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Supplementary Information for Resonantly hybridized excitons in moiré superlattices in van der Waals heterostructures

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I. SUPPLEMENTARY NOTES

1. Model for intralayer-interlayer exciton hybridization and moiré superlattice minibands for excitons

Bright $MoSe_2$ excitons are formed in an $MoSe_2/WS_2$ heterobilayer by $\tau\mathbf{K}_{MoSe_2}$ valley electrons and $-\tau\mathbf{K}_{MoSe_2}$ holes of opposite spins, where $\tau = \pm 1$ is the valley index. For $\tau = 1$, the intralayer exciton state is

$$|\mathrm{X}_s(\mathbf{Q})\rangle = \frac{1}{\sqrt{S}}\sum_{\boldsymbol{\kappa}}\tilde{\varphi}(\boldsymbol{\kappa})c^\dagger_{\mathrm{M},s}(\mathbf{K}_{\mathrm{MoSe}_2} + \tfrac{m_e}{M_\mathrm{X}}\mathbf{Q} + \boldsymbol{\kappa})h^\dagger_{\mathrm{M},-s}(-\mathbf{K}_{\mathrm{MoSe}_2} + \tfrac{m_h}{M_\mathrm{X}}\mathbf{Q} - \boldsymbol{\kappa})\,|\Omega\rangle\,, \quad (1)$$

where $c^\dagger_{\mathrm{M},s}(\mathbf{K}_{\mathrm{MoSe}_2} + \mathbf{k})$ $[h^\dagger_{\mathrm{M},s}(\mathbf{K}_{\mathrm{MoSe}_2} + \mathbf{k})]$ creates an electron (hole) in the $MoSe_2$ spin–s conduction (valence) band, with wave vector $\mathbf{k}$ near $\mathbf{K}_{\mathrm{MoSe}_2}$ ($s =\downarrow$ gives the A exciton, $\mathrm{X_A}$, while $s =\uparrow$ gives the B exciton, $\mathrm{X_B}$. The same is true for WS_2), and $\tilde{\varphi}(\boldsymbol{\kappa})$ is the Fourier transform of the (ground-state) exciton relative-motion wavefunction. m_e and m_h are the electron and hole effective masses; $M_\mathrm{X} = m_e + m_h$, and $|\Omega\rangle$ is the heterobilayer ground state.

$MoSe_2$ electrons tunnel into the WS_2 conduction band through the "hopping term"[1],

$$t = \sum_{s,\tau'=\pm1}\sum_{m,n}\sum_{\mathbf{k},\mathbf{k}'}\delta_{(\mathbf{K}_{\mathrm{MoSe}_2}+\mathbf{k})-(\tau'\mathbf{K}_{\mathrm{WS}_2}+\mathbf{k}'),\mathbf{G}_n^{\mathrm{WS}_2}-\mathbf{G}_m^{\mathrm{MoSe}_2}}\,t_{cc}(\mathbf{G}_m^{\mathrm{MoSe}_2} + \mathbf{K}_{\mathrm{MoSe}_2} + \mathbf{k})$$
$$\times\left[e^{-i\mathbf{G}_m^{\mathrm{MoSe}_2}\cdot\mathbf{r}_0}c^\dagger_{\mathrm{W},s}(\tau'\mathbf{K}_{\mathrm{WS}_2} + \mathbf{k}')c_{\mathrm{M},s}(\mathbf{K}_{\mathrm{MoSe}_2} + \mathbf{k}) + \mathrm{H.c.}\right],$$

where $\mathbf{G}_m^{\mathrm{MoSe}_2}$ and $\mathbf{G}_n^{\mathrm{WS}_2}$ are reciprocal lattice vectors of the corresponding crystals, and $\mathbf{r}_0$ represents the in-plane shift between metal atoms in the two layers, which together with the twist angle θ parametrizes the heterobilayer stacking. The Kronecker delta encodes momentum conservation . Due to symmetry under C_3 rotations, the valley $-\mathbf{K}_{\mathrm{WS}_2}$ is equivalent to $\mathbf{K}'_{\mathrm{WS}_2}$ (see main text Fig. 3a).

Intralayer $MoSe_2$ excitons can hybridize with interlayer excitons (iXs) of same quantum number s, (WS_2 electron and an $MoSe_2$ hole)

$$|\mathrm{Y}_s^{\tau'}(\mathbf{Q}')\rangle = \frac{1}{\sqrt{S}}\sum_{\boldsymbol{\kappa}}\tilde{\psi}(\boldsymbol{\kappa})c^\dagger_{W,s}(\tau'\mathbf{K}_{\mathrm{WS}_2} + \tfrac{m'_e}{M_\mathrm{iX}}\mathbf{Q}' + \boldsymbol{\kappa})h^\dagger_{M,-s}(-\mathbf{K}_{\mathrm{MoSe}_2} + \tfrac{m_h}{M_\mathrm{Y}}\mathbf{Q}' - \boldsymbol{\kappa})\,|\Omega\rangle\,, \quad (2)$$

where m'_e is the WS_2 electron effective mass and $M_\mathrm{iX} = m'_e + m_h$ (see Extended Data Table I).

The relative-motion momentum-space wavefunctions of both exciton species are given by

$$\tilde{\varphi}(\boldsymbol{\kappa}) = \int \mathrm{d}^2\rho\, e^{-i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}}\varphi(\boldsymbol{\rho}), \quad \tilde{\psi}(\boldsymbol{\kappa}) = \int \mathrm{d}^2\rho\, e^{-i\boldsymbol{\kappa}\cdot\boldsymbol{\rho}}\psi(\boldsymbol{\rho}),$$

and we obtained the real–space wavefunctions

$$\varphi(\rho) \approx \sqrt{\frac{2}{\pi a_{\mathrm{X}}^2}}\, e^{-\rho/a_{\mathrm{X}}}, \quad \psi(\rho) \approx \sqrt{\frac{2}{\pi a_{\mathrm{iX}}^2}}\, e^{-\rho/a_{\mathrm{iX}}},$$

by solving numerically the two–body problem with bilayer Keldysh–type interactions [2–6], finding a_{X} and a_{iX} from the solutions. Then, we obtain the bright inter–intra exciton mixing term

$$T = \sum_{s,\tau'} \sum_{m,n} \sum_{\mathbf{Q},\mathbf{Q}'} T_{\tau'}(\mathbf{G}_m^{\mathrm{MoSe_2}}, \mathbf{G}_n^{\mathrm{WS_2}}) \delta_{\mathbf{Q}-\mathbf{Q}', \Delta\mathbf{K}_{\tau'}+\mathbf{G}_n^{\mathrm{WS_2}}-\mathbf{G}_m^{\mathrm{MoSe_2}}} Y_s^{\tau'\dagger}(\mathbf{Q}') X_s(\mathbf{Q}) + \mathrm{H.c.}$$

$$T_{\tau'}(\mathbf{G},\mathbf{G}') \approx \frac{4t_{cc}(\mathbf{K}_{\mathrm{MoSe_2}}+\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{r}_0}}{a_{\mathrm{X}}a_{\mathrm{iX}}} \left(\frac{a_{\mathrm{X}}+a_{\mathrm{iX}}}{a_{\mathrm{X}}a_{\mathrm{iX}}}\right) \left[\left(\frac{a_{\mathrm{X}}+a_{\mathrm{iX}}}{a_{\mathrm{X}}a_{\mathrm{iX}}}\right)^2 + \frac{m_h^2}{M_{\mathrm{iX}}^2}(\Delta\mathbf{K}_{\tau'}+\mathbf{G}'-\mathbf{G})^2\right]^{-3/2}, \tag{3}$$

where $\Delta\mathbf{K}_{\tau'} = \tau'\mathbf{K}_{\mathrm{WS_2}} - \mathbf{K}_{\mathrm{MoSe_2}}$; $\Delta\mathbf{K} \equiv \Delta\mathbf{K}_+$ and $\Delta\mathbf{K}' \equiv \Delta\mathbf{K}_-$; and $X_s(\mathbf{Q})$, $Y_s^{\tau'}(\mathbf{Q}')$ are exciton annihilation operators.

The coupling function $t_{cc}(\mathbf{q})$ decays rapidly with wave vector for $|\mathbf{q}| > |\mathbf{K}_{\mathrm{MoSe_2}}|$ [1, 7], which allows us to set it as a constant t_{cc} for $|\mathbf{q}| \lesssim |\mathbf{K}_{\mathrm{MoSe_2}}|$, and zero otherwise. This makes $T_{\tau'}(\mathbf{G},\mathbf{G}')$ finite only for $\mathbf{G}=0$ and the two other $\mathrm{MoSe_2}$ Bragg vectors shown in Extended Data Fig. 3c. For closely aligned ($\theta \approx 0°$) configurations, when $\mathbf{G} = \mathbf{G}_n^{\mathrm{MoSe_2}}$, the hopping term gives significant contributions only if $\tau' = 1$ and $\mathbf{G}' = \mathbf{G}_n^{\mathrm{WS_2}}$, and is vanishingly small otherwise. Thus, the allowed Bragg vector combinations give

$$\Delta\mathbf{K} + \mathbf{G}' - \mathbf{G} = \begin{cases} \Delta\mathbf{K} \ , & \mathbf{G}' = \mathbf{G} = 0 \\ C_3\Delta\mathbf{K} \ , & \mathbf{G}' = \mathbf{G}_2^{\mathrm{WS_2}},\ \mathbf{G} = \mathbf{G}_2^{\mathrm{MoSe_2}} \\ C_3^2\Delta\mathbf{K} \ , & \mathbf{G}' = -\mathbf{G}_1^{\mathrm{WS_2}},\ \mathbf{G} = -\mathbf{G}_1^{\mathrm{MoSe_2}} \end{cases} .$$

Therefore, to a good approximation,

$$T = \sum_s \sum_{\mathcal{D}} \sum_{\mathbf{Q},\mathbf{Q}'} \delta_{\mathbf{Q}-\mathbf{Q}',\mathcal{D}\Delta\mathbf{K}}\, T_{\mathcal{D}}\, Y_s^{+\dagger}(\mathbf{Q}') X_s(\mathbf{Q}) + \mathrm{H.c.},$$

$$T_{\mathcal{D}} = e^{i\mathbf{K}\cdot\mathbf{r}_0} \frac{4t_{cc}e^{-i\mathcal{D}\mathbf{K}\cdot\mathbf{r}_0}}{a_{\mathrm{X}}a_{\mathrm{iX}}} \left(\frac{a_{\mathrm{X}}+a_{\mathrm{iX}}}{a_{\mathrm{X}}a_{\mathrm{iX}}}\right) \left[\left(\frac{a_{\mathrm{X}}+a_{\mathrm{iX}}}{a_{\mathrm{X}}a_{\mathrm{iX}}}\right)^2 + \frac{m_h^2}{M_{\mathrm{iX}}^2}\Delta K^2\right]^{-3/2},$$

where we define $\mathcal{D} \in \{E,\, C_3,\, C_3^2\}$, with C_3^n a rotation by $\frac{2n\pi}{3}$ and E the identity.

For $\theta \approx 60°$ one must choose $\tau' = -1$ and for each Bragg vector $\mathbf{G} = \mathbf{G}_n^{\mathrm{MoSe_2}}$ take $\mathbf{G}' = -C_3\mathbf{G}_n^{\mathrm{WS_2}}$, resulting in

$$\tilde{T} = \sum_s \sum_{\mathcal{D}} \sum_{\mathbf{Q},\mathbf{Q}'} \delta_{\mathbf{Q}-\mathbf{Q}',\mathcal{D}\Delta\mathbf{K}'}\, \tilde{T}_{\mathcal{D}}\, Y_s^{-\dagger}(\mathbf{Q}') X_s(\mathbf{Q}) + \mathrm{H.c.}$$

From the above analysis, we get for $\tau = 1$ the exciton Hamiltonians

$$H = \sum_s \sum_{\mathbf{Q}} \left[\mathcal{E}_{\mathrm{X,s}}(\mathbf{Q}) X_s^\dagger(\mathbf{Q}) X_s(\mathbf{Q}) + \mathcal{E}_{\mathrm{iX,s}}^{+}(\mathbf{Q}) Y_s^{+\dagger}(\mathbf{Q}) Y_s^{+}(\mathbf{Q}) \right] + T; \quad \theta < 30^\circ, \tag{4a}$$

$$H = \sum_s \sum_{\mathbf{Q}} \left[\mathcal{E}_{\mathrm{X,s}}(\mathbf{Q}) X_s^\dagger(\mathbf{Q}) X_s(\mathbf{Q}) + \mathcal{E}_{\mathrm{iX,s}}^{-}(\mathbf{Q}) Y_s^{-\dagger}(\mathbf{Q}) Y_s^{-}(\mathbf{Q}) \right] + \tilde{T}; \quad \theta > 30^\circ, \tag{4b}$$

where

$$\mathcal{E}_{\mathrm{X,s}}(\mathbf{Q}) = E_{\mathrm{X}}^0 + s(\Delta_{\mathrm{SO}}^{\mathrm{v}} + \Delta_{\mathrm{SO}}^{\mathrm{c}}) + \frac{\hbar^2 Q^2}{2M_{\mathrm{X}}},$$

$$\mathcal{E}_{\mathrm{iX,s}}^{\tau'}(\mathbf{Q}) = E_{\mathrm{iX}}^0 + s(\Delta_{\mathrm{SO}}^{\mathrm{v}} + \tau' \Delta_{\mathrm{SO}}^{\mathrm{c}}{}') + \frac{\hbar^2 Q^2}{2M_{\mathrm{iX}}},$$

with $\Delta_{\mathrm{SO}}^{\mathrm{c}}$ and $\Delta_{\mathrm{SO}}^{\mathrm{v}}$ the spin-orbit couplings of the $MoSe_2$ conduction and valence bands, and $\Delta_{\mathrm{SO}}^{\mathrm{c}}{}'$ the WS_2 conduction band spin-orbit coupling. Thus, for $Q = 0$, the A- and B-exciton energies can be written as (see Extended Data Table I) $E_{\mathrm{X_A}} = E_{\mathrm{X}}^0 - (\Delta_{\mathrm{SO}}^{\mathrm{v}} + \Delta_{\mathrm{SO}}^{\mathrm{c}})$ and $E_{\mathrm{X_B}} = E_{\mathrm{X}}^0 + (\Delta_{\mathrm{SO}}^{\mathrm{v}} + \Delta_{\mathrm{SO}}^{\mathrm{c}})$. Analogous terms exist for the $\tau = -1$ valley, given by a time reversal transformation.

The moiré superlattice periodicity, introduced in Eqs. (4a) and (4b) through the terms T and $\tilde{T}$, requires that we fold the X and iX bands onto the moiré Brillouin zone,

$$|\mathrm{X}_s(\mathbf{Q})\rangle_{m,n} \equiv |X_s(\mathbf{Q} + m\mathbf{b}_1 + n\mathbf{b}_2)\rangle,$$

$$|\mathrm{Y}_s^{\tau'}(\mathbf{Q}')\rangle_{m,n} \equiv |Y_s^{\tau'}(\mathbf{Q}' + m\mathbf{b}_1 + n\mathbf{b}_2)\rangle,$$

where $\mathbf{Q}$ is limited to the first moiré Brillouin zone (mBZ, Extended Data Fig. 3e). The intra- and interlayer exciton states $|\mathrm{X}_s(\mathbf{Q})\rangle_{m,n}$ and $|\mathrm{Y}_s^{\tau'}(\mathbf{Q}')\rangle_{m',n'}$ hybridize when $\mathbf{Q} = \mathbf{Q}'$ and

$$(m' - m)\mathbf{b}_1 + (n' - n)\mathbf{b}_2 = \mathbf{b}_j\,;\ j = \pm 1, \pm 2, \pm 3,$$

producing hXs states

$$|\mathrm{hX}_s^{\tau'}(\mathbf{Q})\rangle_{i,j} \equiv \sum_{m,n=0}^{\infty} \left[A_{i,j}^{m,n}(s, \mathbf{Q}) |\mathrm{X}_s(\mathbf{Q})\rangle_{m,n} + B_{i,j}^{m,n}(s, \tau', \mathbf{Q}) |\mathrm{Y}_s^{\tau'}(\mathbf{Q})\rangle_{m,n} \right], \ \mathbf{Q} \in \mathrm{mBZ},$$

with corresponding energies $E_{s;i,j}^{\tau'}(\mathbf{Q})$.

To evaluate the optical spectra of hX states, we use the light-matter interaction Hamiltonian

$$H_{\mathrm{LM}} = \frac{e\gamma}{\hbar c} \sum_s \sum_{\eta=\pm 1} \sum_{\boldsymbol{\xi}, \xi_z} \sum_{\mathbf{k}} \sqrt{\frac{4\pi\hbar c}{V\boldsymbol{\xi}}}\, c_{\mathrm{M,s}}^\dagger(\eta \mathbf{K}_{\mathrm{MoSe_2}} + \mathbf{k} - \boldsymbol{\xi}) h_{\mathrm{M,s}}^\dagger(-\eta \mathbf{K}_{\mathrm{MoSe_2}} - \mathbf{k}) a_\eta^\dagger(\boldsymbol{\xi}, \xi_z) + \mathrm{H.c.}$$

Here, $a_\eta^\dagger(\boldsymbol{\xi}, \xi_z)$ creates a photon of in-plane momentum $\boldsymbol{\xi}$ and out-of-plane momentum ξ_z, and polarization $\eta = \pm 1$, corresponding to counter-clockwise and clockwise, respectively. We obtain the recombination and absorption rates from Fermi's golden rule ($\mathbf{Q}+m\mathbf{b}_1+n\mathbf{b}_2 = \boldsymbol{\xi}$):

$$\Gamma^{\tau'}_{\mathrm{PL;m,n;s}}(\mathbf{Q}) = \frac{4\pi}{\hbar} \sum_{\boldsymbol{\xi},\xi_z} |\langle \eta; \boldsymbol{\xi}, \xi_z | H_{\mathrm{LM}} | \mathrm{hX}^{\tau'}_s(\mathbf{Q})\rangle_{m,n}|^2 n_{\mathrm{B}}(E^{\tau',T}_{s;m,n}) \delta\left(E^{\tau'}_{s;m,n}(\mathbf{Q}) - \hbar c\sqrt{|\boldsymbol{\xi}|^2 + \xi_z^2}\right),$$

$$\Gamma^{\eta}_{\mathrm{A}}(\boldsymbol{\xi}, \xi_z) = \frac{2\pi}{\hbar} \sum_{s} \sum_{m,n} \sum_{\mathbf{Q}} |_{m,n}\langle \mathrm{hX}^{\tau'}_s(\mathbf{Q}) | H_{\mathrm{LM}} | \eta; \boldsymbol{\xi}, \xi_z\rangle|^2 \delta\left(E^{\tau'}_{s;m,n}(\mathbf{Q}) - \hbar c\sqrt{|\boldsymbol{\xi}|^2 + \xi_z^2}\right),$$

For PL, we take into account temperature effects through the Bose-Einstein distribution

$$n_{\mathrm{B}}(E, T) = \frac{1}{e^{(E-E_{\mathrm{gnd}})/k_{\mathrm{B}}T} + 1},$$

where E_{gnd} is the energy of the lowest exciton state. The calculated twist-angle dependence of the activation energy $E_{\downarrow;0,0}(0) - E_{\mathrm{gnd}}$ for hX_1 in $\mathrm{MoSe}_2/\mathrm{WS}_2$, as well as PL spectra at several temperatures, are shown in Extended Data Fig. 8.

For absorption, we find [8]

$$I^s_{\mathrm{A}}(\hbar\omega) = \frac{8\omega\delta\omega}{\hbar\pi c^2} \frac{e^2}{\hbar c} \sum_{m,n} \left| \sum_{i,j} \frac{\gamma A^{i,j}_{m,n}(s,0)}{a_{\mathrm{X}}} \right|^2 \frac{\beta/\pi}{(\hbar\omega - E^{\tau'}_{s;m,n}(0))^2 + \beta^2},$$

where we use $\beta = 5\,\mathrm{meV}$ and $\hbar\delta\omega = 1\,\mathrm{meV}$ to evaluate the spectrum shown in Fig. 3e.

2. Harmonic potential approximation to exciton moiré effects in $\mathrm{MoSe}_2/\mathrm{WS}_2$ heterostructures

The moiré superlattice effects on the band structure [9, 10] and exciton energies [7] of bilayer systems, produced by incommensurability and misalignment of the two lattices, are often described in terms of a minimal harmonic potential [11–13]. In this section we derive the tunnelling contribution to this potential for intralayer excitons in TMD heterobilayers, using $\mathrm{MoSe}_2/\mathrm{WS}_2$ as a case study. We show that a harmonic potential fails to describe the moiré superlattice effects in the close alignment (anti-alignment) regime in the case of near-resonant exciton bands.

For $\theta < 30^\circ$, interlayer tunnelling T allows MoSe_2 intralayer excitons to explore the reciprocal lattice of the WS_2 layer through virtual tunneling of their electrons onto the WS_2 conduction band, and then back onto the MoSe_2 conduction band. These virtual processes introduce momentum-dependent corrections to the intralayer exciton energies, which in real space correspond to a potential.

Focusing on the case of $\theta < 30°$, we perform a canonical transformation $\tilde{H} = e^{iS} H e^{-iS}$ on the intralayer-interlayer exciton Hamiltonian $H = H_0 + T$ presented in main text Eq. (4a), with the condition [14]

$$T = -i\,[S, H_0]\,, \tag{8}$$

which removes from $\tilde{H}$ all terms that are first order in T. A similar procedure is followed for the Hamiltonian of main text Eq. (4b), for $\theta > 30°$. The condition Eq. (8) is achieved by the generator

$$iS = \sum_{s}\sum_{\mathcal{D}}\sum_{\mathbf{Q},\mathbf{Q}'} \delta_{\mathbf{Q},\mathbf{Q}'+\mathcal{D}\Delta\mathbf{K}} \left[\frac{T_{\mathcal{D}}}{\mathcal{E}^{+}_{\mathrm{iX,s}}(\mathbf{Q}') - \mathcal{E}_{\mathrm{X,s}}(\mathbf{Q})} Y^{+\dagger}_{s}(\mathbf{Q}') X_s(\mathbf{Q}) - \mathrm{H.c.} \right] \tag{9}$$

Evaluating $\tilde{H}$ up to second order in T we obtain

$$\begin{aligned} \tilde{H} \approx &\sum_{s}\sum_{\mathbf{Q}} \left[\tilde{E}_{\mathrm{X,s}}(\mathbf{Q}) X^{\dagger}_{s}(\mathbf{Q}) X_s(\mathbf{Q}) + \tilde{E}_{\mathrm{iX,s}}(\mathbf{Q}) Y^{+\dagger}_{s}(\mathbf{Q}) Y^{+}_{s}(\mathbf{Q}) \right] \\ &+ \frac{1}{2}\sum_{s}\sum_{\mathcal{D}\neq\mathcal{D}'}\sum_{\mathbf{Q}} \left[\frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{\mathcal{E}^{+}_{\mathrm{iX,s}}(\mathbf{Q}) - \mathcal{E}^{+}_{\mathrm{X,s}}(\mathbf{Q}+\mathcal{D}\Delta\mathbf{K})} Y^{+\dagger}_{s}(\mathbf{Q}+[\mathcal{D}-\mathcal{D}']\Delta\mathbf{K}) Y^{+}_{s}(\mathbf{Q}) + \mathrm{H.c.} \right] \\ &- \frac{1}{2}\sum_{s}\sum_{\mathcal{D}\neq\mathcal{D}'}\sum_{\mathbf{Q}} \left[\frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{\mathcal{E}^{+}_{\mathrm{iX,s}}(\mathbf{Q}-\mathcal{D}\Delta\mathbf{K}) - \mathcal{E}^{+}_{\mathrm{X,s}}(\mathbf{Q})} X^{\dagger}_{s}(\mathbf{Q}+[\mathcal{D}-\mathcal{D}']\Delta\mathbf{K}) X_s(\mathbf{Q}) + \mathrm{H.c.} \right], \end{aligned} \tag{10}$$

with the renormalized energies

$$\tilde{E}^{\tau}_{\mathrm{X,s}}(\mathbf{Q}) = \mathcal{E}^{\tau}_{\mathrm{X,s}}(\mathbf{Q}) - \frac{1}{2}\sum_{\mathcal{D}} \frac{|T_{\mathcal{D}}|^2}{\mathcal{E}^{\tau}_{\mathrm{Y,s}}(\mathbf{Q}-\mathcal{D}\Delta\mathbf{K}_{\tau}) - \mathcal{E}^{\tau}_{\mathrm{X,s}}(\mathbf{Q})}, \tag{11a}$$

$$\tilde{E}^{\tau\tau'}_{\mathrm{iX,s}}(\mathbf{Q}) = \mathcal{E}^{\tau}_{\mathrm{Y,s}}(\mathbf{Q}) + \frac{1}{2}\sum_{\mathcal{D}} \frac{|T_{\mathcal{D}}|^2}{\mathcal{E}^{\tau}_{\mathrm{Y,s}}(\mathbf{Q}) - \mathcal{E}^{\tau}_{\mathrm{X,s}}(\mathbf{Q}+\mathcal{D}\Delta\mathbf{K}_{\tau})}. \tag{11b}$$

The remaining two terms represent scattering by moiré vectors $\mathbf{b} = (\mathcal{D}-\mathcal{D}')\Delta\mathbf{K}_{\tau}$, as shown in Extended Data Fig. 3e. For exciton momenta near the center of the moiré Brillouin zone we have $Q \ll \Delta K$, and we may approximate

$$\frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{\mathcal{E}^{+}_{\mathrm{iX,s}}(\mathbf{Q}) - \mathcal{E}^{+}_{\mathrm{X,s}}(\mathbf{Q}+\mathcal{D}\Delta\mathbf{K})} \approx \frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{[(E^{0}_{\mathrm{iX}} - \Delta'_{\mathrm{SO}}) - (E^{0}_{\mathrm{X}} - \Delta_{\mathrm{SO}})] - \frac{\hbar^2 \Delta K^2}{2M_{\mathrm{X}}}}, \tag{12a}$$

$$\frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{\mathcal{E}^{+}_{\mathrm{iX,s}}(\mathbf{Q}-\mathcal{D}\Delta\mathbf{K}) - \mathcal{E}^{+}_{\mathrm{X,s}}(\mathbf{Q})} \approx \frac{T^{*}_{\mathcal{D}} T_{\mathcal{D}'}}{[(E^{0}_{\mathrm{iX}} - \Delta'_{\mathrm{SO}}) - (E^{0}_{\mathrm{X}} - \Delta_{\mathrm{SO}})] + \frac{\hbar^2 \Delta K^2}{2M_{\mathrm{iX}}}}. \tag{12b}$$

Finally, an inverse Fourier transform gives the harmonic potential for bright intralayer excitons at valley $\tau = 1$

$$V_{\mathrm{X,s}}(\mathbf{r}) = \sum_{n=1}^{3} \frac{T^{*}_{C_3^{n-1}} T_{C_3^{n-2}} e^{-i\mathbf{d}_n\cdot\mathbf{r}} + T^{*}_{C_3^{n-2}} T_{C_3^{n-1}} e^{i\mathbf{d}_n\cdot\mathbf{r}}}{[(E^0_{\mathrm{iX}} - \Delta'_{\mathrm{SO}}) - (E^0_{\mathrm{X}} - \Delta_{\mathrm{SO}})] + \frac{\hbar^2\Delta K^2}{2M_{\mathrm{iX}}}}, \tag{13}$$

where $C_3^0 = E$, and for convenience we have re-labeled the moiré Bragg vectors as follows: $\mathbf{d}_1 = \mathbf{b}_1$, $\mathbf{d}_2 = \mathbf{b}_3$ and $\mathbf{d}_3 = -\mathbf{b}_2$. A similar analysis for $\theta > 30°$ leads to the potential

$$W_{\mathrm{X,s}}(\mathbf{r}) = \sum_{n=1}^{3} \frac{\tilde{T}^{*}_{C_3^{n-1}} \tilde{T}_{C_3^{n-2}} e^{-i\tilde{\mathbf{d}}_n\cdot\mathbf{r}} + \tilde{T}^{*}_{C_3^{n-2}} \tilde{T}_{C_3^{n-1}} e^{i\tilde{\mathbf{d}}_n\cdot\mathbf{r}}}{[(E^0_{\mathrm{iX}} + \Delta'_{\mathrm{SO}}) - (E^0_{\mathrm{X}} - \Delta_{\mathrm{SO}})] + \frac{\hbar^2\Delta K'^2}{2M_{\mathrm{iX}}}}. \tag{14}$$

Using the values of Extended Data Table I, we find that $W_{\mathrm{X,s}}(\mathbf{r})$ diverges at $\theta \approx 58°$, signaling the breakdown of perturbation theory due to a crossing between the intralayer and interlayer exciton bands at the iX band edge, as shown in Extended Data Fig. 2b. Furthermore, Extended Data Fig. 2c shows that, although $V_{\mathrm{X,s}}(\mathbf{r})$ remains finite for all $\theta < 30°$, the excitation energy in the virtual process becomes smaller than the mixing energy for $\theta < 5°$, indicating that the perturbative approach is no longer valid.

Beyond these angles the intralayer-interlayer exciton mixing strength becomes the dominant energy scale in the problem, such that perturbative methods in general, and a simple description in terms of a potential in particular, cannot describe hX states or the moiré superlattice effects. This is a direct consequence of the near-resonant conduction bands in $MoSe_2/WS_2$ heterostructures.

3. Broadening of the photoluminescence line by random fields in the sample

The dependence on twist angle of the emission line broadening shown in Extended Data Fig. 1b may be explained by the coupling of weak electric fields produced by random strain throughout the sample, with the out-of-plane electric dipole of the mixed intralayer-interlayer exciton states. The field-dipole coupling can be estimated as

$$
\begin{aligned}
H_{\mathrm{E-D}} = &-\frac{ed\,E_z}{2}\sum_s\sum_{\tau=\pm1}\Bigg[\sum_{\mathbf{k}} c^\dagger_{\mathrm{M},s}(\tau\mathbf{K}_{\mathrm{MoSe}_2}+\mathbf{k})c_{\mathrm{M,s}}(\tau\mathbf{K}_{\mathrm{MoSe}_2}+\mathbf{k}) \\
&\qquad - \sum_{\mathbf{k}'} c^\dagger_{\mathrm{W},s}(\tau\mathbf{K}_{\mathrm{WS}_2}+\mathbf{k}')c_{\mathrm{W,s}}(\tau\mathbf{K}_{\mathrm{WS}_2}+\mathbf{k}')\Bigg] \\
&+\frac{ed\,E_z}{2}\sum_s\sum_{\tau=\pm1}\Bigg[\sum_{\mathbf{k}} h^\dagger_{\mathrm{M},s}(\tau\mathbf{K}_{\mathrm{MoSe}_2}+\mathbf{k})h_{\mathrm{M,s}}(\tau\mathbf{K}_{\mathrm{MoSe}_2}+\mathbf{k}) \\
&\qquad - \sum_{\mathbf{k}'} h^\dagger_{\mathrm{W},s}(\tau\mathbf{K}_{\mathrm{WS}_2}+\mathbf{k}')h_{\mathrm{W,s}}(\tau\mathbf{K}_{\mathrm{WS}_2}+\mathbf{k}')\Bigg],
\end{aligned}
\tag{15}
$$

where $c_{\mathrm{M,s}}(\mathbf{q})$ and $c_{\mathrm{W,s}}(\mathbf{q})$ annihilate an electron of momentum $\mathbf{q}$ and spin projection s in $MoSe_2$ and WS_2, respectively; e is the charge unit, d the interlayer distance, and we assume that the out-of-plane electric field E_z is small. In first–order perturbation theory, this gives a correction to the bright, optically–active ($Q = 0$) mixed exciton energy

$$
\delta E = {}_{0,0}\left\langle \mathrm{hX}_\downarrow(0)\left|H_{\mathrm{E-D}}\right|\mathrm{hX}_\downarrow(0)\right\rangle_{0,0} = ed\,E_z\,\left|\langle \mathrm{Y}^{\tau'}_\downarrow(0)|\mathrm{hX}_\downarrow(0)\rangle_{0,0}\right|^2, \tag{16}
$$

where $\tau' = 1$ ($\tau' = -1$) for $\theta < 30°$ ($\theta \geq 30°$), $|\mathrm{hX}_\downarrow(0)\rangle_{0,0}$ is the lowest bright hybridized exciton state, and $\langle \mathrm{Y}^{\tau'}_\downarrow(0)|\mathrm{hX}_\downarrow(0)\rangle_{0,0}$ is its interlayer exciton component (see Methods in main text). Excitons in different parts of the sample will experience different values of E_z. Assuming that the E_z values found throughout the sample follow a Gaussian distribution

$$
\rho(E_z) = \sqrt{\frac{1}{2\pi\sigma^2}}\,e^{-(E_z-E_z^0)^2/2\sigma^2}, \tag{17}
$$

of mean E_z^0 and variance σ^2, the correction δE will also be normally distributed, with mean value

$$
\langle\delta E\rangle_\rho = ed\,E_z^0\,\left|\langle \mathrm{Y}^{\tau'}_\downarrow(0)|\mathrm{hX}_\downarrow(0)\rangle_{0,0}\right|^2, \tag{18}
$$

and a full width at half maximum given by

$$
\mathrm{FWHM}_{\delta E} = 2\sqrt{2\log 2}\sqrt{\langle\delta E^2\rangle_\rho - \langle\delta E\rangle_\rho^2} = 2\sigma\sqrt{2\log 2}\,ed\left|\langle \mathrm{Y}^{\tau'}_\downarrow(0)|\mathrm{hX}_\downarrow(0)\rangle_{0,0}\right|^2. \tag{19}
$$

Allowing for an additive constant, representing the intrinsic broadening of the PL line, we fitted Eq. (19) to the experimental data, and the result is presented in Extended Data Fig. 1b of the main text. The fitting parameters give $\sigma ed = 19.8\,\mathrm{meV}$, or $\sigma \approx 0.03\,\mathrm{V/nm}$, assuming an approximate interlayer distance of 6 Å [15].

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