

Polaron-induced changes in moiré exciton propagation in twisted van der Waals heterostructures

Supplementary Information

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Effective Single Particle Hamiltonian

In our pursuit of evaluating the excitonic band structure within the presence of a moiré potential, we derive an effective single-particle Hamiltonian. In order to accomplish this, we introduce operators for electron-hole pairs, represented as $P_{l\mathbf{k},l'\mathbf{k}'}$. These operators are defined as a summation over excitonic eigenmodes where l represents the layer index [1]. These modes incorporate factors $\alpha_{ll'}/\beta_{ll'}$, accounting for the electron and hole masses in the conduction and valence bands, respectively. For a WSe₂-MoSe₂ bilayer, these values are determined as $m_e/m_0 = 0.36(0.6)$ and $m_h/m_0 = 0.29(0.5)$ based on Ref. [2]. The exciton wave functions satisfy the Wannier equation [3]. In the low-density regime, with a focus on the excitonic ground state, we arrive at the free exciton Hamiltonian [1].

$$H_{ex} = \sum_{ll'\mathbf{Q}} \varepsilon_{\mathbf{Q}}^{ll'} X_{ll'\mathbf{Q}}^\dagger X_{ll'\mathbf{Q}}. \quad (1)$$

where $\varepsilon_{\mathbf{Q}}^{ll'}$ denotes the free exciton dispersion. Additionally, we transform the Hamiltonian for the moiré potential [1] reading

$$H_M = \sum_{ll'\mathbf{Q}\mathbf{q}} M_{\mathbf{q}}^{ll'} X_{ll'\mathbf{Q}+\mathbf{q}}^\dagger X_{ll'\mathbf{Q}} + h.c. \quad (2)$$

with the matrix element $M_{\mathbf{q}}^{ll'} = V_l^c(\mathbf{q})\mathcal{J}_{ll'}(\beta_{ll'}\mathbf{q}) - V_{l'}^v(\mathbf{q})\mathcal{J}_{ll'}^*(\alpha_{ll'}\mathbf{q})$ including the electronic moiré potential $V_l^{v/c}$ in the valence and conduction band respectively, as well as the excitonic form factor $\mathcal{J}_{ll'}(\mathbf{q}) = \sum_{\mathbf{k}} \psi_{ll'}^*(\mathbf{k})\psi_{ll'}(\mathbf{k}+\mathbf{q})$ [1]. For the electronic moiré potentials we employ the microscopic approach developed in Ref. [1] yielding

$$H_M = \sum_{L\mathbf{Q}\mathbf{n}} \zeta_L X_{L\mathbf{Q}+(-1)^{l_e}\mathbf{G}_n}^\dagger X_{L\mathbf{Q}} \quad \text{with} \quad (3)$$

$$\zeta_L = \begin{cases} v_{l_e}^c \mathcal{J}_L(\beta_L \mathbf{G}_0) - v_{l_h}^v \mathcal{J}_L(\alpha_L \mathbf{G}_0) & \text{for } l_e = l_h \\ v_{l_e}^c \mathcal{J}_L(\beta_L \mathbf{G}_0) - v_{l_h}^{v*} \mathcal{J}_L(\alpha_L \mathbf{G}_0) & \text{for } l_e \neq l_h \end{cases}, \quad (4)$$

where $L = (l_e, l_h)$ and the parameters v_l^λ are extracted from first principle computations and read $v_l^\lambda = \alpha_l + \exp(2\pi i\sigma/3)\beta_l$ [1]. In this equation α/β are deduced moiré parameter which can be found in the table below [1], the parameter σ represents the stacking parameter. Throughout this work we consider R-type stacking ($\sigma = 1$) where both layers have a parallel orientation. The moiré potential creates a superlattice

TABLE I: Required DFT input parameters for our microscopic model.

band	α [meV]	β [meV]
vb-1(Mo)	-20	-7.3
vb(W)	-16.1	-8
cb(Mo)	-14.7	-5.2
cb+1(W)	-11.1	-5.4

with reciprocal lattice vectors $\mathbf{G}_n = C_3^n \mathbf{G}_0$, which only allows the mixing between discrete center-of-mass

momenta. We utilise a zone-folding approach to take advantage of the new periodic lattice [4]. Hence, by changing into the in the zone-folded eigenbasis $F_{Ls\mathbf{Q}}^\dagger = \tilde{X}_{L,\mathbf{Q}+\mathbf{G}_s}$ we obtain

$$H = \sum_{Ls\mathbf{Q}} \tilde{\varepsilon}_{L,\mathbf{Q}+s_1\mathbf{G}_1+s_2\mathbf{G}_2} F_{Ls\mathbf{Q}}^\dagger F_{Ls\mathbf{Q}} + \sum_{Lss'\mathbf{Q}} \tilde{\mathcal{M}}_{ss'}^L F_{Ls\mathbf{Q}}^\dagger F_{Ls'\mathbf{Q}} \quad (5)$$

with the modified moiré mixing matrix

$$\begin{aligned} \tilde{\mathcal{M}}_{ss'}^L = & \zeta_L \left(\delta(s_1, s'_1 + (-1)^{l_e}) \delta(s_2, s'_2) + \delta(s_1, s'_1) \delta(s_2, s'_2 + (-1)^{l_e}) + \delta(s_1, s'_1 - (-1)^{l_e}) \delta(s_2, s'_2 - (-1)^{l_e}) \right) \\ & + \zeta_L^* \left(\delta(s_1, s'_1 - (-1)^{l_e}) \delta(s_2, s'_2) + \delta(s_1, s'_1) \delta(s_2, s'_2 - (-1)^{l_e}) + \delta(s_1, s'_1 + (-1)^{l_e}) \delta(s_2, s'_2 + (-1)^{l_e}) \right). \end{aligned} \quad (6)$$

We change to the eigenbasis

$$Y_{L\nu\mathbf{Q}}^\dagger = \sum_s c_{Ls}^{\nu*}(\mathbf{Q}) F_{Ls\mathbf{Q}}^\dagger \quad (7)$$

where the coefficients fulfil the eigenvalue equation

$$\tilde{\varepsilon}_{L,\mathbf{Q}+s_1\mathbf{G}_1+s_2\mathbf{G}_2} c_{Ls}^\nu(\mathbf{Q}) + \sum_{s'} \tilde{\mathcal{M}}_{ss'}^L c_{Ls'}^\nu(\mathbf{Q}) = E_{L\mu\mathbf{Q}} c_{Ls}^\nu(\mathbf{Q}). \quad (8)$$

This new basis leads us to the final diagonal Hamiltonian

$$H = \sum_{L\mu\mathbf{Q}} E_{L\mu\mathbf{Q}} Y_{L\mu\mathbf{Q}}^\dagger Y_{L\mu\mathbf{Q}} \quad (9)$$

which is further discussed in the main text.

Exciton-Phonon Interaction

We introduce the electron-phonon interaction Hamiltonian. We simplify the treatment of phonons by using a Taylor expansion near high symmetry points, incorporating material-specific phonon energies. The phonon dispersion, akin to electronic band structure, is characteristic to each material and can be determined through first principles calculations. These DFPT results are incorporated into the electron-phonon matrix element $D_{\mathbf{q}j}^\lambda$ [5, 6]. The Hamiltonian reads

$$H_{\text{el-ph}} = \sum_{\lambda,\mathbf{q},\mathbf{k},j} D_{\mathbf{q}j}^\lambda a_{\lambda,\mathbf{k}+\mathbf{q}}^\dagger a_{\lambda,\mathbf{k}} \left(b_{\mathbf{q}}^j + b_{-\mathbf{q}}^{\dagger j} \right), \quad (10)$$

with \mathbf{k} and \mathbf{q} denoting electron and phonon momenta, respectively. Here, λ signifies the band index, and j represents the phonon mode index. In this context, the operator $a_{\lambda,\mathbf{k}}$ corresponds to the electron operator, while $b_{\mathbf{q}}^j$ stands for the phonon operator.

By employing again electron-hole pair operator introduced in the previous section we perform a basis transformation into an excitonic basis [7]. We obtain the following Hamiltonian

$$H_{\text{ex-ph}} = \sum_{\mathbf{Q},\mathbf{q},j,\mu,\nu} \mathcal{D}_{\mathbf{q}j}^{\mu\nu} X_{\mu,\mathbf{Q}+\mathbf{q}}^\dagger X_{\nu,\mathbf{Q}} \left(b_{\mathbf{q}}^j + b_{-\mathbf{q}}^{\dagger j} \right) \quad (11)$$

with the transformed exciton-phonon matrix

$$\mathcal{D}_{\mathbf{q}j}^{\mu\nu} = D_{\mathbf{q}j}^c \mathcal{J}^{\mu\nu}(\beta\mathbf{q}) - D_{\mathbf{q}j}^c \mathcal{J}^{\mu\nu}(-\alpha\mathbf{q}). \quad (12)$$

Here once again $\mathcal{J}^{\mu\nu}(-\alpha\mathbf{q})$ denotes the excitonic form factor.

Polaron Transformation

Utilizing the Hamiltonian introduced earlier, we can construct a comprehensive Hamiltonian that encapsulates the entirety of our system's dynamics and interactions. This encompassing Hamiltonian enables us to thoroughly describe and analyze the behavior and properties of our system, taking into account both the free excitonic contributions denoted by H_{ex} and the phonon-related aspects characterized by H_{ph} . Please note that for the sake of simplicity, we omit the phonon mode index j . It's important to emphasize that while we do not explicitly write out this index, it still exists and is applicable in our calculations. Furthermore, it incorporates the critical interaction term, $H_{\text{ex-ph}}$, which embodies the intricate interplay between excitons and phonons, allowing us to gain a deeper understanding of the intricate phenomena occurring within our system.

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}} = H_0 + H_{\text{ex-ph}}, \quad (13)$$

We employ a polaron transformation to facilitate a unitary mapping of Hamiltonians.

$$\begin{aligned} \tilde{H} &= e^{-S} H e^S \\ &= H + [S, H] + \frac{1}{2} [S, [S, H]] + \mathcal{O}(H^3) \\ &= H_0 + H_{\text{ex-ph}} + [S, H_0] + [S, H_{\text{ex-ph}}] + \frac{1}{2} [S, [S, H]] + \mathcal{O}(H^3) \end{aligned}$$

We omit the above Baker-Campbell-Hausdorff in third order. We define the transformation operator

$$S = - \sum_{\mathbf{Q}, \mathbf{q}} \mathcal{D}_{\mathbf{q}} \left(\frac{1}{\mathcal{E}_{\mathbf{Q}+\mathbf{q}} - \mathcal{E}_{\mathbf{Q}} + \hbar\Omega} b_{-\mathbf{q}}^\dagger + \frac{1}{\mathcal{E}_{\mathbf{Q}+\mathbf{q}} - \mathcal{E}_{\mathbf{Q}} - \hbar\Omega} b_{\mathbf{q}} \right) X_{\mathbf{Q}+\mathbf{q}}^\dagger X_{\mathbf{Q}}. \quad (14)$$

As one can easily ascertain, the commutator relation below follows from this transformation

$$[S, H_0] = -H_{\text{ex-ph}}. \quad (15)$$

Thus, we obtain the new Hamiltonian

$$\tilde{H} = H_0 + \frac{1}{2} [S, H_{\text{ex-ph}}]. \quad (16)$$

Using many-particle Fock states of the unperturbed Hamiltonian, denoted as $|n\rangle$ with corresponding eigenvalues E_n , we can derive the matrix elements of the operator S in this eigenbasis from Equation (15).

$$\langle n | S | m \rangle = \frac{\langle n | H_{\text{ex-ph}} | m \rangle}{E_n - E_m} \quad (17)$$

Which yields for our new Hamiltonian [8, 9]

$$\tilde{H} = H_0 - \frac{1}{2} \sum_{lmn} \langle l | H_{\text{ex-ph}} | m \rangle \langle m | H_{\text{ex-ph}} | n \rangle \left(\frac{1}{E_m - E_n} - \frac{1}{E_l - E_m} \right) |l\rangle \langle n| \quad (18)$$

In order to obtain an effective Hamiltonian, we perform a trace over the phonons within a bath approximation. As a consequence, the initial states represented as $|n\rangle$ and the final states represented as $|l\rangle$ must maintain the same phonon configuration. This constrains the processes to involve a two-step sequence where a phonon is first absorbed and then subsequently emitted with the same momentum or vice versa. Additionally, we need to account for energy conservation in these processes. As an example, considering one of these processes, the energy change associated with the absorption of a phonon with energy $\hbar\Omega$ can be expressed as $E_m - E_n = \mathcal{E}_{\mathbf{Q}+\mathbf{q}} - \mathcal{E}_{\mathbf{Q}} - \hbar\Omega$. It's important to note that we intentionally neglect two-particle processes in our calculations. This set of assumptions and considerations ultimately leads us to the final form of the Hamiltonian.

$$\tilde{H} = H_0 - \sum_{\mathbf{Q}, \mathbf{q}} |\mathcal{D}_{\mathbf{q}}|^2 \left(\frac{n_{\mathbf{q}}}{\Delta\mathcal{E} - \hbar\Omega} + \frac{n_{\mathbf{q}} + 1}{\Delta\mathcal{E} + \hbar\Omega} \right) X_{\mathbf{Q}}^\dagger X_{\mathbf{Q}}.$$

where $\Delta\mathcal{E} = \mathcal{E}_{\mathbf{Q}+\mathbf{q}} - \mathcal{E}_{\mathbf{Q}}$. We can identify a polaron renormalized energy as

$$\tilde{\mathcal{E}}_{\mathbf{Q}} = \mathcal{E}_{\mathbf{Q}} - \sum_{\mathbf{q}} |\mathcal{D}_{\mathbf{q}}|^2 \left(\frac{n_q}{\Delta\mathcal{E} - \hbar\Omega} + \frac{n_q + 1}{\Delta\mathcal{E} + \hbar\Omega} \right).$$

Performing a Taylor expansion on the second term for small \mathbf{Q} we obtain

$$\begin{aligned} \tilde{\mathcal{E}}_{\mathbf{Q}} = \mathcal{E}_{\mathbf{Q}} - \sum_{\mathbf{q}} |\mathcal{D}_{\mathbf{q}}|^2 & \left[\frac{n_q}{\mathcal{E}(\mathbf{q}) - \hbar\Omega} \left\{ 1 - \frac{\frac{\hbar^2}{m} \mathbf{Q} \cdot \mathbf{q}}{(\mathcal{E}(\mathbf{q}) - \hbar\Omega)} + \left(\frac{\frac{\hbar^2}{m} \mathbf{Q} \cdot \mathbf{q}}{(\mathcal{E}(\mathbf{q}) - \hbar\Omega)} \right)^2 \right\} \right. \\ & \left. + \frac{(n_q + 1)}{\mathcal{E}(\mathbf{q}) + \hbar\Omega} \left\{ 1 - \frac{\frac{\hbar^2}{m} \mathbf{Q} \cdot \mathbf{q}}{(\mathcal{E}(\mathbf{q}) + \hbar\Omega)} + \left(\frac{\frac{\hbar^2}{m} \mathbf{Q} \cdot \mathbf{q}}{(\mathcal{E}(\mathbf{q}) + \hbar\Omega)} \right)^2 \right\} \right] \end{aligned}$$

Upon integration over \mathbf{q} , the contributions linear in \mathbf{q} vanish. Consequently, we are left with two key terms: one responsible for shifting the original exciton energy, denoted as $\mathcal{E}_{\text{Polaron}}$ (representing the polaron shift), and the other term corresponds to a mass renormalization factor denoted as λ . In a more concise form, we can express the new energy as:

$$\tilde{\mathcal{E}}_{\mathbf{Q}} = -\mathcal{E}_{\text{Polaron}} + \frac{\hbar^2 \mathbf{Q}^2}{2m^*}, \quad (19)$$

with $m^* = (1 + \lambda)m$. The individual terms can be specified as follows:

$$\mathcal{E}_{\text{Polaron}} = \sum_{\mathbf{q}} |\mathcal{D}_{\mathbf{q}}|^2 \left(\frac{n_q}{\mathcal{E}(\mathbf{q}) - \hbar\Omega} + \frac{(n_q + 1)}{\mathcal{E}(\mathbf{q}) + \hbar\Omega} \right) \quad (20)$$

$$\lambda = \frac{2\hbar^2}{m} \sum_{\mathbf{q}} |\mathcal{D}_{\mathbf{q}}|^2 \mathbf{q}^2 \left(\frac{n_q}{(\mathcal{E}(\mathbf{q}) - \hbar\Omega)^3} + \frac{(n_q + 1)}{(\mathcal{E}(\mathbf{q}) + \hbar\Omega)^3} \right). \quad (21)$$

Observing the mass renormalization term, it becomes apparent that the first term vanishes during the integration over \mathbf{q} . This can be confirmed through a residue analysis.

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