$ is the lattice constant mismatch $|a_0 - a'_0|/a_0$ between the two layers [27]. In Eqs. (3), (4) and (5), the spin label is not shown explicitly, and we consider spin up states.
This interlayer tunneling Hamiltonian $H_T$ hybridizes an intralayer exciton $|X\rangle$ with an interlayer exciton $|IX\rangle$, which shares the same angular momentum as $|X\rangle$ and can be written as [12]:

$$|IX\rangle = \frac{1}{\sqrt{3}}(|q_1\rangle_{IX} + |q_2\rangle_{IX} + |q_3\rangle_{IX}).$$

(6)

The energy difference $\delta$ between $|IX\rangle$ and $|X\rangle$ is

$$\delta = E_{IX} - E_X$$

$$= \delta_0 + \frac{\hbar^2 q_1^2}{2M_{IX}}$$

$$= \tilde{\delta}_0 + \left(\frac{4\pi}{3a_0}\right) \frac{\hbar^2 \theta^2}{2M_{IX}},$$

(7)

where the energy $E_{intra}$ of intralayer exciton $|X\rangle$ is assumed to be independent of the twist angle $\theta$, while the energy $E_{inter}$ of interlayer exciton $|IX\rangle$ increases with increasing $\theta$ due to its kinetic energy. Equation [7] provides a quantitative description of the experimentally observed $\theta$ dependence of the detuning $\delta$ when $\theta$ is small.

The coupling $J$ between $|IX\rangle$ and $|X\rangle$ due to the interlayer tunneling is

$$J = \langle IX|H_T|X\rangle = \frac{\sqrt{3}w}{A} \sum_k \phi_k^* \frac{m_{h,IX}}{M_{IX}} q_1 \psi_k,$$

(8)

where $\phi_k$ and $\psi_k$ are respectively the relative-motion wave function for interlayer and intralayer excitons with the normalizations $(1/A) \sum_k |\psi_k|^2 = 1$ and $(1/A) \sum_k |\phi_k|^2 = 1$. Because of the momentum shift $(m_{h,IX}/M_{IX})q_1$ in the integral of Eq. [8], $J$ decreases with increasing $\theta$, which agrees with the experimentally observed $\theta$ dependence of $J$. At $\theta = 0^\circ$, $J$ can be approximated by $\sqrt{3}w$. Using our experimentally measured value of $J$, we can estimate the interlayer tunneling $w$ to be about 14 meV.

We make two remarks about the theory. (1) While $R$ stacking configuration and the MoA hybrid excitons are assumed in the above analysis, Equations [7] and [8] apply equally well to $H$ stacking configuration and other hybrid excitons, but the exact parameter values can be different for different cases. (2) Moiré pattern can in principle lead to additional bright exciton states besides those that are studied above. Here we only consider hybrid exciton states made of $|X\rangle$ and $|IX\rangle$, because this type of hybrid states have the largest oscillator strengths. In summary, the theory presented here lays a microscopic foundation for the phenomenological coupled oscillator model, provides a microscopic explanation for the experimentally observed $\theta$ dependence of $J$ and $\delta$, and allows us to estimate the interlayer exciton total mass $M_{IX}$ and the interlayer tunneling $w$ from the optical spectra.
Data availability Data are available on request from the authors. Competing interests The authors declare that they have no competing financial interests. Author Contributions H.D., L.Z. conceived the experiment. L.Z. and Z.Z fabricated the device and performed the measurements. F.W. performed the modeling and calculations. L.Z. and H.D. performed data analysis. R.G performed tunneling estimation. D.W, S.H, K.K. and T.G assisted the fabrication. K.W. and T.T grew hBN single crystals. H.D. and S.F. supervised the projects. L.Z, F.W. and H.D. wrote the paper with inputs from other authors. All authors discussed the results, data analysis and the paper. Acknowledgment L.Z., R.G, S.H, S.F. and H.D. acknowledge the support by the Army Research Office under Awards W911NF-17-1-0312. F. W. is supported by Laboratory for Physical Sciences. K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan and the CREST (JPMJCR15F3), JST. S.F. also acknowledges support by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0017971.

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FIG. 1: Hybrid excitons in rotationally aligned WS$_2$/MoSe$_2$ bilayers. (a) Optical microscope image of an hBN-encapsulated heterobilayer. Red and blue solid lines outline the MoSe$_2$ and WS$_2$ monolayers, respectively. (b) Top panels illustrate a unit cell of R-stacking (left) and H-stacking (right) WS$_2$/MoSe$_2$ bilayers with a small twist angle. Middle panels depict the corresponding conduction and valence band alignment of WS$_2$ and MoSe$_2$, where X labels the intra-layer transition and IX labels the nearly-resonant inter-layer transition that shares the same hole state. Solid and dashed lines correspond to states of opposite spins. Bottom panels illustrate the alignment between an intra-layer MoSe$_2$ A exciton state (red) and the inter-layer exciton state (blue) that it hybridizes with.

(c) Reflection contrast (RC) spectra for, from bottom to top, a monolayer WS$_2$ (blue), monolayer MoSe$_2$ (red), R-stacking bilayer (orange) and H-stacking bilayer (purple). The dots are data and solid lines are fits by transfer matrix calculations. (d) Summary of the ratio of the oscillator strength between LXH and UHX by fitting the bilayer spectra in c, and the corresponding detuning $\delta$ calculated using the coupled oscillator model.
FIG. 2: Twist angle dependence of the hybrid excitons. (a) RC spectra of bilayers of different twist angles $\theta_i$, for $i = 1$ to 6. The corresponding $\theta_i$ and fitted detuning $\delta_i = E_{IX,i} - E_{X,i}$ are labeled by each spectrum. Two well-resolved, bright hybrid MoA excitons are observed for $\theta_0$ up to $6^\circ$. (b) Schematics of MoA intra-layer (red) and inter-layer (blue) exciton bands at the different twist angles $\theta_i$. The interlayer exciton band is displaced in the momentum space by $Q_i$ with increasing $\theta_i$. The moiré superlattice leads to band folding and formation of a new interlayer exciton state at the $\Gamma$ point $q = 0$ (blue oval), with the same angular momentum as the intralayer exciton state (red oval). (c) Ratio of the oscillator strengths of the hybrid states $LHX_{MoA}$ and $UHX_{MoA}$, detuning, and inter- and intra-layer exciton coupling strength as a function of the twist angle $\theta$, obtained from the RC spectra. The gray solid lines in the middle panel are quadratic fits based on equation [1].
FIG. 3: Hybridization in commensurate moiré lattices compared with aligned bilayers. (a)
RC spectra of bilayers with $\theta = 2.1^\circ, 20.1^\circ, 40.3^\circ$ and 59.8$^\circ$. All show two well-resolved
hybrid excitons. The LHX has a higher (lower) spectral weight than UHX has in bilayers
with $\theta = 2.1^\circ$ and 40.3$^\circ$ ($\theta = 59.8^\circ$ and 20.1$^\circ$). Dots are data, solid lines are fits by transfer
matrix calculation, and dashed lines are the fitted individual hybrid exciton resonances.
(b) Summary of the fitted parameters for the RC spectra in a, showing similarities between
bilayers with $\theta = 2.1^\circ$ and 40.3$^\circ$ and between bilayers with $\theta = 59.8^\circ$ and 20.1$^\circ$.
(c-e) Schematics of the Brillouin zones of twisted bilayers. The red (blue) hexagons depict the
Brillouin zones of MoSe$_2$ (WS$_2$) monolayers. The lattice constant mismatch between
MoSe$_2$ and WS$_2$ is neglected in this figure for the purpose of clear illustration. In (c), the
twist angle is small, at $\theta = 6^\circ$. The green arrows indicate vectors $\mathbf{q}_1$, $\mathbf{q}_2$ and $\mathbf{q}_3$, which
represent the momentum shift between the Brillouin zone corners of the two monolayers.

In (d), $\theta = 21.8^\circ$, a commensurate moiré lattice is formed, with the corresponding
moiré Brillouin zone depicted by the black hexagons. The yellow arrow represents the
moiré reciprocal lattice base vector that connects $\mathbf{K}_M$ and $\mathbf{K}_W'$. In (e), $\theta = 38.2^\circ$, which is
another commensurate angle dual to 21.8$^\circ$, and $\mathbf{K}_M$ and $\mathbf{K}_W$ become equivalent states in
the moiré Brillouin zone.
FIG. 4: Comparison of MoA and WA hybrid states. (a) Band diagram of R-stacking MoSe₂/WS₂ bilayers. The conduction and valence bands are represented by broad continuous bands. Exciton states are represented by the horizontal solid lines. Arrows represent spin-conserved exciton transitions, which are lowered in energy from the band-to-band transition by a binding energy. \( E_{BX} \) and \( E_{BIX} \) denote the binding energies for the intra- and inter-layer transitions, respectively. (c) RC spectra of both MoA and WA hybrid excitons from bilayers with \( \theta \sim 0^\circ \). Dots are data and solid lines are fits by transfer matrix calculations. The corresponding \( \theta \) and detuning \( \delta_M \) and \( \delta_W \) obtained from fitting are labeled by each spectrum.