Theory of moiré localized excitons in transition-metal dichalcogenide heterobilayers

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Transition-metal dichalcogenide heterostructures exhibit moiré patterns that spatially modulate the electronic structure across the material’s plane. For certain material pairs, this modulation acts as a potential landscape with deep, trigonally symmetric wells capable of localizing interlayer excitons, forming periodic arrays of quantum emitters. Here, we study these moiré localized exciton states and their optical properties. By numerically solving the two-body problem for an interacting electron-hole pair confined by a trigonal potential, we compute the localized exciton spectra for different pairs of materials. We derive optical selection rules for the different families of localized states, each belonging to one of the irreducible representations of the potential’s symmetry group $C_{3v}$, and numerically estimate their polarization-resolved absorption spectra. We find that the optical response of localized moiré interlayer excitons is dominated by states belonging to the doubly-degenerate $E$ irreducible representation. Our results provide new insights into the optical properties of artificially confined excitons in two-dimensional semiconductors.

I. INTRODUCTION

Atomically thin layers of semiconducting transition-metal dichalcogenides (TMDs) have emerged as a promising optoelectronics platform, based on their valley-dependent optical selection rules and enhanced optical activity mediated by strongly-bound excitons. Among these, so-called interlayer excitons (IXs) form in band-mismatched heterobilayers, where electrons and holes preferentially localize in different material planes. Being delocalized across the two crystals, IXs are especially susceptible to the heterostructure’s stacking configuration. For instance, it has been shown that the IX energies can be tuned by means of the interlayer twist angle by their Stark shift in the presence of out-of-plane electric field as well as hybridization with bright intralayer exciton states. These and other examples suggest that manipulating IXs may constitute a viable way of tuning the optical properties of TMD-based heterostructures.

In closely aligned TMD heterobilayers, the slight incommensurability between the two lattices produces a moiré pattern, an approximately periodic spatial modulation of the relative shift between the two materials. Due to the long-range periodicity of the moiré pattern, different regions of the heterostructure have an approximately commensurate stacking that determines the local value of the heterostructure’s band gap, and consequently the IX energy. Thus, the moiré pattern acts as an approximate superlattice potential for IXs, leading to zone folding and miniband formation, visible in experiments as a complex fine structure in the material’s optical spectrum.

For certain material pairs, such as WSe$_2$/MoSe$_2$ and WSe$_2$/MoS$_2$, the moiré potential exhibits deep potential wells capable of localizing IXs, effectively forming tunable quantum emitter arrays with the periodicity of the moiré pattern. The optical response of such states is governed by their symmetry, inherited from that of the potential well and from the carrier Bloch functions at the localization center, giving rise to optical selection rules distinct from those of extended exciton states.

Here, we numerically study the localization and optical spectra of IX states confined by moiré potential wells in TMD heterobilayers. We focus on closely aligned, nearly commensurate structures, where the moiré supercell length is much larger than the exciton Bohr radius. This allows us to separate the exciton’s center of mass (COM) and relative (RM) motions, and solve each problem individually by direct diagonalization methods to compute the low-energy exciton spectrum and wavefunctions. We report a sequence of localized exciton levels identified by their $C_{3v}$ quantum numbers, which is robust for the different material pairs studied in this paper, based on ab initio parametrizations of their moiré potentials reported by Yu et al. We give detailed account of these states’ optical selection rules for twisted heterobilayers close to parallel (R) and anti-parallel (H) stacking, and estimate the corresponding absorption spectra by considering the dominant processes mediated by hybridization with intralayer excitons. Our analysis reveals that the heterostructure’s optical response is dominated by states with orbital wave functions belonging to the $E$ irreducible representation of the group $C_{3v}$. Our results shed new light on the optical properties of IX states in 2D semiconductors confined by artificial potentials.

The rest of this paper is organized as follows: we discuss our theoretical model and its constraints in Sec. II. In Sections IIIA and IIIB we describe our numerical treatment of the IX relative-motion and center-of-mass problems, respectively, and present calculated spectra for moiré localized interlayer excitons in WSe$_2$/MoSe$_2$ and WSe$_2$/MoS$_2$ heterobilayers. The symmetry properties and optical selection rules of these states are discussed in Sec. III, and their numerical absorption spectra are presented in Sec. IV. Our concluding remarks appear in Sec. V.

II. MODEL

Our focus will be on semiconducting TMD heterobilayers with staggered band alignment, whose conduction- and valence-band edge states are localized in different layers. We
Heterostructure

MoSe$_2$

MoSe$_2$

WSe$_2$

WSe$_2$

IX potential

U

range approximation defined by

TMD layer are screened. For simplicity, we adopt the long-

below which electrostatic interactions in the corresponding

A broader side view of the heterostructure within a moiré supercell.

moiré potential. The moiré potential is shown, with an IX localized at its minimum.

use the nomenclature MX$_2$/M'X'$_2$, where M'X'$_2$ (MX$_2$) is

the TMD layer to which the bottom of the conduction band (top of

the valence band) belongs, as sketched in Fig. 1(a). To
describe interlayer excitons in the heterostructure, formed by

an M'X'$_2$ electron of effective mass $m'_e$ and an MX$_2$ hole of
effective mass $m_h$, we use the two-body Hamiltonian

$$H_{e-h} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + U_{K}(\mathbf{r}_e - \mathbf{r}_h) + V_M(\mathbf{r}_e, \mathbf{r}_h).$$  \hspace{0.5cm} (1)

Here, $\mathbf{P}$ and $\mathbf{p}$ represent the total and relative momenta;

$$M = m'_e + m_h, \quad \mu = \frac{m'_e m_h}{m'_e + m_h},$$ \hspace{0.5cm} (2)

ter the total and reduced masses of the electron-hole system;

$U_{K}$ is the electrostatic interaction between the electron and

hole at positions $\mathbf{r}_e$ and $\mathbf{r}_h$; and $V_M$ represents the periodic

moiré potential.

The system is assumed to be embedded in an environment

with average dielectric constant $\varepsilon$, which together with the

in-plane electric susceptibilities $\kappa$ and $\kappa'$ of the two layers
defines the length scales (Table I) $r_s = 2\pi\kappa/\varepsilon$ and $r'_s = 2\pi\kappa'/\varepsilon$, below which electrostatic interactions in the corresponding

TMD layer are screened. For simplicity, we adopt the long-

range approximation defined by $\rho \equiv |\mathbf{r}_e - \mathbf{r}_h| \gg r_s, r'_s$, which gives the electron-hole interaction in the Keldysh form

$$U_{K}(\rho) = -\frac{e^2}{2\varepsilon r_{\text{eff}}} \left[ H_0\left(\frac{\rho}{r_{\text{eff}}}\right) - Y_0\left(\frac{\rho}{r_{\text{eff}}}\right) \right].$$  \hspace{0.5cm} (3)

where $H_0$ and $Y_0$ are a Struve function and a Bessel function of
the second kind, respectively, and $e$ is the elementary charge.
The effective screening length $r_{\text{eff}} = r_s + r'_s + d$ accounts for
the dielectric response of the additional layer, and in the case
of IXs for the out-of-plane separation between their carriers,
d [Fig. 1(b)]. For intralayer excitons in the heterostructure, the
appropriate definition is $r_{\text{eff}} = r_s + r'_s$, whereas in a mono-
layer $r_{\text{eff}} = r_s$. As discussed in Ref. [25] this approximation
overestimates the short-range interactions in the case of IXs,
and the binding energies (Bohr radii) computed from (3) must
be interpreted as an upper (lower) limit.

The moiré potential $V_M$ varies over length scales of the or-
der of the moiré superlattice constant [Fig. 1(c)]

$$a_M = \frac{a_{>}}{\sqrt{\delta^2 + \theta^2}}, \hspace{1cm} (4)$$

defined by the interlayer twist angle $\theta \ll 1$ and lattice mis-
match $\delta = 1 - a_{<}/a_{>}$, where $a_{<}$ ($a_{>}$) is the larger (smaller)
lattice constant of the two TMD layers. Based on Eq. (4) and

the known lattice constants of the four main semiconductor TMDs
(Table I), we estimate $a_M$ for both $R$ and $H$ structures to be of order 10nm for heterobilayers with different chalco-
gens, and 100nm for those with matching chalcogens, like

WSe$_2$/MoSe$_2$ and WS$_2$/MoS$_2$. By contrast, $U_{K}$ binds elec-
trons and holes into excitons with Bohr radii $\delta_{25,26}$ $a_{\theta} \approx 10-$

20Å, over which $V_M$ varies slowly. This allows us to treat the

electron-hole pair as point-like, and located at the COM

position $\mathbf{R}$. The moiré potential then becomes

$$V_M(\mathbf{r}_e, \mathbf{r}_h) \approx V_M(\mathbf{R}) = \frac{m_e r_e + m_h r_h}{M},$$  \hspace{0.5cm} (5)

neglecting any RM dependence, and making the Hamilton-

ian (1) separable into a COM part and a RM part. This

approach is especially well suited for studying excitons in

WSe$_2$/MoSe$_2$ and WS$_2$/MoS$_2$ heterostructures with small

twist angles, and less so in the case of strong misalignment

TABLE I. In-plane lattice constants $a$, effective electron and hole

masses $m_e$ and $m_h$, and screening lengths $r_s$ (in vacuo) for the main

semiconductor TMDs, extracted from the experimental and ab ini-
tio literature. We also show the (maximum) moiré superlattice pa-

Table from saved PDF text.

| TMD       | $a$ [Å] | $m_e/m_0$ | $m_h/m_0$ | $r_s$ [Å] | $d$ [Å] | $a_M$ [nm] |
|-----------|---------|-----------|-----------|-----------|--------|-----------|
| MoSe$_2$  | 3.160$^a$ | 0.70$^d$  | 0.70$^b$  | 38.62$^d$ | 6.97$^c$ | 7.54$^c$  |
|           | 3.140$^b$ |           |           |           |        |           |
| MoSe$_2$  | 3.299$^b$ | 0.80$^c$  | 0.50$^c$  | 39.79$^c$ | 6.83$^d$ | 8.05$^d$  |
|           | 3.288$^a$ |           |           |           | 7.02$^b$ | 108.50$^b$ |
| WS$_2$    | 3.154$^{a,c}$ | 0.27$^c$ | 0.50$^c$  | 37.89$^c$ | 6.86$^d$ | 8.30$^d$  |
| WS$_2$    | 3.286$^a$ | 0.50$^b$  | 0.45$^b$  | 45.11$^b$ | 6.76$^d$ | 248.70$^d$ |

$^a$Reference [27], $^b$Reference [28], $^c$Reference [29], $^d$Reference [30].

$^a$Reference [31], $^b$Reference [32], $^c$Reference [33], $^d$Reference [34].

$^a$Reference [35], $^b$Reference [36], $^c$Reference [37].

$^a$Reference [38], $^b$Reference [39], $^c$Reference [40].

$^a$Reference [41], $^b$Reference [42], $^c$Reference [43].

$^a$Reference [44], $^b$Reference [45], $^c$Reference [46].

$^a$Reference [47], $^b$Reference [48], $^c$Reference [49].

$^a$Reference [50], $^b$Reference [51], $^c$Reference [52].

$^a$Reference [53], $^b$Reference [54], $^c$Reference [55].
angles and for heterobilayers formed with TMDs containing different chalcogens. In the following we shall focus on the former case, setting the twist angle to zero.

With \( \mathbf{r}_a - \mathbf{r}_b \), solutions to the Hamiltonian \( H \) have the form

\[
\Psi(\mathbf{r}_a, \mathbf{r}_b) = F(\mathbf{R}) f(\rho),
\]

where \( \rho \equiv \mathbf{r}_a - \mathbf{r}_b \). Since the Keldysh potential is isotropic in the plane it preserves angular momentum, and the second factor in (6) can be written as

\[
f(\rho) \equiv f_m(\rho, \phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \chi_m(\rho),
\]

where the integer \( m \) is the RM angular momentum quantum number, \( \rho \equiv |\rho| \) and \( \phi \) is the azimuthal angle of vector \( \rho \). Operating on (6) with \( \mu \) and dividing by the same wavefunction yields the two eigenvalue problems

\[
\begin{align}
\left[ -\left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} - \frac{m^2}{\rho^2} \right) + \frac{2\mu}{\hbar^2} \left( U(\rho) - E^m_f \right) \right] f(\rho) &= 0, \tag{8a} \\
\left[ -\nabla^2 + \frac{2M}{\hbar^2} \left( V_M(\mathbf{R}) - E_F \right) \right] F(\mathbf{R}) &= 0, \tag{8b}
\end{align}
\]

with the total energy of state \( \Psi \) given by \( E = E_F + E^m_f \).

**A. The relative motion problem**

Equation (8a) represents a two-dimensional hydrogenic problem with a non-trivial interaction whose form is logarithmic in the short-range limit\(^{33}\) and of Coulomb type at long distance.\(^{31}\) Different approaches have been taken to solve this equation in the context of exciton formation in TMDs, including variational methods\(^{43}\), quantum Monte Carlo simulations\(^{44,45}\), and finite elements calculations\(^{46}\).

Here, we adopt an economical numerical method based on direct diagonalization in a truncated basis, first introduced in nuclear physics\(^{34}\) and more recently used in the context of acceptor states in semiconductors\(^{43,45}\). The basis functions

\[
\chi^m_j(\rho) \equiv (\beta \rho)^{|m|} e^{-\beta \rho}, \quad 1 \leq j \leq N,
\]

are inspired by analytical solutions to the 2D hydrogen atom problem\(^{34}\), and share their general behavior at \( \rho = 0 \) and \( \rho \to \infty \). Each basis element is defined by its decay length \( \beta = \beta_0 \) which varies discretely between two values \( \beta_0 \) and \( \beta_1 \). An arbitrary length scale \( \beta_0 \) has also been introduced, to make each function dimensionless. We have chosen \( \beta_0 \leq r_{\text{eff}} \ll \beta_1^{-1} \) to cover the entire range of Bohr radii that the low-energy excitons are likely to take. The values of \( \beta \) are spaced logarithmically as

\[
\beta_j = \beta_0 e^{\xi (j - 1)}, \quad \xi = (N - 1)^{-1} \log(\beta_N/\beta_1),
\]

with \( \beta_0 \leq r_{\text{eff}} \leq \beta_1^{-1} \) to cover more densely length scales of the order of the screening lengths and below. Then, the radial part of the RM wavefunction can be expanded in this basis as

\[
\chi^m(\rho) = \sum_{j=1}^{N} A^m_j \chi^m_j(\rho).
\]

Substituting (11) into (8a), left-multiplying by \( \chi^m(\rho) \) and integrating leads to the generalized eigenvalue problem

\[
[H^m - E^m_f] A^m = 0,
\]

where we have defined the column vector \( A^m = (A_1^m, \ldots, A_N^m)^T \), and the matrices \( H^m \) and \( S^m \) are shown explicitly in Appendix A. Equation (12) is solved numerically to obtain a set of eigenvalues \( \{E^m_f\} \) and eigenvectors \( \{A^m\} \), where \( n \) is the principal quantum number.

To test this method, we have evaluated the intralayer exciton spectrum of WS\(_2\) on a SiO\(_2\) substrate by setting \( \varepsilon = (\varepsilon_{\text{vacuum}} + \varepsilon_{\text{SiO}_2})/2 = 2.4 \), and \( r_{\text{eff}} = 2\pi k_W \varepsilon_{\text{SiO}_2}/\varepsilon = 15.79 \text{ Å} \) in Eq. (3). The first few energies and radial wavefunctions are presented in Fig. 2. The obtained values reproduce the non-Rydberg sequence reported experimentally in Ref. 46 and theoretically in Ref. 47. Moreover, the energy spacings between states 1s, 2s and 3s are a good match\(^{48}\) to those reported in Ref. 39.

Table I shows our results for the low-energy interlayer excitons in all TMD heterobilayers formed with Mo, W, S and Se, also between a SiO\(_2\) substrate and air/vacuum. The band alignment of each structure, which determines to which material the electron and hole making up the IX belong, has been taken from \textit{ab initio} calculation\(^{49}\).

**B. The center-of-mass motion problem**

The moiré potential \( V_M \) appearing in Eq. (8b) has been modeled and parametrized by Yu \textit{et al.} in Ref. 15 based on \textit{ab initio} results for the band-gap and band alignment variation.
TABLE II. Calculated binding energies of the lowest-lying interlayer excitons for different semiconducting TMD heterobilayers on a typical SiO$_2$ substrate. All heterostructures shown have type-II (staggered) band gap. The electron and hole masses are taken from Table II according to which layer contains the highest valence-band edge and the lowest conduction-band edge, as reported in Ref. [49].

| Heterostructure | Binding energy [meV] |
|-----------------|---------------------|
| MoSe$_2$/MoS$_2$ | 195 100 79 61 33 45 |
| MoSe$_2$/WS$_2$ | 167 78 61 44 39 32 |
| WS$_2$/MoSe$_2$ | 185 94 75 57 50 42 |
| WS$_2$/MoS$_2$  | 185 96 76 59 51 43 |
| WS$_2$/WS$_2$   | 159 75 58 42 37 31 |
| WS$_2$/MoS$_2$  | 199 101 80 61 54 45 |

FIG. 3. (a) Ab initio moiré potential for interlayer excitons in a fully aligned, R-stacked WSe$_2$/MoSe$_2$ heterobilayer, as calculated by Yu et al. The moiré supercell is shown in white, with the two primitive moiré vectors represented by white arrows. (b) Potential profile around one of the minima, resembling a C$_3v$-symmetric harmonic potential below the saddle point energy. Our fitting of this potential well with Eq. (13) is shown in green, offset out of the plane for clarity. (c) Top view of the local stacking configurations at the moiré potential minima for R-stacked (BA) and H-stacked (BB') TMD heterobilayers. In each case, the shortest in-plane vector $r_0$ joining the W atom to the M atom is shown.

across different TMD heterobilayers. Fig. 3(a) shows the superlattice potential for interlayer excitons in one such case: R-stacked WSe$_2$/MoSe$_2$, where at zero twist angle the moiré lattice constant is about 100 nm. The potential landscape contains periodic potential wells interconnected by saddle points and surrounded by three maxima. Each of these wells is $C_{3v}$ symmetric about its minimum, and for energies below the saddle point they can be modeled by a simple trigonally-warped harmonic potential of the form

$$\tilde{V}_M(R, \Phi) = V_0 + \frac{M\omega^2}{2} R^2 [1 - \delta \cos(3\Phi + \varphi)],$$

centered at the well minimum, where $R$ and $\Phi$ are the magnitude and polar angle of the COM vector $\mathbf{r}$, and $\omega$, $\delta$ and $\varphi$ are fitting parameters. This is exemplified in Fig. [3]b. The corresponding fitting parameters for interlayer excitons in this and other TMD heterobilayers are reported in Table III.

TABLE III. Fitting parameters for the model Eq. (13), corresponding to the wells appearing in the moiré potentials reported in Ref. [15] based on DFT calculations. The localized state width $R_0$ and the barrier energy $E_s$ are also reported.

| Heterostructure | $\hbar \omega$ [meV] | $\delta$ | $R_0$ [Å] | $E_s$ [meV] | $\varphi$ |
|-----------------|-------------------|--------|--------|-----------|--------|
| R-WSe$_2$/MoSe$_2$ | 2.12 | 0.290 | 53.64 | 28 | $\pi/2$ |
| H-WSe$_2$/MoSe$_2$ | 1.23 | 0.292 | 70.52 | 14 | $-\pi/2$ |
| R-WSe$_2$/MoS$_2$ | 54.83 | 0.330 | 10.99 | 28 | $-\pi/2$ |
| H-WSe$_2$/MoS$_2$ | 30.88 | 0.019 | 14.65 | 58 | $-\pi/2$ |

Unlike the true potential $V_M$, Eq. (13) is unbounded and will always produce localized states, the lowest of which will appear at an energy $E_{F,1} \approx \hbar \omega$ above the potential bottom. Nonetheless, as long as the energy eigenvalue $E_{F,1}$ is well below the saddle point energy $E_s$ [see Fig. [3]b] and the wavefunction decays rapidly enough, the corresponding state will be a good approximation to a localized state of the finite potential well. This is, indeed, the case for R-WSe$_2$/MoSe$_2$, where $\hbar \omega = 2$ meV is much lower than the saddle point barrier, and the state width, defined by $R_0 = \sqrt{\hbar M^{-1} \omega^2}$, is a full order of magnitude shorter than the moiré superlattice constant (Table III). This suggests that the moiré localized IXs recently reported experimentally by Seyler et al. and Tran et al. are well described by the potential (13). Incidentally, we note that our estimated values for $\hbar \omega$ are consistent with the shortest energy differences between moiré localized IX resonances reported in Ref. [21] for both R- and H-stacked WSe$_2$/MoSe$_2$. By contrast, the parameters reported in Table III indicate that chalcogen-mismatched heterostructures like WSe$_2$/MoS$_2$ may not be well described by this approach, since their moiré periodicities are comparable to the localized state width $R_0$. A notable case is R-WSe$_2$/MoS$_2$, for which $\hbar \omega$ greatly exceeds the saddle-point energy, such that localized IXs are not to be expected in this heterostructure.

To find the energies of IXs localized by the potential (13), we numerically solve the eigenvalue problem (8b) by direct diagonalization over the basis of eigenstates of the 2D harmonic oscillator (2DHO), expressed in cylindrical coordinates as

$$\Psi_{j,m}(R, \Phi) = \frac{e^{iM\Phi}}{\sqrt{2 \pi N_{j,m}}} \left( \frac{R}{R_0} \right)^{|M|} L_j^{|M|} (R^2/R_0^2).$$

Here, $L_j^{|M|}$ are associated Laguerre polynomials, and the nor-
nalization factors are
\[ N_{j,M} = \frac{R_0^2}{2} (\frac{j - |M|}{2} + 1)^{|M|}, \]
with \((x)_n = \Gamma(x+n)/\Gamma(x)\) the Pochhammer symbol. The principal quantum number \(j\) is a positive integer or zero, and determines the state energy as \(E_f^0 = \hbar \omega (j + 1)\). The angular momentum quantum number \(M\) is restricted such that \(|M| \leq j\) and \(j - |M|\) is an even number, giving a total degeneracy of \(j + 1\) for the basis state \(\psi_{f,M}\).

Unlike the case of electron-hole interactions, the \(C_{3v}\)-symmetric potential \(V_M\) only preserves angular momentum \(M\) modulo 3, and matrix elements between states with different angular momenta must be considered. The appropriate quantum number is then
\[ \tilde{M} = M \mod 3, \]

taking the values \(-1, 0, 1\) for states belonging to different irreducible representations (irreps) of group \(C_{3v}\).

Substituting \(\psi_{f,M}\) into Eq. (5b), left-multiplying by \(\psi_{f',M'}\) and integrating, we get the eigenvalue problem
\[
\langle E_F - \hbar \omega (j + 1) \rangle_{j,M} + \delta \frac{\hbar \omega V_{j,M}^{M',M}}{\sqrt{(j - |M|)(j - |M|)}} = 0.
\]

Explicit formulae for \(V_{j,M}^{M',M}\) are provided in Appendix B. Equation (17) may be divided into three independent blocks with different \(M\) eigenvalue, each of which can be solved numerically by truncating the basis at principal quantum number \(j_{\text{max}} \approx 10\), determined by convergence of the low-lying eigenvalues. Such convergence is guaranteed, as it can be numerically shown that for any given \(M' = M \pm 3\), \(V_{j,j}^{M',M}\) decays rapidly with \(|j' - j|\).

Figure 4(a) shows the low-energy spectrum \(\{E_{f,M}\}\) of moiré bound interlayer excitons in R-WSe\(_2\)/MoSe\(_2\), as well as the wavefunctions \(\Phi_{0,0,M}\) for the first six states. The corresponding energies for this and other TMD heterostructures are listed in Table II. For simplicity, in both cases we take the potential bottom \(V_0\) as the energy reference. As may be expected by analogy with the isotropic case (2DHO), the ground state, labeled \(F_{0,0}\), originates from block \(M = 0\). This state can be viewed as the 2DHO state \(\psi_{0,0}\), weakly modified by second-order perturbations from states \(\psi_{j,3,M \pm 3}\), the lowest of which appear \(3\hbar \omega\) higher in energy. The perturbative parameter is then \(\delta / \hbar \omega \approx 10^{-2}\), and \(E_{0,0}^F \approx \hbar \omega\) to within less than 0.1%. The situation is qualitatively similar for the next two energy levels, a degenerate doublet formed by a state from block \(M = 1\) and one from block \(M = -1\), with energies \(E_{\pm 1}^F \approx 2\hbar \omega\) to within 5% accuracy. Finally, the 2DHO degenerate triplet formed by \(\psi_{-2,0}, \psi_{2,0}\), and \(\psi_{2,2}\) is split by trigonal warping of the potential into a lower singlet \(F_{0,2}\) and a higher degenerate doublet \(F_{-1,2}\), separated by a gap of \(\approx 0.2\hbar \omega\) or 0.5 meV. Similar level splittings appear for the entire spectrum from this point on. By comparison, Ref. 21 reports IX photoluminescence (PL) peaks as narrow as 100 μeV, indicating that experimental observation of the predicted broken degeneracies is currently possible. The same sequence of quantum numbers is found also for \(H\)-WSe\(_2\)/MoSe\(_2\) and \(H\)-WSe\(_2\)/MoS\(_2\), as reported in Table IV.

### Table IV. Calculated energies of the lowest-lying moiré localized IXs in different semiconducting TMD heterobilayers. All energies are measured with respect to the corresponding potential well bottom \(V_0\) in Eq. (15). For \(H\)-WSe\(_2\)/MoS\(_2\) only the first energy is below the saddle-point barrier.

| Heterostructure | Localized IX energy [meV] |
|-----------------|--------------------------|
|                 | \(E_{F,1}^F\)          | \(E_{F,1}^{+1,1}\) | \(E_{F,2}^{+1,2}\) | \(E_{F,3}^{+1,3}\) | \(E_{F,3}^{+1,3}\) |
| R-WSe\(_2\)/MoSe\(_2\) | 2.105 | 4.153 | 6.095 | 6.303 | 8.158 | 8.406 |
| H-WSe\(_2\)/MoSe\(_2\) | 1.221 | 2.140 | 3.535 | 3.656 | 4.731 | 4.876 |
| H-WSe\(_2\)/MoS\(_2\) | 30.877 | 61.754 | 92.621 | 92.637 | 123.498 | 123.517 |

The six wavefunctions discussed above are plotted in Figures 4(b)-(g). From inspection of their symmetries, we deduce that \(F_{0,1}\) and \(F_{0,2}\) transform according to the one-dimensional irrep \(A_1\) of group \(C_{3v}\). That is, \(F_{0,1}\) and \(F_{0,2}\) do not acquire a phase under \(C_3\) rotations or mirror operations about
the axes sketched in Fig. 4(c). Similarly, the degenerate doublets \( F_{\pm 1,1} \) and \( F_{\pm 1,2} \) belong to the two-dimensional irrep \( E \).

In general, we find that degenerate states of irrep \( E \) originate from the \( M = \pm 1 \) blocks, whereas the \( \bar{m} = 0 \) block produces states belonging to \( A_1 \) and \( A_2 \). The first two states belonging to the latter are \( F_{0,3} \) and \( F_{0,6} \), which acquire a \((-1)\) phase factor under mirror operations (see Fig. 5 in Appendix D). While IXs are—due to their permanent electric dipole moment—mainly susceptible to out-of-plane electric fields, the in-plane symmetry of the wavefunctions shown in Fig. 4 will determine the localized IX’s interaction with perturbations such as impurities with non-trivial symmetry properties, as well as phonons.

### III. SYMMETRY CONSIDERATIONS AND OPTICAL SELECTION RULES

Having computed the RM and COM parts of the wave function, we are now in a position to construct the full excitonic state. For COM quantum numbers \((\bar{M}, \ell)\) and RM quantum numbers \((m, n)\), and taking the bottom of the moiré potential well as the origin of coordinates, the localized IX wave function is given by

\[
|\text{IX}^{c,s}_{\bar{M},\ell} m,n\rangle = \int d^2r_e \int d^2r_h \phi^{c,s}_{\bar{M},\ell}(r_e, r_h) \phi^m_n(r_e, r_h)
\]

where \(\phi^{c,s}_{\bar{M},\ell}(r)\) is the field operator for an electron of band \(\alpha\) with spin and valley quantum numbers \(s\) and \(\tau\), respectively; \(K\) (\(K'\)) is the valley vector \(M'X_2\) (\(M'X'_2\)); and \(|\Omega\rangle\) represents the charge-neutral many-body ground state. The two-body state \((18)\) is formed by an electron and a hole of opposite spin projections, and thus can recombine in the absence of spin-flip mechanisms \((11,12)\) which we shall ignore in our discussion.

In addition, we shall restrict the relative values of \(\tau\) and \(\tau'\) in order to form exciton states that can recombine without inter-valley scattering. This is achieved by setting \(\tau' = \tau\) for configurations close to \(R\) stacking, and \(\tau' = -\tau\) for cases close to \(H\) stacking. The optical activity of excitons that meet these criteria is then solely dependent on the symmetry properties of the exciton state, which we address next.

In Sec. [11B](#) we have identified the relation between \(\bar{M}\) and the COM states’ irreducible representation, which immediately yields the symmetry rules

\[
C_3 F_{\bar{M},\ell} = e^{-i\frac{2\pi}{3}} F_{\bar{M},\ell},
\]

\[
C_3 \psi_{m,n} = e^{-i\frac{2\pi}{3}} \psi_{m,n},
\]

\[
C_3 \phi^{c,s}_{\bar{M},\ell} = e^{-i\frac{2\pi}{3}} \phi^{c,s}_{\bar{M},\ell},
\]

where the second expression stems trivially from Eq. (7). Using Eq. (19), it can be shown that (18) transforms under \(C_3\) rotations as (Appendix C)

\[
C_3 |\text{IX}^{c,s}_{\bar{M},\ell} m,n\rangle = e^{-i\frac{2\pi}{3} (\bar{M} + m)} \phi^{c,s}_{\bar{M},\ell} |\text{IX}^{c,s}_{\bar{M},\ell} m,n\rangle,
\]

with \(\phi^{c,s}_{\bar{M},\ell}\) and \(\phi^c_{\bar{M},\ell}\) the \(C_3\) eigenvalues of the conduction- and valence-band Bloch functions and the state \(|\Omega\rangle\), respectively.

The values of \(\phi^{c,s}_{\bar{M},\ell}\) and \(\phi^c_{\bar{M},\ell}\) are determined by the local interlayer registry at the bottom of the potential well. In
the case of R-WSe$_2$/MoSe$_2$ ($\tau' = \tau$), this corresponds to BA stacking [Fig. 3(c)], where the W atom of the WSe$_2$ layer is aligned with the hollow site of the MoSe$_2$ layer, while Se atoms in the WSe$_2$ layer coincide with the Mo atoms of the MoSe$_2$. By contrast, for H-WSe$_2$/MoSe$_2$ and H-WSe$_2$/MoS$_2$ ($\tau' = -\tau$) the local stacking is BB’ [Fig. 3(d)], where once again the W atom aligns with the MoSe$_2$ hollow site, while the chalcogens in both layers coincide. In both cases, we may take the bottom-layer W atom as the common rotation center, such that the electron Bloch function rotates about the top-layer hollow site, resulting in

$$\phi_{\tau, \nu} = e^{\frac{2\pi i}{3}}, \quad (21a)$$

$$\phi_{\tau', \nu'} = e^{-\frac{2\pi i}{3}} = \begin{cases} e^{i\frac{2\pi i}{3}}, & R \text{ stacking} \\ e^{-\frac{2\pi i}{3}}, & H \text{ stacking} \end{cases} \quad (21b)$$

This finally gives

$$C_3 |IX_{\tau', \nu'; m, n}^{\prime} \rangle = \begin{cases} e^{-\frac{2\pi i}{3}(\bar{m}+m-\tau)} \phi_{\eta} |IX_{\tau', \nu'; m, n}^{\prime} \rangle, & R \text{ stacking} \\ e^{-\frac{2\pi i}{3}(\bar{m}+m)} \phi_{\eta} |IX_{\tau', \nu'; m, n}^{\prime} \rangle, & H \text{ stacking} \end{cases} \quad (22)$$

Optical transitions are possible only between states with the same $C_3$ eigenvalue. For a state

$$|\eta, \xi\rangle = a^\dagger_{\eta}(\xi)|\Omega\rangle, \quad (23)$$

where the boson operator $a^\dagger_{\eta}(\xi)$ creates a single photon of wave vector $\xi$ and in-plane circular polarization $\eta = \pm 1$ (for right- and left-handed, respectively), the corresponding $C_3$ eigenvalue is $\phi_{\eta} e^{\frac{2\pi i}{3}\eta}$. The optical selection rules for localized IXs and in-plane polarized photons are then summarized as

$$|\eta, \xi\rangle = \left\{ \begin{array}{ll} (\tau - \bar{M} - m) \mod 3, & R \text{ stacking} \\ -(\bar{M} + m) \mod 3, & H \text{ stacking} \end{array} \right. \quad (24)$$

and illustrated in Fig. 5 for $m = 0$ in the context of photoluminescence. In R-type structures [Fig. 5(a)], $M = 0$ states at valley $\tau$ produce PL of polarization $\eta = \tau$, opposite to the well known selection rule for intralayer excitons ($\eta = -\tau$), as recently reported by Seyler et al.\[21] and Tran et al.,\[22] whereas states with $\bar{M} = -\tau$ give PL of polarization $\eta = -\tau$. For $\bar{M} = \tau$ the IX $C_3$ eigenvalue is one, which is incompatible with the two possible values of $\eta$; these states are dark for in-plane polarized photons, and couple instead to out-of-plane polarized ones that propagate along the heterostructure plane. Since these photons are missed by most optical experiments,\[21] we label them as “dark”. Moving on to the case of H-type structures [Fig. 5(b)], we find that the optical selection rules are valley independent, since the valley-dependent orbital angular momenta of the electron and hole Bloch states cancel each other out. Equation (24) shows that $\bar{M} = 0$ states at either valley are dark, while $\bar{M} \neq 0$ states produce PL of polarization $\eta = -\bar{M}$.

IV. ABSORPTION SPECTRUM OF MOIRÉ LOCALIZED INTERLAYER EXCITONS

Due to the spatial separation between their constituting carriers, direct interaction of IXs with light is weak\[24,23] and the IX oscillator strength comes mainly from mixing with bright intralayer excitons\[18,24]. Such mixing can be taken into account perturbatively, given the weak tunneling strengths and large interlayer CB and VB detunings\[37,49] typical of type-II TMD heterostructures. The dominant contributions to the photon absorption rate are given by the two processes sketched in Fig. 6, where an incoming photon, depicted as a wavy line, is shown to interact with either of the two TMD layers to create a virtual intralayer exciton. Then, one of the two carriers can tunnel into the opposite layer to form a moiré localized IX, shown as mid-gap levels for the electron and the hole.

This process introduces additional constraints on top of the selection rules obtained in Sec. III. Firstly, formation of the intermediate exciton state in either layer is constrained by the intralayer optical selection rule $\eta = -\tau$ if it forms in the MX$_2$ layer, or $\eta = -\tau'$ if it forms in the M’X’$_2$ layer. Moreover, the intermediate exciton must have an angular momentum quantum number $m = 0$, which sets the same quantum number for the moiré localized IX. In other words, $s$-type IXs will dominate the absorption spectrum associated to moiré localized excitons.

To compute the probability amplitudes of the processes in Fig. 6, we first evaluate the corresponding mixed intralayer-interlayer exciton wavefunction, to first order in perturbation...
theory:

\[ |\text{hX}_{v,r}^{a,n}(Q)| = |\text{IX}_{v,r}^{a,n}(Q)| \]

\[ + \sum_{Q,R} \frac{\phi(Q)\phi(R)}{E_{0,v,R} - E_{v,r}^{0,0}(Q)} \]

\[ + \sum_{Q,R} \frac{\phi(Q)\phi(R)}{E_{0,v,R} - E_{v,r}^{0,0}(Q)} \]

where \(|\text{hX}_{v,r}^{a,n}(Q)|\) and \(|\text{hX}_{v,r}^{a,n}(Q)|\) are the wave functions of s-type intralayer excitons with COM wave vector Q in MX₂ and M'X₂, respectively. We have also introduced the intralayer exciton dispersions

\[ E_{r,v}^{0,0}(Q) = E_{0,v}^{0,0} + \frac{h^2 Q^2}{2(m_e + m_h)} \]

\[ E_{r,v}^{0,0}(Q) = E_{0,v}^{0,0} + \frac{h^2 Q^2}{2(m_e + m_h)} \]

with \(m_e\) and \(m_h\) are the electron and hole masses in the MX₂ and M'X₂ layers, respectively. The interlayer tunneling Hamiltonian for the moiré heterostructure is

\[ H_T = \sum_s \sum_{\eta=0} \sum_{v,r} \sum_{k,k'\mathbf{K}} \delta_{v'k-k} e^{i\mathbf{k}r_0} \left( \eta v', r, k' \right) \left( \eta v, r, k \right) \text{H.c.} \]

where \(\Delta K' = \tau K' - \tau K\) is the interlayer valley mismatch; \(\eta v\) and \(\eta v'\) are hopping parameters; and \(r_0\) is the shortest interlayer vector joining the metal atoms of the two layers at the localization site. For BA and BB' stacking we have \(r_0^{BA} = 0\) and \(r_0^{BB'} = -\alpha a_0 \sqrt{3}/\beta\); these vectors are shown in Fig. 3(c).

The compiled results in Table V: Energies of A (\(\tau = -1\)) and B (\(\tau = +1\) intra- and interlayer excitons in WSe₂/MoSe₂, relevant to photon absorption through the processes of Fig. 6. The A-exciton energies were extracted from Refs. [21] and [22]. The B-exciton values were estimated by adding the experimental spin-orbit splittings reported in Ref. [23] to the A-exciton energies.

| A exc. energy [eV] | B exc. energy [eV] |
|---------------------|---------------------|
| \(\bar{n} = 1\) | \(\bar{n} = 2\) |
| WSe₂ | 1.715 \^b | 1.837 | 1.872 | 2.163 \^b | 2.285 | 2.320 |
| MoSe₂ | 1.630 \^a | 1.758 | 1.796 | 1.871 | 1.999 | 2.037 |

\(R\) stacking [eV] \(H\) stacking [eV]

| IX | 1.320 \(^a\) | 1.392 \(^a\) |
| --- | --- | --- |

\(^a\)Reference [21], \(^b\)Reference [22].

Next, we compute the decay rate of state (23) into every possible weakly hybridized exciton (25) with Fermi’s golden rule

\[ \Gamma_{\eta}(\xi) = \frac{2\xi}{\hbar} \sum_{\eta_{\nu},s,\mu} \left| \langle \eta, \xi | H_L M | \text{hX}_{v,r}^{a,n} \rangle \right|^2 \]

with a relaxed energy conservation condition to allow for a phenomenological Lorentzian broadening \(\xi\) caused by impurities and disorder. The light-matter interaction Hamiltonian is

\[ H_L M = \frac{e\gamma}{\hbar c} \sum_{\eta_{\nu},s,\mu} \sqrt{\frac{4\pi}{L S}} c_{\eta_{\nu},s,\mu}(k + \xi \xi) c_{\eta_{\nu},s,\mu}(k) a_{-\eta}(\xi) \]

\[ + \frac{e\gamma}{\hbar c} \sum_{\eta_{\nu},s,\mu} \sqrt{\frac{4\pi}{L S}} c_{\eta_{\nu},s,\mu}(k + \xi \xi) c_{\eta_{\nu},s,\mu}(k) a_{-\eta}(\xi) + \text{H.c.} \]

with \(\gamma (\gamma')\) the matrix element of the in-plane momentum operator between the WSe₂ (MoSe₂) conduction and valence bands at the \(K (K')\) point.

Finally, the absorption rate \(A(\xi)\) for photons of energy \(\epsilon\) and circular polarization \(\eta\) can be estimated by multiplying (25) by the number of localizing centers per unit area—one per moiré unit cell—and by the number of available photon states within a range \(\Delta \epsilon\) of that energy (28), which may be identified with the energy resolution of the measurement. For simplicity, we consider only \(1s\) states for both the localized IX and the virtual intralayer excitons [\(\bar{n} = n = 1\) in the sum of Eq. (28)]. This gives

\[ A(\xi) = \frac{e^2}{\hbar c} \frac{16 \Delta \epsilon}{\sqrt{3} \Delta M^2 \hbar^3} \sum_{s, \nu, \mu} \left| \sum_{\eta_{\nu},s,\mu} \phi_{\eta_{\nu},s,\mu} \phi_{\eta_{\nu},s,\mu} \right|^2 \]

\[ \left( \frac{2\gamma}{\hbar c} \sum_{\nu, s, \mu} \sqrt{\frac{4\pi}{L S}} c_{\nu, s, \mu}(k + \xi \xi) c_{\nu, s, \mu}(k) a_{-\eta}(\xi) + \text{H.c.} \right) \]
where \( X_{\tau',\tau,\beta}^{c,v}(\rho) \) and \( X_{\tau',\tau,\beta}^{c',v'}(\rho) \) are the MX2 and M'X'2 intralayer exciton real-space RM wave functions, and we have defined

\[
\Phi_{\tilde{M},\ell}^{c',\tau,\mu} = F_{\tilde{M},\ell}(\tau) e^{-ic_{\ell,\tau}} k_{\tau},
\]

\[
I_\tau = \int d^2 \rho X_{\tau',\tau,1}^{c,v}(\rho) f_{0,1}(\rho),
\]

\[
I'_{\tau'} = \int d^2 \rho X_{\tau',\tau,1}^{c',v'}(\rho) f_{0,1}(\rho).
\]

The intra- and interlayer exciton RM wave functions were computed using the numerical method of Sec. II A and numerically integrated to evaluate \( I_\tau \) and \( I'_{\tau'} \).

**A. Optical selection rules for absorption**

Equation (30) encodes the optical selection rules for absorption through the processes of Fig. 6. We begin with the case of \( H \)-stacked structures, where the individual layer contributions to absorption are

\[
A^{(H)}_{\eta = -\tau} = \frac{e^2}{\hbar c} \frac{16 \epsilon \Delta \e [\Gamma_{\tau}^{1/2} X_{\tau',\tau,1}^{c,v}(0)]^2}{\sqrt{3} \Delta k^2 \hbar^3 c^2} \sum_{\tilde{M},\ell,\mu} \left| I_\tau \right|^2
\]

\[
\times \left\{ \sum_{\mu = 0}^2 \Phi_{\tilde{M},\ell}^{c',\tau,\mu} \right\}^2 \left( \frac{\zeta / \pi}{(\epsilon - E_{0,1,s}^\ell)^2 + \zeta^2} \right)^2
\]

\[
A^{(H)}_{\eta = \tau} = \frac{e^2}{\hbar c} \frac{16 \epsilon \Delta \e [\Gamma_{\tau}^{1/2} X_{\tau',\tau,1}^{c,v}(0)]^2}{\sqrt{3} \Delta k^2 \hbar^3 c^2} \sum_{\tilde{M},\ell,\mu} \left| I'_{\tau'} \right|^2
\]

\[
\times \left\{ \sum_{\mu = 0}^2 \Phi_{\tilde{M},\ell}^{c',\tau,\mu} e^{-i2\pi \mu / 3} \right\}^2 \left( \frac{\zeta / \pi}{(\epsilon - E_{0,1,s}^\ell)^2 + \zeta^2} \right)^2
\]

In each case, the sum over \( \mu \) can be simplified by noting that

\[
F_{\tilde{M},\ell}(C_3 q) = e^{i2\pi \tilde{M}} F_{\tilde{M},\ell}(q),
\]

yielding the same rule for \( \Phi_{\tilde{M},\ell}^{c',\tau} \). This gives

\[
\sum_{\mu = 0}^2 \Phi_{\tilde{M},\ell}^{c',\tau,\mu} = F_{\tilde{M},\ell}^{c',\tau}(0).
\]

Expression (35) is non zero only for \( \tilde{M} = -\tau = \eta \) in agreement with Eq. (24), corresponding to the inverse process to that in the bottom panel of Fig. 5(b). Though allowed by symmetry in \( R \)-stacked structures, absorption by \( \tilde{M} = 0 \) states cannot be mediated by intralayer excitons, as it violates the intralayer optical selection rules.
The above analysis leads to the important conclusion that the dominant absorption processes favor localized IXs of the $E$ irrep of group $C_{3v}$, by contrast to more homogeneous states on which most interpretations of the optics of localized moiré IXs have been based thus far. The symmetry properties of these states are expected to play an important role when considering how they are influenced by impurities and other perturbations, as well as possible means to modify their optical response.

### B. Numerical results

Equations (33a), (33b) and (35) show that the localized IX’s oscillator strength is determined by the Fourier transform of the COM wave function evaluated at a single wave vector $-\Delta K_{\tau,\tau}$. Note that, while the latter vector is determined by the moiré supercell vectors [Fig. 8(a)], the wave function $\tilde{F}_{\Delta K_{\tau,\tau}}$ is given by the trigonally symmetric potential well, whose orientation in the moiré pattern is given by the phase factor $\phi$ appearing in Eq. (13).

Figure 8(a) shows two sample functions $F_{0,3}$ and $F_{0,4}$ for R-WSe$_2$/MoSe$_2$, with arrows indicating the vectors $-c_3^{\ell} \Delta K_{1,1}$. In the former case the three vectors coincide with lobes of the function, giving a finite oscillator strength, whereas in the latter they align with nodes, resulting in a dark state. Figure 8(b) shows the corresponding prefactors $|\tilde{F}_{\Delta K_{\tau,\tau}}|^{2}$ for the first few localized IXs, indicating that the states with $M = 0$ and $\ell = 7$ and $\ell = 10$, and those with $M = \pm1$ and $\ell = 3, 7$ and 10 are also dark. This effect is, in a sense, accidental, as it is independent of the potential well symmetry. Further ab initio studies of TMD heterostructures are necessary to ascertain whether different pairs of TMDs will produce the same moiré potential landscape for IXs when similarly stacked into a heterostructure. Here, we simply focus on the cases of R- and H-stacked WSe$_2$/MoSe$_2$, which we consider to be of interest for experiments.

Figure 8 shows the polarization-resolved absorption spectra of moiré localized IXs in R- and H-stacked WSe$_2$/MoSe$_2$. The curves were constructed based on the selection rules of Sec. IV A, our numerical results for $\tilde{F}_{\Delta K_{\tau,\tau}}$, and the experimental data of Table V. For the tunnelling strengths entering Eq. (27), we use $t_{\tau} = 2t_{e} = 52$ meV motivated by earlier work on TMD heterobilayers, which should suffice for an order-of-magnitude estimation. The corresponding localized IX spectra are shown in the bottom panels to highlight the absence of absorption signatures from $M = 0$ states, as dictated by symmetry, as well as from some $M \neq 0$ states for which $\tilde{F}_{\Delta K_{\tau,\tau}} \approx 0$. The absorption profiles for right- and left-circularly polarized light are identical, as guaranteed by time reversal symmetry.

### V. Conclusions

We have presented an in-depth study of interlayer exciton localization by trigonally symmetric moiré potentials in type-II transition-metal dichalcogenide heterostructures. Our numerical results for the localized exciton spectra are in good qualitative agreement with recent experiments, and the associated wave functions have allowed us to identify each state’s symmetry properties as inherited from the localizing potential and the carrier Bloch functions. We have derived general
optical selection rules for such states that generalize early theoretical description, and which are in full agreement with experimental results. By pairing these rules with the dominant exciton-photon interaction processes, we have predicted that the moiré-localized-state sector of the optical absorption in these materials is dominated by states belonging to the irreducible representation of the group $C_3v$. These results are fundamental to understanding how general perturbations influence moiré localized exciton states, and lay the groundwork for the manipulation of their optical response.

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Appendix A: Matrix elements of the relative motion problem

Taking the basis states of \( |s\rangle \), the RM Hamiltonian matrix elements can be written as

\[
H_{jj'}^{m} = K_{jj'}^{m} - \frac{2\mu e^2}{\hbar^2 \varepsilon_{eff}} U_{jj'}^{m},
\]

with auxiliary matrix elements

\[
K_{jj'}^{m} = \int_{0}^{\infty} d\rho \rho \chi_{jj'}^{m}(\rho) \left[ \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} - \frac{m^2}{\rho} \right] \chi_{jj'}^{m}(\rho) = -[2|m| + 1] \beta_2^{|m|} \beta_{j j'} \frac{\Gamma(2|m| + 1)}{(\beta_j + \beta_{j j'})^{2|m| + 1}} \Gamma(2|m| + 2),
\]

\[
U_{jj'}^{m} = \frac{\pi}{2} \int_{0}^{\infty} d\rho \rho \chi_{jj'}^{m}(\rho) \left[ H_0 \left( \frac{\rho}{\varepsilon_{eff}} \right) - Y_0 \left( \frac{\rho}{\varepsilon_{eff}} \right) \right] \chi_{jj'}^{m}(\rho) = \frac{\beta_2^{|m|}}{\varepsilon_{eff}} \frac{\Gamma(2|m| + 3)}{\beta_{jj'}^{2|m| + 3}} F_2 \left( |m| + 1, |m| + \frac{3}{2}, |m| + 2; \frac{3}{2}, \frac{3}{2}; -\varepsilon_{eff} \beta_{jj'}^2 \right)
\]

\[-4\varepsilon_{eff}^2 \cos((|m|) \Gamma^2(|m| + 1)) F_1 \left( |m| + 1, |m| + \frac{1}{2}, |m| + \frac{1}{2}; -\varepsilon_{eff} \beta_{jj'}^2 \right) \]

where $F_q(a_1,\ldots,a_p,b_1,\ldots,b_q;x)$ are generalized hypergeometric functions, and we have defined $\beta_{jj'} = \beta_j + \beta_{j j'}$. Similarly, the RM overlap matrix elements are given by

\[
S_{jj'}^{m} = \int_{0}^{\infty} d\rho \rho \chi_{jj'}^{m}(\rho) \chi_{jj'}^{m}(\rho) = \beta_2^{|m|} \frac{(2|m| + 2)}{\beta_{jj'}^{2|m| + 2}}.
\]

Appendix B: Matrix elements of the center-of-mass problem

The COM part of the Hamiltonian [13] with the trigonally-warped harmonic potential [13] can be written in cylindrical coordinates as

\[
H_{COM} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial R^2} + \frac{1}{R} \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \Phi^2} \right) + \frac{M \omega^2}{2} R^2 + \delta V,
\]

where $\delta V$ is the trigonal warping term.

\[
V = \frac{M \omega^2}{2} R^2 \cos(3\Phi + \phi).
\]

Using the basis states \( |s\rangle \), which are eigenstates of the isotropic part of \( H_{COM} \), we get the matrix elements

\[
\langle \psi_{s',M'} | H_{COM} | \psi_{s,M} \rangle = \hbar \omega (j + 1) \delta_{s,j} \delta_{M,M'} - \frac{\hbar \omega}{4} \frac{V_{s',M'}^{M,M} \delta_{|M'|-|M|,3}}{\sqrt{\left( j - |M'|^2 \right) + 1, |M'| + 1, |M|}}.
\]

where

\[
V_{s',j}^{M,M'} = \frac{2}{R_0} \int_{0}^{\infty} dR R^3 \left( \frac{R}{R_0} \right)^{|M'|+|M|} e^{-R^2/R_0^2} \times L_{|M'|/2}(R^2/R_0^2) L_{|M|/2}(R^2/R_0^2).
\]

As discussed in the main text, the trigonal distortion of the potential leads to coupling between states with quantum numbers $M' = M \pm 3$, conserving angular momentum only module 3.
\[ \Psi_{M,M}^{j} = \int_{0}^{\infty} dx x^{\frac{[M']+[\bar{M}]}{2}} e^{-xL (|M'|+1)_{\frac{[M']}{2}}} (x) L_{\frac{[M]}{2}} (x) \]

\[ = \Gamma \left( \frac{|M'|+|\bar{M}|}{2} + 2 \right) (|M'|+1)_{\frac{|M'|}{2}} \sum_{m=0}^{\frac{|M'|}{2}} \sum_{k=0}^{\frac{|M'|}{2}} \frac{(-|M'|)}{(|M'|+1)_{m}!} \frac{(-|\bar{M}|)}{(|\bar{M}|+1)_{k}!} \right). \]

**Appendix C: Symmetry of the exciton wave function under \( C_3 \) rotations**

Let \( u_{\alpha,\tau,s,k}(r) \) be the Bloch wave function of a \( \tau K \)-valley electron of band \( \alpha \) and spin \( s \), belonging to the symmetry group \( C_{3b} \). This function transforms under \( C_3 \) rotations as \( C_3 u_{\alpha,\tau,s,k}(r) = \phi_{\alpha,\tau,s}(C_3 r) \), where the eigenvalue \( \phi_{\alpha,\tau} \) depends on the symmetry point in the lattice about which the rotation is performed [metal atom, chalcogen atom or hollow site; see Eq. (21)]. Accordingly, the creation operator for such an electron transforms as

\[ C_3 c^\dagger_{\alpha,\tau,s,k}(k)C_3^{-1} = \phi_{\alpha,\tau,s}(C_3 r) \]

From the field operator definition

\[ \phi_{\alpha,\tau,s}(r) = \sum_{k} \frac{e^{i(\tau K + k) \cdot r}}{\sqrt{S}} c_{\alpha,\tau,s}(k), \]

we find that

\[ e^{-iK r} C_3 \phi_{\alpha,\tau,s}(r)C_3^{-1} = \phi_{\alpha,\tau,s}^* e^{-iK C_3 r} \phi_{\alpha,\tau,s}(C_3 r). \]

Substituting \( C_3 \) into Eq. (18) gives

\[ C_3 |X_{\alpha,\tau,s,n}^{M,M} > = \phi_{\alpha,\tau,s}^* e^{-iK C_3 r} \phi_{\alpha,\tau,s}(C_3 r) \Omega \]

\[ \times \Psi_{\alpha,\tau,s}^{m,n} (r, r_0) \phi_{\alpha,\tau,s}(C_3 r_0) \Omega \]

\[ \times |X_{\alpha,\tau,s,n}^{M,M} > = \phi_{\alpha,\tau,s}^* e^{-iK C_3 r} \phi_{\alpha,\tau,s}(C_3 r) \Omega \]

\[ \times \Psi_{\alpha,\tau,s}^{m,n} (r_0, r_0) \phi_{\alpha,\tau,s}(C_3 r_0) \Omega \]

\[ \times |X_{\alpha,\tau,s,n}^{M,M} > = \phi_{\alpha,\tau,s}^* e^{-iK C_3 r} \phi_{\alpha,\tau,s}(C_3 r) \Omega \]

\[ \times \Psi_{\alpha,\tau,s}^{m,n} (r_0, r_0) \phi_{\alpha,\tau,s}(C_3 r_0) \Omega \]

where \( r_0 = C_3 r_0 \). From Eq. (19) we get

\[ \Psi_{\alpha,\tau,s}^{m,n} (C_3^{-1} r_0, C_3^{-1} r_0) = C_3 \Psi_{\alpha,\tau,s}^{m,n} (r_0, r_0) = e^{-iK C_3 r} \]

\[ \Psi_{\alpha,\tau,s}^{m,n} (r_0, r_0) = e^{-iK C_3 r}. \]

The many-body state \( \Omega \) must also be an eigenstate of the \( C_3 \) operator with some eigenvalue \( \phi_{\Omega} \), resulting in Eq. (20).

**Appendix D: Further moiré localized states**

Figure 5 shows the COM wave functions of states \( F_{\ell,\ell} \) for \( \bar{M} = 0, \ell = 3,4,5,6,7,8 \) and \( \bar{M} = \pm 1, \ell = 3,4,5 \). States \( F_{0,0}, F_{0,5}, F_{0,7} \) and \( F_{0,8} \) belong to irrep \( A_1 \) of group \( C_{3v} \), whereas \( F_{0,3}, F_{0,6} \) belong to irrep \( A_2 \). This can be inferred from the former’s invariance under \( \sigma_v \) mirror operations, the latter’s acquisition of a \( \pm 1 \) phase factor under the same, and all states’ invariance under \( C_3 \) rotations. States \( F_{\pm 1,3}, F_{\pm 1,4} \) and \( F_{\pm 1,5} \) belong to the two dimensional irreps \( E \). We have numerically verified their properties under \( C_3 \) rotations and \( \sigma_v \) mirror transformations.
FIG. 9. Wavefunctions of moiré bound states in $R$-$\text{WSe}_2/\text{MoSe}_2$. As in Fig. 4, each function has been normalized to its maximum value for illustration purposes, and the color blue (red) indicates positive (negative) values, whereas white means a zero value. (a)-(f) $F_{0,\ell}$ for $3 \leq \ell \leq 8$. For $\ell = 4, 5, 7$ and 8 the functions are even under the mirror operations $\sigma_v$, $\sigma'_v$ and $\sigma''_v$ shown in Fig. 4(c), and belong to irrep $A_1$ of point group $C_{3v}$. By contrast, $F_{0,3}$ and $F_{0,6}$ belong to irrep $A_2$, and are odd under the same mirror operations. (g)-(l) $F_{1,\ell}$ for $\ell \leq 3 \leq 5$, all of which belong to the two-dimensional irrep $E$. The corresponding wave functions from block $\bar{m} = -1$ can be obtained by complex conjugation.
As mentioned in Sec. II, short-ranged interlayer interactions are overestimated by the Keldysh formula (3). This results in overestimation of the binding energies of the lowest energy states, particularly 1s.

M. Danovich, D. A. Ruiz-Tijerina, R. J. Hunt, M. Szniszewski, N. D. Drummond, and V. I. Fal’ko, Phys. Rev. B 97, 195452 (2018).

As long as these heterostructures are chalcogen mismatched and possess short moiré periodicities, making them poor candidates for high-quality electronic devices. This is of particular importance because of the strong interlayer hybridization of carriers which has been predicted and/or observed experimentally. Nonetheless, these heterostructures are chalcogen mismatched and possess short moiré periodicities, making them poor candidates for high-quality electronic devices.