Supplementary Information
Hybridized intervalley moiré excitons and flat bands in twisted WSe_2 bilayers

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I. DENSITY MATRIX FORMALISM

A. Electronic Hamiltonian

The Starting point is the electronic Hamiltonian in second quantization with monolayer eigenstates as basis function. Here the wave functions of conduction ($\lambda = c$) and valence band electrons ($\lambda = v$) in layer l are described with tight-binding wave functions in the vicinity of high symmetry points ζ of the Brillouin zone. Using compound indices $i = (l_i, \zeta_i)$ these read [1]:

$$\Psi^{\lambda}_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_i} e^{\mathrm{i}(\zeta_i + \mathbf{k})\mathbf{R}_i} \Phi^{\lambda}_i(\mathbf{r} - \mathbf{R}_i). \tag{1}$$

Here Φ represents the effective orbital composing the respective band. Within this basis, the interaction-free part of the bilayer Hamiltonian reads

$$\begin{aligned} H &= H_0 + H_{\mathrm{T}} \\ &= \sum_{\lambda,i,\mathbf{k}} \varepsilon^{\lambda}_{i\mathbf{k}} \lambda^{\dagger}_{i\mathbf{k}} \lambda_{i\mathbf{k}} + \sum_{\lambda,\mathbf{k},\mathbf{q},i\neq j} T^{\lambda}_{ij}(\mathbf{q},\mathbf{k}) \lambda^{\dagger}_{i\mathbf{k}+\mathbf{q}} \lambda_{j\mathbf{k}} \end{aligned} \tag{2}$$

In the close vicinity of ζ_i the band structure is approximated parabolic $\varepsilon^{\lambda}_{i\mathbf{k}} = \varepsilon^{\lambda}_{i0} \pm \hbar^2\mathbf{k}^2/(2m^{\lambda}_i)$ and the tunneling matrix element $T^{\lambda}_{ij}(\mathbf{q},\mathbf{k}) = \langle \lambda i, \mathbf{k}+\mathbf{q}|V_l|\lambda j, \mathbf{k}\rangle$ depends on the bilayer lattice potential V_l. To determine the tunnelling matrix element, we follow the derivation in Ref. [1] which yields

$$\begin{aligned} T^{\lambda}_{ij}(\mathbf{q},\mathbf{k}) = \sum_{\mathbf{G}_i\mathbf{G}_j} & h^{\lambda}_{ij}(\mathbf{k} + \zeta_j + \mathbf{G}_j)\delta_{\mathbf{q},\zeta_j+\mathbf{G}_j-\zeta_i-\mathbf{G}_i} \\ & \times e^{\mathrm{i}(\mathbf{G}_j\mathbf{r}^0_j - \mathbf{G}_i\mathbf{r}^0_i)} \end{aligned} \tag{3}$$

Here $\mathbf{G}_i$ and $\mathbf{r}^0_i$ denote the reciprocal lattice vector and a constant lattice shift in real space respectively. The tunnelling strength is given by the hopping integral in momentum space $h^{\lambda}_{ij}(\mathbf{k}) = 1/A_{uc} \int d\mathbf{R} e^{\mathrm{i}\mathbf{k}\mathbf{R}} \int d\mathbf{r} \Phi^{\lambda}_i(\mathbf{r}) \hat{V}_l \Phi^{\lambda}_i(\mathbf{r} - \mathbf{R})$. Equation 3 can be further simplified by assuming a long range interlayer interaction, viz. quickly decaying hopping integrals in momentum space. In this case, we only sum over reciprocal vectors with $|\zeta_j + \mathbf{G}_j| = |\zeta_j|$, which for valleys deep within the Brillouin zone yield [1],

$$T^{\lambda}_{ij}(\mathbf{q},\mathbf{k}) \approx h^{\lambda}_{\zeta_j} \delta_{\mathbf{q},\zeta_j-\zeta_i}, \quad \text{for } \zeta_i, \zeta_j = \Lambda, \Lambda', \Gamma. \tag{4}$$

In contrast, for electrons at the K point we have to consider the reciprocal vectors connecting two corners of the Brillouin zone, e.g. K and the 120° rotated C_3K. In this case we have to account for the angular symmetry of the d-orbitals composing states at the K point. Hence we find [1, 2]

$$T^{\lambda}_{ij}(\mathbf{q}) \approx \sum_{n=0}^{2} h^{\lambda}_{\zeta_j} \theta^{\lambda n}_{ij} \delta_{\mathbf{q},C^n_3(\zeta_j-\zeta_i)}, \ \zeta_i, \zeta_j = K, K'. \tag{5}$$

The additional phase factors account for orbital symmetries at the K point, as well as phase cancellations resulting from lateral shifts of the two layers: $\theta^{\lambda n}_{ij} = exp(in2\pi/3\Delta l + i(C^n_3\zeta_j - \zeta_j)\mathbf{r^0}_j - i(C^n_3\zeta_i - \zeta_i)\mathbf{r^0}_i)$, with $\Delta l = \pm 1$ for $\lambda = c$ and anti-parallel stacking (AP), but $\Delta l = 0$ else. In the following we will use the more general form in Eq. 5 but keep in mind that for $\zeta_i, \zeta_j = \Lambda, \Lambda', \Gamma$ we have to set $\theta^{\lambda n}_{ij} = \delta_{n,0}$. The interlayer hopping strength h for different bands and high symmetry points can be extracted from band splittings obtained in DFT calculations (cf. Section II).

B. Exciton Transformation and Hybridization

We transform the Hamiltonian into the exciton basis in order to account for the Coulomb interaction on Hartree-Fock level. The Hamiltonian reflecting the attraction between electrons and holes reads,

$$H_{\mathrm{C}} = \sum_{ij\mathbf{k}\mathbf{k}'\mathbf{q}} W^{ij}_{\mathbf{q}} c^{\dagger}_{i\mathbf{k}+\mathbf{q}} v^{\dagger}_{j\mathbf{k}'-\mathbf{q}} v_{j\mathbf{k}'} c_{i\mathbf{k}}. \tag{6}$$

The matrix element $W^{ij}_{\mathbf{q}}$ is treated within a semi-classical approach analogous to the Keldysh potential, however assuming two anisotropic dielectric slabs to model the screening created by the TMD bilayer system [3, 4]. Here we use ab initio parameters from Ref. [5] for the dielectric tensor of WSe_2 and $\epsilon_{\mathrm{sub}} = (3.9 + 1)/2$ for a SiO_2 substrate. To diagonalize the full Hamiltonian, we first transform into the eigenbasis of $H = H_0 + H_{\mathrm{C}}$ by using the exciton Hamiltonian formalism [6, 7]. To this end we define electron-hole pair operators

$$P^{\dagger}_{i\mathbf{k},j\mathbf{k}'} = c^{\dagger}_{i\mathbf{k}} v_{j\mathbf{k}'}, \tag{7}$$

together with the low density pair expansion

$$c^\dagger_{i\mathbf{k}}c_{j\mathbf{k}'} \approx \sum_{l\mathbf{p}} P^\dagger_{i\mathbf{k},l\mathbf{p}}P_{j\mathbf{k}',l\mathbf{p}} \tag{8}$$

$$v^\dagger_{i\mathbf{k}}v_{j\mathbf{k}'} \approx \delta^{ij}_{\mathbf{k}\mathbf{k}'} - \sum_{l\mathbf{p}} P^\dagger_{l\mathbf{p},j\mathbf{k}'}P_{l\mathbf{p},i\mathbf{k}} \tag{9}$$

After expressing the problem in terms of pair operators, we can diagonalize $H = H_0 + H_\mathrm{C}$ by expanding the pairs in terms of excitons $X^{ij}_{\mu\mathbf{Q}}$ with center-of-mass momentum $\mathbf{Q}$:

$$P^\dagger_{i\mathbf{k},j\mathbf{k}'} = \sum_\mu X^\mu_{ij,\mathbf{k}-\mathbf{k}'}{}^\dagger \psi^\mu_{ij}(\alpha_{ij}\mathbf{k}' + \beta_{ij}\mathbf{k}) \tag{10}$$

with mass factors $\alpha_{ij}(\beta_{ij}) = m^\mathrm{c}_i(m^\mathrm{v}_j)/m^\mathrm{c}_i + m^\mathrm{v}_j$ and the wave function $\psi^\mu_{ij}(\mathbf{k})$ for intra- ($l_i = l_j$) and interlayer excitons ($l_i \neq l_j$). The latter fulfil the bilayer Wannier equation

$$\frac{\hbar^2k^2}{2m^\mathrm{r}_{ij}}\psi^\mu_{ij}(\mathbf{k}) - \sum_\mathbf{q} W^{ij}_\mathbf{q}\psi^\mu_{ij}(\mathbf{k}+\mathbf{q}) = E^\mu_{ij\mathbf{0}}\psi^\mu_{ij}(\mathbf{k}), \tag{11}$$

with the binding energy $E^\mu_{ij\mathbf{0}}$ depending on the reduced mass $m^\mathrm{r}_{ij} = (m^c_i m^v_j)/(m^c_i + m^v_j)$. In the following, we restrict our consideration to the exciton ground state $\mu = 1s$. Hence, the excitonic Hamiltonian reads

$$\begin{aligned} H = &\sum_{ij\mathbf{Q}} E_{ij\mathbf{Q}}X^\dagger_{ij\mathbf{Q}}X_{ij\mathbf{Q}} \\ &+ \sum_{i\neq j,l,\mathbf{Q},\mathbf{q}} \tilde{T}^c_{il,jl}(\mathbf{q})X^\dagger_{jl,\mathbf{Q}+\mathbf{q}}X_{il,\mathbf{Q}} \\ &- \sum_{i\neq j,l,\mathbf{Q},\mathbf{q}} \tilde{T}^v_{li,lj}(\mathbf{q})X^\dagger_{lj,\mathbf{Q}+\mathbf{q}}X_{li,\mathbf{Q}} \end{aligned} \tag{12}$$

with exciton tunnelling matrix elements

$$\tilde{T}^c_{il,jl}(\mathbf{q}) = T^c_{ji}(\mathbf{q})\mathcal{F}_{il,jl}(\beta_{jl}\mathbf{q}) \tag{13}$$

$$\tilde{T}^v_{li,lj}(\mathbf{q}) = T^v_{ij}(\mathbf{q})\mathcal{F}_{li,lj}(-\alpha_{jl}\mathbf{q}) \tag{14}$$

$$\mathcal{F}_{ij,nm}(\mathbf{q}) = \sum_\mathbf{k} \psi_{ij}(\mathbf{k})^*\psi_{nm}(\mathbf{k}+\mathbf{q}). \tag{15}$$

Now the Hamiltonian in Eq. 12 is diagonalized numerically. Here it is convenient to transform the discrete mixing of periodic momenta, cf. Eq. 5, into an interaction of subbands created through the moiré superlattice. To this end we introduce a valley specific zone folding with exciton subbands $\tilde{X}^\dagger_{\zeta\alpha,\mathbf{Q}} = X^\dagger_{\zeta_e l_e \zeta_h l_h,\mathbf{Q}-\zeta_e+\zeta_h+n\mathbf{b}_1+m\mathbf{b}_2}$. Here we have introduced new compounds $\zeta = (\zeta_e,\zeta_h)$ and $\alpha = (l_e, l_h, n, m)$ containing valley ζ_e (ζ_h) and layer l_e (l_h) of the electron (hole) as well as the discrete subband index $n, m = 0, 1, 2, ...$ Here the introduced vectors $\mathbf{b}_n = (C^n_3 - 1)(K_2 - K_1)$ correspond to the reciprocal lattice vectors of the moiré lattice and depend on the mismatch between the K point of the upper (K_2) and the lower layer (K_1). Due to the new periodicity of the resulting problem, we can restrict our consideration to momenta $\mathbf{Q}$ within the first mini-Brillouin zone spanned by $\mathbf{b}_1$ and $\mathbf{b}_2$. In the subband basis the Hamiltonian becomes diagonal in $\mathbf{Q} \in$ 1st mBZ and reads

$$H = \sum_{\alpha\mathbf{Q}}(E^\zeta_{\alpha\mathbf{Q}}\tilde{X}^\dagger_{\zeta\alpha,\mathbf{Q}} + \sum_\beta \mathcal{T}^\zeta_{\alpha\beta}\tilde{X}^\dagger_{\zeta\beta,\mathbf{Q}})\tilde{X}_{\zeta\alpha,\mathbf{Q}} \tag{16}$$

with the tunnelling matrix $\mathcal{T}^\zeta_{\alpha\beta}$ containing the valley specific selection rules (Eq. 4 and 5) for the mixing of different subbands and layer configurations. Finally, we introduce new hybrid moiré exciton operators $Y^\dagger_{\zeta\nu\mathbf{Q}} = \sum_\alpha C^{\zeta\nu}_\alpha(\mathbf{Q})^*\tilde{X}^\dagger_{\zeta\alpha,\mathbf{Q}}$, with mixing coefficients fulfilling $E^\zeta_{\alpha\mathbf{Q}}C^{\zeta\nu}_\alpha(\mathbf{Q}) + \sum_\beta \mathcal{T}^\zeta_{\alpha\beta}C^{\zeta\nu}_\beta(\mathbf{Q}) = \mathcal{E}^\zeta_{\nu\mathbf{Q}}C^{\zeta\nu}_\alpha(\mathbf{Q})$ in order to diagonalize the Hamiltonian

$$H = \sum_{\zeta\nu\mathbf{Q}} \mathcal{E}^\zeta_{\nu\mathbf{Q}}Y^\dagger_{\zeta\nu\mathbf{Q}}Y_{\zeta\nu\mathbf{Q}} \tag{17}$$

The resulting eigenstates are valley specific superpositions of different layer configurations as well as integer multiples of center-of-mass momenta $\mathbf{Q} + n\mathbf{b}_1 + m\mathbf{b}_2$ yielding moiré periodic wave functions. Alternative to the diagonalization procedure outlined above, we could have also first diagonalized the interaction-free part of the Hamiltonian of the bilayer, and subsequently considered excitonic effects resulting from the Coulomb interaction. However, the resulting Schroedinger equation for the exciton would be numerically much more demanding than the problem in Eq. 16. Moreover, the above chosen approach allows to conveniently interpret the bilayer physics as consequence of the hybridization of intra- and interlayer excitonic states.

C. Exciton-Phonon and -Photon Interaction

In the following we will transform the electron-phonon and electron-photon interaction, whose parametrisation is known for a monolayer system, into the basis of hybridized moiré excitons derived in the last section. In the above specified monolayer basis, the electron-photon interaction reads,

$$H_{el-pt} = \sum_{i\mathbf{k},\sigma\mathbf{q}} \mathbf{m}^i\hat{\mathbf{e}}_{\sigma\mathbf{q}}c^\dagger_{i,\mathbf{k}+\mathbf{q}_\parallel}v_{i\mathbf{k}}b_{\sigma\mathbf{q}} + \mathrm{h.c.}, \tag{18}$$

with the annihilation operator for σ-polarized photons $b_{\sigma\mathbf{q}}$, normalization of the photon field $\hat{\mathbf{e}}_{\sigma\mathbf{q}}$ and the electron-light matrix element $\mathbf{m}^i$. Note, that the photon momentum $\mathbf{q}$ is three dimensional(with projection $\mathbf{q}_\parallel$ to the monolayer plane), while the electronic momentum $\mathbf{k}$ is strictly two dimensional. We first transform into an exciton Hamiltonian using the above explained pair operators, which yields

$$H_{x-pt} = \sum_{i\sigma\mathbf{q}} \mathbf{M}^i\hat{\mathbf{e}}_{\sigma\mathbf{q}}X^\dagger_{ii,\mathbf{q}_\parallel}b_{\sigma\mathbf{q}} + \mathrm{h.c.}. \tag{19}$$

$$\mathbf{M}^i = \mathbf{m}^i\sum_\mathbf{k}\psi_{ii}(\mathbf{k}) \tag{20}$$

Finally, we expand in terms of hybrid moiré excitons after regrouping indices into exciton valley ζ and layer subband α, giving rise to the convenient form

$$H_{x-pt} = \sum_{\zeta\nu,\sigma\mathbf{q}} \tilde{\mathbf{M}}^{\zeta\nu} \hat{\mathbf{e}}_{\sigma\mathbf{q}} Y^{\dagger}_{\zeta\nu,\mathbf{q}_\parallel} b_{\sigma\mathbf{q}} + \text{h.c.}. \quad (21)$$

$$\tilde{\mathbf{M}}^{\zeta\nu} = \sum_{\alpha} \mathbf{M}^{l_e\zeta_e} C^{\zeta\nu}_{\alpha}(\mathbf{0}) \delta_{\zeta_e\zeta_h} \delta_{l_e l_h} \delta_{n,0} \delta_{m,0} \quad (22)$$

From Eq. 21 we can directly see some interesting new features of the bilayer system. In the monolayer case only intra layer excitons with centre-of-mass momenta within the light cone $X^{\dagger}_{ii,\mathbf{q}_\parallel}$ contribute to the interaction with light (cf. Eq. 19). In contrast, the mixing of different layer configurations as well as subbands in the bilayer yield a whole series of bright states. Thereby, the oscillator strength of a given state ν depends on how strongly the bright intralayer exciton state is contributing to the hybrid. From the form of the Hamiltonian in Eq. 21 we can directly deduce the linear optical response of the system. We can in a straightforward manner generalize the excitonic Elliot formula, so that the absorption coefficient for σ-polarized light reads,

$$\alpha_\sigma(\omega) \propto \sum_{\zeta\nu} \Im\mathrm{m}\left(\frac{|\tilde{M}^{\zeta\nu}_{\sigma}|^2}{\mathcal{E}^{\zeta}_{\nu\mathbf{0}} - \hbar\omega - \mathrm{i}(\gamma^{\zeta}_{\nu} + \Gamma^{\zeta}_{\nu})} \right), \quad (23)$$

where we have introduced a radiative and non-radiative dephasing γ^{ζ}_{ν} and Γ^{ζ}_{ν} determining the broadening of excitonic resonances [8].

Next, we determine the exciton-phonon interaction for the bilayer system. Starting point is again the electronic Hamiltonian in monolayer basis, which for interaction with a single phonon mode $B^{\dagger}_{\mathbf{q}}$ reads,

$$H_{el-ph} = \sum_{\lambda ij\mathbf{kq}} g^{\lambda}_{ij\mathbf{q}} \lambda^{\dagger}_{i,\mathbf{k}+\mathbf{q}} \lambda_{j,\mathbf{k}} (B_{\mathbf{q}+\zeta_{ij}} + B^{\dagger}_{-\mathbf{q}-\zeta_{ij}}) \quad (24)$$

where $\zeta_{ij} = \zeta_i - \zeta_j$ denotes the connection vector of two valleys and $g^{\lambda}_{ij\mathbf{q}}$ corresponds to the electron-phonon matrix element for the intervalley scattering $j \to i$ with phonon momentum $\mathbf{q} + \zeta_{ij}$. The latter is parametrized in zeroth (first) order deformation potential in case of optical (acoustic) phonons. The corresponding parameters for electrons and holes are taken from the DFPT based calculation in Ref. [9] for all relevant intervalley scattering processes. Moreover, direct interlayer hopping via phonon scattering has been neglected by setting $g^{\lambda}_{ij\mathbf{q}} \propto \delta_{l_i,l_j}$. Following the same procedure as for the tunnelling Hamiltonian, we arrive at the exciton-phonon Hamiltonian

$$H_{x-ph} = \sum_{ijl\mathbf{Qq}} (G^{c}_{jl,il}(\mathbf{q}) X^{\dagger}_{il,\mathbf{Q}+\mathbf{q}} X_{jl,\mathbf{Q}} - G^{v}_{li,lj}(\mathbf{q}) X^{\dagger}_{lj,\mathbf{Q}+\mathbf{q}} X_{li,\mathbf{Q}}) (B_{\mathbf{q}+\zeta_{ij}} + B^{\dagger}_{-\mathbf{q}-\zeta_{ij}}) \quad (25)$$

Here we have again introduced excitonic matrix elements [10, 11] analogue to the tunnelling Hamiltonian, $G^{c}_{jl,il}(\mathbf{q}) = g^{c}_{ij\mathbf{q}} \mathcal{F}_{jl,il}(\beta_{il}\mathbf{q})$ and $G^{v}_{li,lj}(\mathbf{q}) = g^{v}_{ij\mathbf{q}} \mathcal{F}_{li,lj}(-\alpha_{lj}\mathbf{q})$. Next, we expand the Hamiltonian in terms of bilayer hybrid excitons Y again using valley and subband compound indices, which yields the final expression

$$H_{x-ph} = \sum_{\zeta\zeta'\nu\nu'\mathbf{Qq},\Delta n,\Delta m} \tilde{G}^{\zeta\nu,\zeta'\nu'}_{\Delta n,\Delta m}(\mathbf{Q},\mathbf{q}) \times Y^{\dagger}_{\zeta'\nu'\mathbf{Q}+\mathbf{q}} Y_{\zeta\nu\mathbf{Q}} (B_{\tilde{\mathbf{q}}} + B^{\dagger}_{-\tilde{\mathbf{q}}}) \quad (26)$$

with the transferred phonon momentum $\tilde{\mathbf{q}} = \mathbf{q} + \Delta n \mathbf{b}_1 + \Delta m \mathbf{b}_2$ and the interaction matrix element for hybridized states

$$\begin{aligned} \tilde{G}^{\zeta\nu,\zeta'\nu'}_{\Delta n,\Delta m}(\mathbf{Q},\mathbf{q}) = \sum_{\alpha\alpha'} & (G^{c}_{\zeta\alpha,\zeta'\alpha'}(\tilde{\mathbf{q}} - \Delta Q_{\zeta\zeta'}) \delta_{\zeta_h\zeta'_h} \\ & - G^{v}_{\zeta\alpha,\zeta'\alpha'}(\tilde{\mathbf{q}} - \Delta Q_{\zeta\zeta'}) \delta_{\zeta_e\zeta'_e}) \\ & \times C^{\zeta\nu}_{\alpha}(\mathbf{Q})^* C^{\zeta'\nu'}_{\alpha'}(\mathbf{Q}+\mathbf{q}) \\ & \times \delta_{l_e l'_e} \delta_{l_h l'_h} \delta_{n'-n,\Delta n} \delta_{m'-m,\Delta m}. \end{aligned} \quad (27)$$

Here the original exciton-phonon matrix elements G are evaluated at the momentum transfer measured in local valley coordinates, so that $\Delta Q_{\zeta\zeta'} = \zeta'_e - \zeta'_h - \zeta_e + \zeta_h$. Note, that although the electron-phonon scattering set up initially was conserving the layer of the electron, the hybridization of excitonic states does effectively allow for a phonon-assisted transfer of charges between layers. Equation 26 indicates that in principle scatterings between all hybrid states ν are allowed, including e.g. those between a state with the electron mostly localized in the upper layer and a state where the electron is predominantly in the lower layer. The strength of such a process is however given by a superposition of the scattering strengths between the underlying intra- and interlayer exciton states composing the hybrids (Eq. 27). Given the generic form of Eq. 26 we can in analogy to Ref. [12] determine the photoluminescence signal of the bilayer, including phonon-assisted recombination processes. Assuming Boltzmann distributions $N^{\zeta}_{\nu\mathbf{Q}}$ for the hybridized excitons and phonon occupation factors $\eta^{\pm}_{\mathbf{q}} = 1/2 \mp 1/2 + n_B(\Omega_{\mathbf{q}})$ (with Bose-distribution n_B at the phonon energy $\Omega_{\mathbf{q}}$) the luminescence intensity perpendicular to the bilayer plane reads

$$I_\sigma(\omega) \propto \sum_{\zeta\nu} \frac{|\tilde{M}^{\zeta\nu}_{\sigma}|^2}{(\mathcal{E}^{\zeta}_{\nu\mathbf{0}} - \hbar\omega)^2 + (\gamma^{\zeta}_{\nu} + \Gamma^{\zeta}_{\nu})^2} \left(\gamma^{\zeta}_{\nu} N^{\zeta}_{\nu\mathbf{0}} + \sum_{\zeta'\nu'\tilde{\mathbf{q}},\pm} |\tilde{G}^{\zeta'\nu',\zeta\nu}_{\Delta n,\Delta m}(\mathbf{0},\mathbf{q})|^2 N^{\zeta'}_{\nu'\mathbf{q}} \eta^{\pm}_{\tilde{\mathbf{q}}} \frac{\Gamma^{\zeta'}_{\nu'}}{(\mathcal{E}^{\zeta'}_{\nu'\mathbf{q}} \pm \Omega_{\tilde{\mathbf{q}}} - \hbar\omega)^2 + (\Gamma^{\zeta'}_{\nu'})^2} \right), \quad (28)$$

where the sum over $\tilde{\mathbf{q}}$ abbreviates summing over $\mathbf{q}$, Δn and Δm. Our numerical implementation of Eq. 28 shows that for recombination processes of K-K excitons assisted by acoustic Γ-phonons, the contribution of terms with $\Delta n, \Delta m > 0$ are negligible due to the weak hybridization at the K point (see main text). For all other phonon-assisted recombination processes the phonon energy is almost independent of the momentum (Einstein approximation), so that the sum over $\tilde{\mathbf{q}}$ can be simlified: $\sum_{\tilde{\mathbf{q}}} |\tilde{G}^{\zeta' \nu', \zeta \nu}_{\Delta n, \Delta m}(\mathbf{0}, \mathbf{q})|^2 f(\tilde{\mathbf{q}}) \approx \sum_{\mathbf{q}} |D^{\zeta' \zeta}_{\nu' \nu}(\mathbf{q})|^2 f(\mathbf{q})$ with the effective cross section $|D^{\zeta' \zeta}_{\nu' \nu}(\mathbf{q})|^2 = |\tilde{G}^{\zeta' \nu', \zeta \nu}_{0,0}(\mathbf{0}, \mathbf{q})|^2$ for acoustic Γ-phonons and $|D^{\zeta' \zeta}_{\nu' \nu}(\mathbf{q})|^2 = \sum_{\Delta n, \Delta m} |\tilde{G}^{\zeta' \nu', \zeta \nu}_{\Delta n, \Delta m}(\mathbf{0}, \mathbf{q})|^2$ else.

The dephasing rates γ^{ζ}_{ν} and Γ^{ζ}_{ν} determining the broadening in the absorption (Eq. 23) and luminescence spectrum (Eq. 28) can in principle be microscopically calculated in analogy to the method used in [8] using the modified electron-phonon and -photon matrix elements derived for the layer hybridized moiré excitons Y. However, in this work we focus on the energetic position and general spectral shape of resonances and therefore choose a phenomenological temperature dependence of the linewidth in Fig. 4a-d in the main text. To this end, we choose a constant radiative dephasing $\gamma_{K-K} = 1$ meV and temperature dependent phonon-induced dephasing of $\Gamma_{K-K}(T) = 5$ meV+(50 μeV/K) T. Since the momentum dark K-Λ exciton does not have any lower lying phonon emission channels, the phonon-induced dephasing is set to be significantly lower $\Gamma_{K-\Lambda} = \Gamma_{K-K}/2$. This set of dephasing rates is in qualitative agreement with the microscopically calculated dephasing rates in monolayer WSe_2 [12] and yields a good qualitative agreement with the experiment.

II. DENSITY FUNCTIONAL THEORY

The valley and band dependent interlayer hopping strength h^{λ}_{ζ} (Eq.4) can be extracted from splittings in the AA-stacked bilayer single particle dispersion as discussed in Ref. [1]. We calculate the electronic band structures of the WSe_2 bilayer based on density functional theory (DFT) in the Perdew-Burke-Ernzerhof (PBE) approximation implemented in the Quantum ESPRESSO package [13]. For the integrations we used a Monkhorst-Pack grid of 12x12x1 points to sample the Brillouin zone and replaced core electrons with norm-conserving pseudo-potentials from the Pseudo Dojo library [14]. In the latter, the s and p semi-core electrons of the W and the semi-core d electrons of the Se have been considered in the set of valence electrons. For the employed plane wave basis set a cut-off energy of 90 Ry (1224 eV) was chosen ensuring converged ground state densities and wave functions. Based on these parameters the atomic positions and in-plane lattice constants of an AA-stacked bilayer WSe_2 was optimized, until the inter-atomic forces and the stress were below thresholds of 0.01 eV/Å and 0.01 GPa. Interactions with out-of-plane images were minimized by adding a vacuum layer of at least 25 Å. Moreover, a semi-empirical van-der-Waals correction for the PBE+D3 [15] was included, yielding excellent predictions for lattice constants of layered systems [16, 17].

Based on the optimized geometry of AA-stacked bilayer WSe_2 we determine the interlayer hopping parameter h^{λ}_{ζ} from the splitting of electronic bands (without spin-orbit interaction) at different high symmetry points[1]. For the results shown in the main text, the most important hopping parameters are $h^{c}_{\Lambda} \approx 170$ meV and $h^{c}_{K} \approx 0.2$ meV. In contrast to the conduction band, we also find a significant hopping for holes at the K-point $h^{v}_{K} \approx 10$ meV. All found values are comparable to the order of magnitude found for different valleys and bands in MoS_2 bilayer [1].

III. EXPERIMENTAL METHODS

A. Sample preparation

We obtain WSe2 monolayers from a bulk WSe2 crystal (HQ Graphene) through mechanical exfoliation with blue Nitto tape (Nitto Denko, SPV 224P) [18]. WSe2 monolayers were first exfoliated onto thin PDMS films (Gel-Pak, Gel-film X4) on glass slides, and then transferred onto silicon chips with 300 nm of thermal oxide on top. To fabricate twisted bilayer WSe2, we transferred one section of the monolayer onto the substrate and then stamped the remaining section of the monolayer on top after rotating the substrate orientation by the chosen stacking angle. The substrate was generally heated up to 65 °C by a small Peltier heating plate during stamping. The twist angle was confirmed by measuring the relative crystal orientation through SHG [19].

B. Optical spectroscopy

We measured the one-photon photoluminescence (PL) of twisted bilayer WSe2 using the 488 nm line of an argon-ion laser (Spectra-Physics, 2045E). The configuration of the setup can be found in Ref. [19]. A power of 500 nW was generally used for excitation and the laser line was filtered out by a 488 nm long-pass edge filter (Semrock, LP02-488RU). The signal was dispersed by a 150 grooves mm-1 grating and then detected by a charge-coupled device (CCD) camera (Princeton Instruments, PIXIS 100).

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