

Many-body Rashba spin-orbit interaction and exciton spin relaxation in atomically thin semiconductor structures

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We propose a pair spin-orbit interaction mechanism by establishing a mesoscopic many-particle Rashba Hamiltonian. In lowest order, this Hamiltonian self-consistently describes exciton spin relaxation in monolayer transition metal dichalcogenides (TMDC) due to local electric fields caused by spatial asymmetries in the dielectric environment. For a monolayer MoSe₂ on a sapphire or SiO₂ substrate above 77 K showing a bright-dark splitting in the meV range, the local electric field causes fast intravalley spin relaxation on a sub-picosecond time scale, whereas it is negligible for other TMDCs with larger bright-dark splitting.

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I. INTRODUCTION

Atomically thin semiconductors [1] host a broad variety of incoherent exciton scattering mechanisms. Based on the valley-selective optical selection rules, next to spin-conserving exciton-phonon scattering [2–5], Coulomb scattering mechanisms such as spin-conserving Dexter interaction [6] and spin-nonconserving intra- and intervalley exchange [7–12] via double spin flips are relevant. Moreover, single spin flips can occur via, e.g., spin-Zeeman interaction induced by externally applied in-plane magnetic fields [13–17] or Rashba interaction [18,19]. Rashba spin-orbit interaction (SOI) can already affect linear optical spectra of a spin-forbidden mixture of *s*-*p* orbital excitons in monolayers [20,21]. However, these signatures are very weak and have not been measured until now. For *s*-orbital excitonic states, which are usually measured in absorption or photoluminescence due to their large optical oscillator strength, no brightening of spin-dark excitonic states in out-of-plane electric fields can occur, since Rashba spin coupling vanishes at zero center-of-mass (COM) momentum within the light cone [22]. In contrast, in-plane magnetic fields already brighten spin-forbidden *s*-orbital excitons at zero COM momentum [13,14,23]. Thus, Rashba spin coupling is only relevant for incoherent *s*-orbital excitons occupying COM momenta well beyond the light cone. In contrast to Coulomb-exchange-induced double spin flips or Zeeman-interaction-induced single spin flips, single-spin-flip scattering mechanisms induced by electric fields are less understood, as they are often included via external parameters [24–27] or resulting from a complex band structure [28–31].

Recently, chiral phonons have been identified as an important single spin-flip mechanism [32–34]. Besides the one-body SOI, it has been shown, that many-body-, Breit- or pair spin-orbit interaction (PSOI) due to self-induced Coulomb fields also occurs [35–40], which completes the electron-electron interaction picture. In particular, such process can induce a superconducting phase in thin films under suitable conditions [41].

In this work, we derive a many-body Rashba PSOI mechanism [18,38,42,43], which results from self-consistently described out-of-plane electric fields $\mathbf{E}(\mathbf{r}, z)$ induced by the dielectric environment and examine its consequences for excitons in atomically thin semiconductors.

The nonrelativistic limit of the Dirac equation results in the Pauli equation, where the spin-orbit interaction appears. The corresponding Hamiltonian reads [19]:

$$H_{\text{BR}} = -\frac{\alpha_{\text{BR}}}{\hbar} \boldsymbol{\sigma} \cdot (\mathbf{E}(\mathbf{r}) \times \mathbf{p}), \quad (1)$$

where $\boldsymbol{\sigma} = (\sigma_x \ \sigma_y \ \sigma_z)^\top$ is the vector of the Pauli matrices σ_i , $\mathbf{E}(\mathbf{r})$ is an electric field, $\mathbf{p} = \frac{\hbar}{i} \nabla$ is the momentum operator and α_{BR} is the Rashba coupling constant. Note that, in solids, the Rashba coupling constant α_{BR} is greatly enhanced compared to the atomic constant in vacuum [19,42]. In Eq. (1), the electric field $\mathbf{E}(\mathbf{r})$ acts on the electrons and couples the spin $\boldsymbol{\sigma}$ to the orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. In contrast to atoms, where the electric field occurs due to the nucleus and exhibits radial symmetry, in mesoscopically structured semiconductors, the electric field $\mathbf{E}(\mathbf{r})$ acting on Bloch electrons is not necessarily radial [44], and, hence, induces distinct physical effects depending on the geometric arrangement of atoms: E.g., in-plane microscopic fields induced by the ionic background, which vary on the scale of the unit cell, are responsible for the SOI-induced spin-splitting of valence- and conduction bands [45–47], while out-of-plane fields, external or intrinsic, induce spin flips [42]. Recently, it has been shown, that PSOI, which is often not considered in *ab initio* calculations for solids, is non-negligible in determining the

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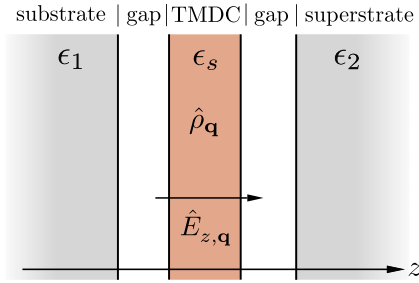


FIG. 1. Sketch of the sample geometry. $\epsilon_{1/2}$ is the static dielectric constant of substrate/superstrate and ϵ_s is the dielectric constant of the thin semiconductor, which are separated by a vacuum gap of width l . $\hat{\rho}_q$, cf. Eq. (7), is the charge density and $\hat{E}_{z,q}$ is the (operator-valued) electric field induced by surface charges at the boundaries, cf. Eq. (6).

valence- and conduction-band splitting in WSe₂ monolayers [48].

Starting from Eq. (1), we derive a second-quantized description of the Rashba interaction caused by the optically induced charge density resulting in an electric field $\mathbf{E}(\mathbf{r}, z)$ due to spatial asymmetries in the dielectric environment of an atomically thin semiconductor (Sec. II). Using an excitonic description (Sec. III) in combination with exciton-phonon-interaction-generating non-zero COM-momentum excitons (Sec. IV), the described PSOI leads to a phonon-assisted exciton spin relaxation. We illustrate the new mechanism for a monolayer MoSe₂ and quantify its impact on the incoherent exciton dynamics via microscopic calculations (Sec. V).

II. ELECTRON-HOLE MANY-PARTICLE RASHBA HAMILTONIAN DUE TO SELF-CONSISTENT FIELDS IN AN INHOMOGENEOUS DIELECTRIC ENVIRONMENT

We consider the following geometry, cf. Fig. 1: A monolayer transition metal dichalcogenides (TMDC) (ϵ_s) is sandwiched between a substrate (ϵ_1) and superstrate (ϵ_2) dielectric material with a small vacuum gap in between due to van der Waals interaction [49,50]. An induced charge density $\hat{\rho}_q$ via, e.g., optical excitation, accumulates surface charges at dielectric boundaries, which induce a net out-of-plane electric field $\hat{E}_{z,q}$ in an inhomogeneous dielectric environment ($\epsilon_1 \neq \epsilon_2$).

To investigate the consequences thereof, we employ the method of second quantization for Bloch electrons [51]. The Rashba Hamiltonian from Eq. (1) reads

$$\hat{H}_{\text{BR}} = \sum_{\substack{\mathbf{k}, \mathbf{q}, \\ \lambda_1, \lambda_2, \\ \xi, \xi', s}} \hat{E}_{z, \mathbf{q} + \mathbf{K}^{\xi} - \mathbf{K}^{\xi'}} S_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi', \xi, \bar{s}, s} \hat{a}_{\lambda_1, \mathbf{k} + \mathbf{q}}^{\dagger \xi', \bar{s}} \hat{a}_{\lambda_2, \mathbf{k}}^{\xi, s}. \quad (2)$$

A detailed derivation of Eq. (2) is given in Appendix A. Here, $\hat{E}_{z,q}$ is the spatially inhomogeneous, quantum-confined out-of-plane (z direction) oriented electric field, cf. Fig. 1, defined as

$$\hat{E}_{z,q} = \frac{1}{\mathcal{A}} \int dz |\zeta(z)|^2 \hat{E}_{z,q}(z), \quad (3)$$

where $\mathcal{A}$ is the in-plane area of the atomically thin semiconductor, $\zeta(z)$ are the electronic confinement wave functions and $\hat{E}_{z,q}(z)$ is the in-plane wave vector $\mathbf{q}$ -dependent Fourier transform of the real-space field $\hat{E}_z(\mathbf{r}, z)$, $\mathbf{r}$ being the in-plane coordinate. We note, that we neglect Umklapp processes, i.e., we neglect spatial variations of the electric field on the scale of a unit cell. Also, we note, that the quantum-confined electric field $\hat{E}_{z,q}$ in Eq. (3) carries equal units of V nm^{-1} as the electric field in real space $E_z(\mathbf{r}, z)$ [in contrast to the true Fourier transform $\hat{E}_{z,q}(z)$], since it is defined over the semiconductor area $\mathcal{A}$. In Eq. (2), $\mathbf{K}^{\xi}$ is a valley momentum at valley ξ , with reference point $\mathbf{K}^{\Gamma} = \mathbf{0}$ at the Γ valley, $\hat{a}_{\lambda, \mathbf{k}}^{(\dagger)\xi, s}$ is the annihilation (creation) operator of an electron in band λ with momentum $\mathbf{k}$ relative to valley ξ and spin s . Note that, if $s = \uparrow$, then $\bar{s} = \downarrow$ and vice versa. The Rashba matrix element $S_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi, \xi', \bar{s}, s}$ results from the expansion of the Rashba coupling in single-particle Bloch wave functions:

$$\Psi_{\mathbf{k}, \lambda}^{\xi, s}(\mathbf{r}, z) = \frac{1}{\sqrt{\mathcal{A}}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{\lambda, \mathbf{k}}^{\xi, s}(\mathbf{r}) \zeta(z) \chi_s, \quad (4)$$

with Bloch factor $u_{\lambda, \mathbf{k}}^{\xi, s}(\mathbf{r})$ and spin wave function χ_s and is defined as

$$S_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi, \xi', \bar{s}, s} = -\frac{\alpha_{\text{BR}}}{\hbar} (i(\delta_{s, \uparrow} - \delta_{s, \downarrow})) (\mathbf{p}_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi', \xi, \bar{s}, s})_x - (\mathbf{p}_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi', \xi, \bar{s}, s})_y, \quad (5)$$

where $\mathbf{p}_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_2, \xi', \xi, \bar{s}, s}$ is the in-plane momentum matrix element, cf. Eq. (A13) in Appendix A. At first glance, Eq. (5), and therefore Eq. (2), seem to break the rotational symmetry in the x - y plane. Actually, this is not the case, as a rotation in the x - y plane simultaneously acts on both the spin vector $\boldsymbol{\sigma}$ and the cross product of field and momentum $\mathbf{E}(\mathbf{r}, z) \times \mathbf{p}$, which always ensures rotational invariance of the Rashba Hamiltonian in Eq. (2). In Eq. (2), an external electric field $\hat{E}_{z,q}(z)$ can be applied in z direction with vanishing in-plane variation, so that $\hat{E}_{z,q}(z) \equiv E_z^{\text{ext}} \mathcal{A} \delta_{\mathbf{q}, \mathbf{0}}$, where E_z^{ext} can be generated by, e.g., static electrical gating [52], or it can be an in-plane propagating optical field [53] with an almost vanishing in-plane photon momentum. Static fields couple mainly via the intraband Rashba interaction with $\lambda_1 = \lambda_2$, whereas optical fields couple mainly via the interband Rashba interaction with $\lambda_1 \neq \lambda_2$.

In the case considered here, i.e., without electrical gating or in-plane propagating optical fields, the electric field is induced by a self-arranging charge-density fluctuation of electrons and holes $\hat{\rho}_q(z)$ within the atomically thin semiconductor itself. The occurring charge distribution $\hat{\rho}_q(z)$ results from the dielectric boundary conditions for the longitudinal fields $\mathbf{E}^{\parallel}$ and $\mathbf{D}^{\parallel}$ implied by the macroscopic Maxwell equations. The boundary conditions for the normal vector $\mathbf{n}$ in z direction read: $\mathbf{n} \times \mathbf{E}_i^{\parallel} = \mathbf{n} \times \mathbf{E}_j^{\parallel}$ and $\mathbf{n} \cdot \mathbf{D}_i^{\parallel} = \mathbf{n} \cdot \mathbf{D}_j^{\parallel}$ at the interface, cf. Fig. 1, between layer i and layer j inducing electronic charges $\hat{\rho}_q$ in the heterostructure, that have to be adjusted self-consistently. To account for this self-consistency in the charge $\hat{\rho}_q$, we solve the inhomogeneous Poisson equation for a layered dielectric environment with the operator-valued charge density $\hat{\rho}_q(z)$ as a source. The solution can be obtained by the Green's function $G_q(z, z')$ of Poisson's equation. The

local, quantum-confined electric field can be expressed as, cf. Appendix B:

$$\hat{E}_{z,\mathbf{q}} = -\frac{1}{\mathcal{A}} \int dz |\zeta(z)|^2 \partial_z \int dz' G_{\mathbf{q}}(z, z') \hat{\rho}_{\mathbf{q}}(z'). \quad (6)$$

The occurring source charge density reads

$$\hat{\rho}_{\mathbf{q}}(z) = -e |\zeta(z)|^2 \sum_{\substack{\mathbf{k}, \xi, \xi', s, \\ \lambda, \lambda'}} \bar{\Upsilon}_{\lambda, \lambda', \mathbf{k}-\mathbf{q}, \mathbf{k}}^{\xi, \xi', s, s} \hat{a}_{\lambda, \mathbf{k}-\mathbf{q}}^{\dagger \xi, s} \hat{a}_{\lambda', \mathbf{k}}^{\xi', s}, \quad (7)$$

where e is the elementary charge and $\bar{\Upsilon}_{\lambda, \lambda', \mathbf{k}-\mathbf{q}, \mathbf{k}}^{\xi, \xi', s, s}$ is the (reduced) form factor, given by

$$\bar{\Upsilon}_{\lambda, \lambda', \mathbf{k}-\mathbf{q}, \mathbf{k}}^{\xi, \xi', s, s} = \frac{1}{\mathcal{A}_{\text{UC}}} \int_{\mathcal{A}_{\text{UC}}} d^2r u_{\lambda, \mathbf{k}-\mathbf{q}}^{* \xi, s}(\mathbf{r}) u_{\lambda', \mathbf{k}}^{\xi', s}(\mathbf{r}), \quad (8)$$

with unit cell area $\mathcal{A}_{\text{UC}}$ and integration over the lattice-periodic Bloch factor $u_{\lambda, \mathbf{k}}^{\xi, s}(\mathbf{r})$. In contrast to Ref. [22], where the charge density is treated in a classical mean-field limit, the crucial point of the present work is to preserve the operator-valued character and thus quantum fluctuations in Eq. (7). This way, not only Hartree contributions but also Fock- or higher correlations can be considered and improve the treatment of many-body interactions. Using Eqs. (6)–(8), we arrive at the following form of the Rashba Hamiltonian from Eq. (2):

$$\begin{aligned} \hat{H}_{\text{BR}} = & \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q}, \\ \lambda_1, \lambda_2, \lambda_3, \lambda_4, \\ \xi, \xi', \xi'', s, s'}} E_{z, \mathbf{q} + \mathbf{K}^{\xi'} - \mathbf{K}^{\xi}}^{\text{loc}} \bar{\Upsilon}_{\lambda_2, \lambda_3, \mathbf{k}' - \mathbf{q}, \mathbf{k}'}^{\xi'' + \xi - \xi', s', s'} \\ & \times S_{\mathbf{k} + \mathbf{q}, \mathbf{k}}^{\lambda_1, \lambda_4, \xi', \xi, s, s'} (\hat{a}_{\lambda_1, \mathbf{k} + \mathbf{q}}^{\dagger \xi', s} \hat{a}_{\lambda_2, \mathbf{k}' - \mathbf{q}}^{\dagger \xi'' + \xi - \xi', s'} \hat{a}_{\lambda_3, \mathbf{k}}^{\xi'', s'} \hat{a}_{\lambda_4, \mathbf{k}}^{\xi, s} \\ & + \delta_{\mathbf{k}', \mathbf{k} + \mathbf{q}}^{\lambda_3, \lambda_1} \delta_{s', s}^{\xi', \xi''} \hat{a}_{\lambda_2, \mathbf{k}}^{\dagger \xi', s} \hat{a}_{\lambda_4, \mathbf{k}}^{\xi, s}). \end{aligned} \quad (9)$$

Equation (9) is the full many-body Rashba Hamiltonian, which, at this level, accounts for various single spin-flip scattering $s \rightarrow \bar{s}$ analog to the many-body Coulomb Hamiltonian [54], e.g., intraband ($\lambda_1 = \lambda_4$ and $\lambda_2 = \lambda_3$), interband ($\lambda_1 \neq \lambda_4$ and $\lambda_2 \neq \lambda_3$) and Auger-like ($\lambda_1 = \lambda_4$ and $\lambda_2 \neq \lambda_3$ or vice versa) electron-electron, hole-hole and electron-hole intravalley ($\xi = \xi'$) and intervalley ($\xi' \neq \xi$) scattering. Note, that in contrast to the spin-conserving many-body Coulomb interaction, the one-particle contribution [$\mathbf{r} = \mathbf{0}$ -self-energy, second term in Eq. (9)] arising from normal ordering [55] *does* contribute to the dynamics, since – in low-wave-number approximation – it is not simply proportional to the particle number operator $\hat{N} = \hat{a}_{\lambda, \mathbf{k}}^{\dagger \xi, s} \hat{a}_{\lambda, \mathbf{k}}^{\xi, s}$ but describes a spin-flip process $s \rightarrow \bar{s}$ via $\hat{a}_{\lambda, \mathbf{k}}^{\dagger \xi, s} \hat{a}_{\lambda, \mathbf{k}}^{\xi, s}$.

As mediating quantity, in Eq. (9), the (classical) local electric field $E_{z, \mathbf{q}}^{\text{loc}}$ can be identified:

$$E_{z, \mathbf{q}}^{\text{loc}} = \frac{e}{\mathcal{A} 2 \epsilon_0 \epsilon_{s, \perp}} \frac{g_{\mathbf{q}}}{f_{\mathbf{q}}}, \quad (10)$$

where ϵ_0 is the vacuum permittivity and $\epsilon_{s, \perp}$ is the relative out-of-plane dielectric constant of the thin semiconductor. The unitless functions $g_{\mathbf{q}}$ and $f_{\mathbf{q}}$, which encode the momentum dependence determined by the dielectric structure, are given in Eq. (B13) and Eq. (B14) in Appendix B, respectively. The electric field in Eq. (10) stems solely from the homogeneous solution of the Poisson equation, which arises due

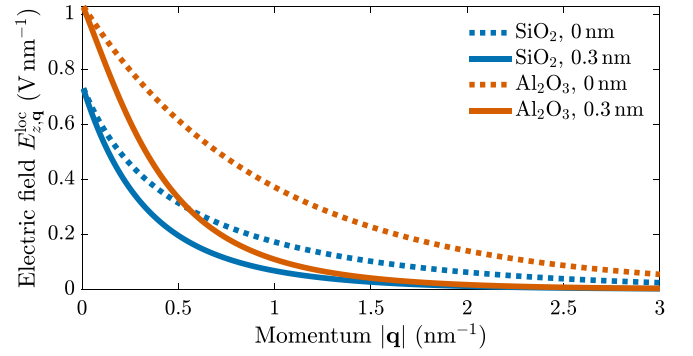


FIG. 2. Local electric field $E_{z, \mathbf{q}}^{\text{loc}}$ from Eq. (10) for an example MoSe₂ monolayer ($\epsilon_{s, \perp} = 7.2$ [59]) on a SiO₂ substrate ($\epsilon_1 = 3.9$ [60], $\epsilon_2 = 1$) and on a sapphire substrate ($\epsilon_1 = \sqrt{\epsilon_{1, \parallel} \epsilon_{1, \perp}} = \sqrt{11.6 \times 9.4}$ [61], $\epsilon_2 = 1$) for a substrate distance l of 0 nm and 0.3 nm.

to surface charges determined by the electrostatic boundary conditions. Out-of-plane fields induced by the corresponding real charge, which corresponds to the inhomogeneous solution of the Poisson equation, vanish under z integration within our assumptions of a symmetric out-of-plane charge distribution $|\zeta(z)|^2$ in Eq. (6) or Eq. (3). We note, that this is not always the case, since, e.g., chalcogen vacancies can induce spatial asymmetries in z direction in the charge distribution [56,57].

To evaluate Eq. (9), we assume a perfectly flat TMDC monolayer with a z -dependent dielectric environment $\epsilon(z)$ without any vacancies [58]. Consequently, if we set $\epsilon_1 = \epsilon_2$, i.e., equal substrate and superstrate material in Fig. 1, the field in Eq. (10) vanishes

$$E_{z, \mathbf{q}}^{\text{loc}}|_{\epsilon_1 = \epsilon_2} = 0. \quad (11)$$

On the other hand, if substrate and superstrate differ in their respective dielectric constants $\epsilon_1 \neq \epsilon_2$, the local electric field is nonzero:

$$E_{z, \mathbf{q}}^{\text{loc}}|_{\epsilon_1 \neq \epsilon_2} \neq 0. \quad (12)$$

This is the situation depicted in Fig. 1.

In Fig. 2, we depict the local electric field in Eq. (10) for an example MoSe₂ monolayer on a SiO₂ and sapphire substrate for different substrate distances. Here, the local electric field is well-localized in momentum space and reaches values larger than 1 V nm⁻¹ at $\mathbf{q} = \mathbf{0}$ on a sapphire substrate. At first glance, the calculated fields are in the range of V nm⁻¹ and appear to be rather strong. However, the strength of the local electric field cannot be directly compared to the total field acting in the sample, since it is weighted within the momentum sum in Eq. (9), so that the overall impact of the local electric field is provided by the momentum integral of the curves in Fig. 2 times the semiconductor area $\mathcal{A}$. Typical weighted internal fields are discussed versus applied external fields in Sec. III. Moreover, a distance l between the atomically thin semiconductor and the substrate, which always occurs to some degree in van der Waals-bound TMDC samples on substrates on the order of $l = 0.3$ nm [49,50], affects the localization. The larger the distance l , the stronger the electric field is localized around zero momentum resulting in a decreased overall impact of the local electric field on the electrons and

holes. Due to the relatively strong localization around small in-plane momenta $\mathbf{q}$, intervalley scattering occurring due to the derived Rashba interaction, cf. Eq. (9), at large valley momenta $|\mathbf{q}| = K = \frac{4\pi}{3a_0} = 12.6 \text{ nm}^{-1}$ (K valley-momentum transfer with lattice constant a_0 [45]) is strongly suppressed.

III. EXCITONIC RASHBA HAMILTONIAN

To illustrate the basic impact of the spin-flip processes introduced by the charge- and field fluctuations of the dielectric environment, we restrict the analysis to intraband electron-electron, hole-hole and electron-hole scattering mediated by the Rashba Hamiltonian in Eq. (9) in full analogy to the four-particle Coulomb interaction [62,63]. For optical excitation at the K points, we apply the low-wave-number approximation to the scattering matrix elements in Eq. (9), which is valid for small momentum transfers $\mathbf{q}$, and obtain

$$\hat{H}_{\text{BR}} = \sum_{\substack{\mathbf{k}, \mathbf{q}, \lambda, \lambda' \\ \xi, \xi', s, s'}} E_{z, \mathbf{q}}^{\text{loc}} S_{\mathbf{k}}^{\lambda, \xi, \bar{s}, s} \hat{a}_{\lambda, \mathbf{k}+\mathbf{q}}^{\dagger \xi, \bar{s}} \hat{a}_{\lambda', \mathbf{k}'-\mathbf{q}}^{\dagger \xi', s'} \hat{a}_{\lambda', \mathbf{k}}^{\xi', s} \hat{a}_{\lambda, \mathbf{k}}^{\xi, s}, \quad (13)$$

where $S_{\mathbf{k}}^{\lambda, \xi, \bar{s}, s} \equiv S_{\mathbf{k}, \mathbf{k}}^{\lambda, \xi, \bar{s}, s}$ from Eq. (5). In the excitonic picture, using the approach and definitions in Ref. [64], the Hamiltonian in Eq. (13) transforms as follows, cf. Appendix C:

$$\begin{aligned} \hat{H}_{\text{BR-X}} = & \sum_{\substack{\mu, \nu, \mathbf{Q} \\ \xi, \xi', s, s'}} (S_{\mu, \nu, \mathbf{Q}}^{h, \xi, \bar{s}, s'} \hat{P}_{\mu, \mathbf{Q}}^{\dagger \xi, \bar{s}, s'} \hat{P}_{\nu, \mathbf{Q}}^{\xi, s, s'}) \\ & - S_{\mu, \nu, \mathbf{Q}}^{e, \xi, \bar{s}, s'} \hat{P}_{\mu, \mathbf{Q}}^{\dagger \xi, \bar{s}, s'} \hat{P}_{\nu, \mathbf{Q}}^{\xi, s, s'}), \end{aligned} \quad (14)$$

which closely resembles the Hamiltonian describing the Rashba interaction on interlayer excitons derived in Ref. [22]. In contrast to our many-body density-independent description in Eq. (14), however, the Rashba interaction in Ref. [22] originates from a density-dependent Hartree limit. The latter should naturally emerge from Eq. (9), if we also included higher-order contributions in the expansion in electron-hole pairs in Appendix C. In Eq. (14), $\hat{P}_{\mu, \mathbf{Q}}^{(\dagger) \xi, \bar{s}, s'}$ are the excitonic annihilation (creation) operators, μ is the excitonic quantum number and $\mathbf{Q}$ is the center-of-mass momentum. Regarding the index pairs of valley ξ, ξ' and spin s, s' , the first index always belongs to the hole and the second to the electron.

The many-particle Rashba Hamiltonian in Eq. (14) encodes single hole spin-flip processes between spin-bright A and spin-dark B excitons, cf. Fig. 3(a) and between spin-dark A and spin-bright B excitons, cf. Fig. 3(b), as well as single electron spin-flip processes between spin-bright A and spin-dark A excitons, cf. Fig. 3(c), and between spin-bright B and spin-dark B excitons, cf. Fig. 3(d). Note, that, in Fig. 3, we only depict the Rashba intravalley spin-flip processes for intravalley excitons at the K valley with $\xi = \xi' = K$, while intravalley spin-flip processes are equally possible for intravalley excitons at the K' valley with $\xi = \xi' = K'$ or for any intervalley configuration with $\xi \neq \xi'$, e.g., for $\xi = K$ and $\xi' = K'$.

The corresponding excitonic Rashba matrix elements occurring in Eq. (14) for single hole spin flips, cf. Figs. 3(a) and

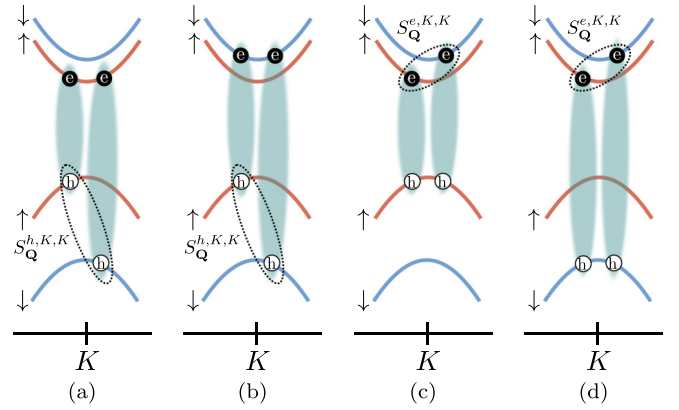


FIG. 3. Scheme of hole spin coupling between spin-bright A and spin-dark B excitons (a), hole spin coupling between spin-dark A and spin-bright B excitons (b), electron spin coupling between spin-bright and spin-dark A excitons (c) and electron spin coupling between spin-dark B and spin-bright B excitons (d) at the K valley induced by the corresponding Rashba coupling matrix elements $S_Q^{h/e, K, K}$ in Eqs. (15) and (16).

Fig. 3(b), read

$$\begin{aligned} S_{\mu, \nu, \mathbf{Q}}^{h, \xi, \bar{s}, s'} = & \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \alpha_{\text{BR}, v}^{\xi} (i(\delta_{\bar{s}, \uparrow} - \delta_{\bar{s}, \downarrow})q_x - q_y) \\ & \times (E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}, h} \delta_{\mathbf{q}'', \mathbf{q}'} + E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}, e} \delta_{\mathbf{q}'', \mathbf{q}} + E_z^{\text{ext}} \delta_{\mathbf{q}'', \mathbf{q}}) \\ & \times \varphi_{\mu, \mathbf{q}''}^{* \xi, \bar{s}, s'} \varphi_{\nu, \mathbf{q}'}^{\xi, \bar{s}, s'} \varphi_{\nu, \mathbf{q}+\mathbf{q}'}^{\xi, s, s'}, \end{aligned} \quad (15)$$

the excitonic Rashba matrix elements for single electron spin flips, cf. Fig. 3(c) and Fig. 3(d), read

$$\begin{aligned} S_{\mu, \nu, \mathbf{Q}}^{e, \xi, \bar{s}, s'} = & \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \alpha_{\text{BR}, c}^{\xi'} (i(\delta_{s', \uparrow} - \delta_{s', \downarrow})q_x - q_y) \\ & \times (E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}, h} \delta_{\mathbf{q}'', \mathbf{q}'} + E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}, e} \delta_{\mathbf{q}'', \mathbf{q}} + E_z^{\text{ext}} \delta_{\mathbf{q}'', \mathbf{q}}) \\ & \times \varphi_{\mu, \mathbf{q}''}^{* \xi, \bar{s}, s'} \varphi_{\nu, \mathbf{q}-\mathbf{q}'}^{\xi, \bar{s}, s'} \varphi_{\nu, \mathbf{q}}^{\xi, s, s'}. \end{aligned} \quad (16)$$

Here, $\alpha_{\text{BR}, v/c}^{\xi}$ is the Rashba coupling constant for holes/electrons at high-symmetry point ξ [42], $\varphi_{\mu, \mathbf{q}}^{\xi, \bar{s}, s'}$ is the excitonic wave function as a solution of the Wannier equation, cf. Eq. (C5), where the first (second) index always belongs to the hole (electron), $\mathbf{q}$ is the relative momentum and $\alpha_{\xi, \xi'}^{\bar{s}, s'}$, $\beta_{\xi, \xi'}^{s, s'}$ are the effective-mass ratios of the corresponding exciton configuration [64]:

$$\alpha_{\xi, \xi'}^{s, s'} = \frac{m_e^{\xi', s'}}{m_h^{\xi, s} + m_e^{\xi', s'}}, \quad \beta_{\xi, \xi'}^{s, s'} = \frac{m_h^{\xi, s}}{m_h^{\xi, s} + m_e^{\xi', s'}}, \quad (17)$$

with effective mass $m_{e/h}^{\xi, s}$ of the involved electron/hole [45]. The use of α and β in the transformation to $\mathbf{q}$ and $\mathbf{Q}$ avoids mixed terms in the kinetic energy. Notably, the local fields $E_{z, \mathbf{q}}^{\text{loc}, i}$ for $i = e, h$ in Eqs. (15) and (16) are defined as

$$E_{z, \mathbf{q}}^{\text{loc}, i} = (\delta_{i, e} - \delta_{i, h}) E_{z, \mathbf{q}}^{\text{loc}}, \quad (18)$$

with $E_{z, \mathbf{q}}^{\text{loc}}$ from Eq. (10). In Eq. (18), i denotes the (quasi-) particle, which induces the field, which is not necessarily

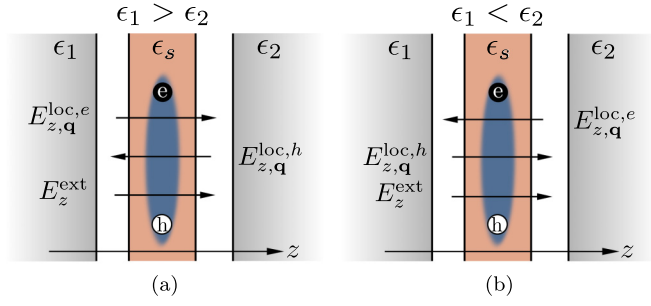


FIG. 4. Alignment of the respective local electric field $E_{z,q}^{loc,i}$ induced by the individual hole ($i = h$) and electron ($i = e$) of an exciton (shaded ellipse) in a thin semiconductor ϵ_s for different dielectric environments ϵ_1 and ϵ_2 . E_z^{ext} is an external electric field chosen as polarized in positive z direction.

equivalent to the (quasi-) particle the field *acts* upon. We rewrote Eq. (15) and Eq. (16) in a way that they can address a more general situation than the dielectric-environment-induced field fluctuations by including a spatially homogeneous external electric field E_z^{ext} arising from electrical gating. This way, the excitonic Rashba Hamiltonian in Eq. (14) combines two physically distinct fields, a local electric field $E_{z,q}^{loc,i}$ due to many-particle interactions inducing PSOI and an arbitrary in-plane spatially homogeneous external electric field E_z^{ext} inducing SOI, in one consistent description. The external electric field E_z^{ext} and the local electric fields $E_{z,q}^{loc,i}$ acting on the corresponding electron/hole may amplify or counteract each other, depending on the dielectric environment and the direction of E_z^{ext} .

To examine this aspect in more detail, in Fig. 4, we depict the alignment of the local electric fields $E_z^{loc,i}$ for $i = e, h$ induced by the corresponding electron (e) or hole (h) of the exciton, cf. Eq. (18), in comparison to an arbitrary external electric field E_z^{ext} polarized in the positive z direction. We observe, that the individual local fields induced by the negatively charged electrons $E_z^{loc,e}$ and positively charged holes $E_z^{loc,h}$ point in opposite directions. Even though these local fields are of fully quantum-mechanical origin, as they represent electron-hole interactions and self-energy corrections arising from Fock contributions, cf. Appendix C, they are in line with a classical interpretation: Within a classical picture, negative (positive) charges located in the TMDC-monolayer region ϵ_s induce net electric fields pointing towards a positive (negative) z direction if $\epsilon_1 > \epsilon_2$ [Fig. 4(a)] and vice versa if $\epsilon_1 < \epsilon_2$ [Fig. 4(b)] as a usual behavior caused by the electrostatic boundary conditions, where high- ϵ regions accumulate surface charges at the boundaries. Hence, an external electric field can amplify or suppress the total field acting on the electron or hole depending on its direction. However, care must be taken regarding specific values, since the interaction mechanisms between electrons and holes regarding specific local fields $E_z^{loc,i}$ differ: Electron- (hole-) induced local electric fields $E_z^{loc,e/h}$ interact with electrons (holes) via self-interaction and with holes (electrons) via electron-hole interaction, which are not the same.

In Fig. 5, we depict the individual contributions via self-interaction (“ e ”) with local fields induced by the electrons themselves and electron-hole interaction (“ h ”) with local

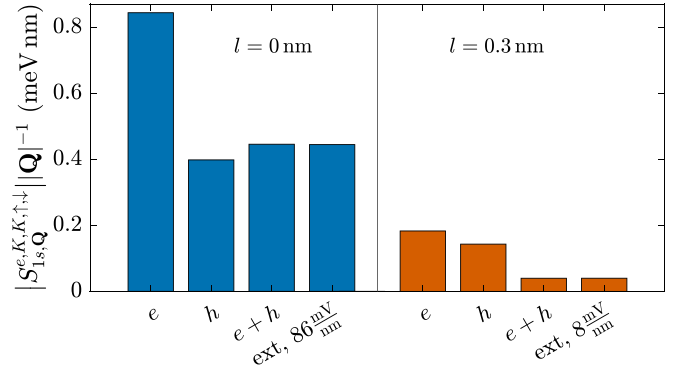


FIG. 5. Excitonic Rashba matrix element due to local electron-induced fields $E_{z,q}^{loc,e}$ (“ e ”), local hole-induced fields $E_{z,q}^{loc,h}$ (“ h ”) and total local fields (“ $e + h$ ”), cf. Eq. (18), from Eq. (16) for interlayer distances l of 0 nm and 0.3 nm (blue and orange coloring) in a MoSe₂ monolayer on a sapphire substrate. “ext” denotes the external contribution from Eq. (16), where the magnitude of the external field E_z^{ext} is chosen to match the total local-field interaction strength (“ $e + h$ ”).

fields induced by the holes and their combined contribution (“ $e + h$ ”) for electron spin flips in terms of the Rashba energy length:

$$\text{Energy length} = |S_{1s,Q}^{e,K,K,\uparrow,\downarrow}| |Q|^{-1}, \quad (19)$$

for two different interlayer distances l of 0 nm and 0.3 nm. “ext” denotes the Rashba energy length due to an externally applied electric field tuned to match the total local-field contribution (“ $e + h$ ”). Since the absolute value of the Rashba matrix element (energy) $|S_{1s,Q}^{e,K,K,\uparrow,\downarrow}|$ is well linear over a wide range of center-of-mass momenta Q , we can safely use the energy length, i.e., the Rashba matrix element divided by the center-of-mass momentum, cf. Eq. (19), for comparison. We stress that comparing the individual field strengths of the local field $E_{z,q}^{loc,i}$ and an externally applied electric field E_z^{ext} is meaningless, as their net influence on the spin hybridization of the involved excitons for a given field strength is quite different. Hence, the only meaningful comparison is obtained via the corresponding excitonic Rashba matrix elements directly. In Fig. 5, the electron-electron self-energy contribution (“ e ”) outcompetes the hole-electron contribution (“ h ”), so that the overall Rashba energy length (“ $e + h$ ”) is even slightly larger than the individual hole-electron contribution at $l = 0$ nm and is equivalent to an external electric field of $E_z^{ext} = 86 \text{ mV nm}^{-1}$. This value, while already substantial, is much lower than the $q = 0$ values of the local electric field $E_{z,q}^{loc}$ at approximately 1 V nm^{-1} in Fig. 2. At larger van der Waals distances of $l = 0.3 \text{ nm}$ [49,50], not only both individual contributions decrease, but also their difference shrinks, so that the overall Rashba energy length is greatly reduced and corresponds to an equivalent external electric field of $E_z^{ext} = 8 \text{ mV nm}^{-1}$. Note that, for the conditions in Fig. 5, to counteract (amplify) the local-field interaction, the external field has to be applied in the negative (positive) z direction if $\epsilon_1 > \epsilon_2$, as the self-energy contribution caused by $E_z^{loc,e}$, which points in positive z direction, cf. Fig. 4, always dominates. For $\epsilon_1 < \epsilon_2$, vice versa.

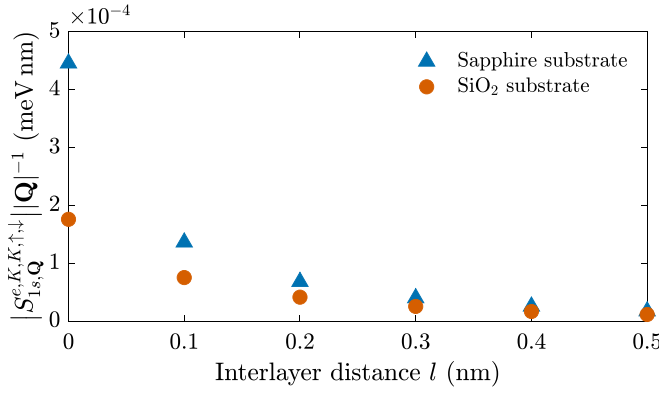


FIG. 6. Excitonic Rashba matrix element with a local electric field $E_{z,q}^{\text{loc}}$ from Eq. (16) for different interlayer distances l in a MoSe₂ monolayer on a sapphire substrate (blue triangles) and on a SiO₂ substrate (orange circles).

In Fig. 6, we depict the (total) Rashba energy length, cf. Eq. (19), of a local electric field from Eq. (16) depending on the interlayer distance l for a MoSe₂ monolayer on a sapphire substrate (blue triangles) and on a SiO₂ substrate (orange circles), cf. also “ $e + h$ ”-case in Fig. 5. Overall, as already indicated by Fig. 5, the magnitude of the excitonic Rashba matrix element for a local electric field decreases by increasing interlayer separation, cf. Fig. 6. This behavior stems from the fact, that a larger interlayer distance l leads to a stronger localization of the local electric field $E_{z,q}^{\text{loc}}$ in momentum space, cf. Fig. 7 (left), which entails a weaker localization in real space, i.e., the increasing interlayer distance gradually causes the local electric field being less spatially inhomogeneous. This, in turn, reduces the overlap with the excitonic wave functions $\varphi_{\mu,q}^{K,K,s,s'}$ on the one hand, cf. Eq. (16), which exhibit an opposite behavior, i.e., a weaker localization in momentum space, cf. Fig. 7 (right), with respect to an increasing interlayer separation due to decreased substrate screening, and, on the other hand, it causes the individual competing contributions $E_{z,q}^{\text{loc},e}$ and $E_{z,q}^{\text{loc},h}$ in Eq. (16) [and similarly regarding hole spin flips in Eq. (15)] to approach each other, since they exactly compensate each other in the limit of a spatially homogeneous

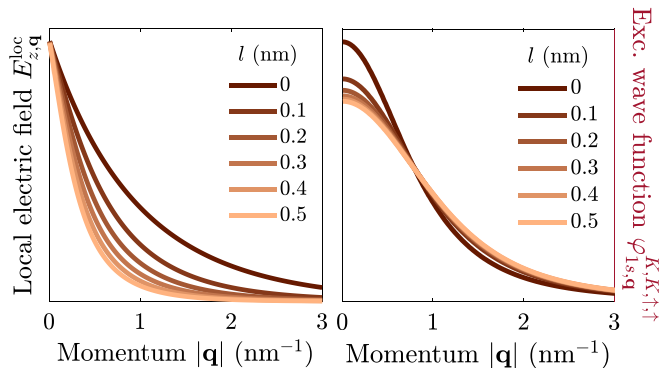


FIG. 7. Local electric field from Eq. (10) (left) and excitonic wave functions obtained by solving Eq. (C5) (right) for a MoSe₂ monolayer on a sapphire substrate for different interlayer distances l .

local electric field $E_{z,q}^{\text{loc}} \rightarrow E_z^{\text{loc}} \delta_{q,0}$, where it holds that

$$S_{\mu,v,Q}^{e/h,\xi,\xi',s,s'} \Big|_{E_{z,q}^{\text{loc}} \rightarrow E_z^{\text{loc}} \delta_{q,0}} \rightarrow 0. \quad (20)$$

Hence, the most relevant tuning knobs of the local-field driven spin-orbit interaction are the dielectric mismatch between superstrate ϵ_1 and substrate ϵ_2 as well as the van der Waals distance l . While the former can be relatively easily adjusted by exfoliating or growing the monolayer TMDC on the desired substrate, tuning the latter involves, e.g., applying pressure in the out-of-plane direction [65].

IV. EQUATIONS OF MOTION FOR EXCITON-PHONON SCATTERING

To activate the Rashba spin-flip process, the occurrence of excitonic occupations $N_{\mu,Q}$ at $Q \neq 0$ is necessary, cf. Eq. (15) and Eq. (16). For this, we choose exciton-phonon scattering as the most relevant scattering mechanism to generate incoherent excitonic occupations $N_{\mu,Q}$ [2,3,5,66]:

$$N_{\mu,Q}^{\xi,\xi',s,s'} = \langle \hat{P}_{\mu,Q}^{\dagger,\xi,\xi',s,s'} \hat{P}_{\mu,Q}^{\xi,\xi',s,s'} \rangle_c, \quad (21)$$

at above-cryogenic temperatures after optical excitation. To formulate the theory in an appropriate basis for exciton-phonon scattering, we perform a diagonalization of the excitonic Rashba Hamiltonian from Eq. (14) into the spin-diagonal basis $s, s' \rightarrow S$ analog to Ref. [22]. Here, S is the excitonic spin-diagonal quantum number, which emerges by diagonalizing the excitonic spin eigenvalue equation. For details, we refer to Appendix D. By adding the exciton-phonon Hamiltonian, the Boltzmann-type equations [2,5] in the spin-hybrid basis for $\mu = 1s$ excitonic states can be derived [22]:

$$\begin{aligned} \partial_t N_Q^{\xi,\xi',S} = & \sum_{\substack{\mathbf{K}, S' \\ \xi'', \xi'''}} (\Gamma_{\mathbf{K},Q}^{\text{in},\xi'',\xi''',S',\xi,\xi',S} N_{\mathbf{K}}^{\xi'',\xi''',S'} \\ & - \Gamma_{\mathbf{K},Q}^{\text{out},\xi'',\xi''',S',\xi,\xi',S} N_Q^{\xi,\xi',S}). \end{aligned} \quad (22)$$

Here, $\Gamma_{\mathbf{K},Q}^{\text{in/out},j,i}$ denote the phonon-assisted scattering rates between states Q, i and K, j , which encode intra- ($\xi'' = \xi$ and $\xi''' = \xi'$) as well as intervalley ($\xi'' \neq \xi$ or $\xi''' \neq \xi'$) scattering of the corresponding holes and electrons, respectively, forming the exciton. All phonon-related parameters such as phonon modes and electron-phonon coupling elements in deformation potential approximation for the corresponding materials are taken from density functional theory calculations [67,68]. Due to Rashba coupling-induced mixing of electron/hole spins in the conduction/valence bands, reflected by the excitonic spin-diagonal quantum number S , phonon-assisted scattering in Eq. (22) does not conserve the spin anymore and phonon-assisted spin relaxation can occur. We note, that the excitonic spin-diagonal quantum number S corresponds to the old spins s, s' at zero center-of-mass momentum $Q \rightarrow 0$ or in case of a vanishing out-of-plane electric field $E_{z,q}^{\text{tot}} \rightarrow 0$: $S \rightarrow s, s'$.

From the spin-hybrid excitonic occupations $N_Q^{\xi,\xi',S}$ obtained by solving Eq. (22), the total momentum-integrated excitonic occupations in the old spin basis $N^{\xi,\xi',s,s'}$ can be

retrieved

$$N_{\mathbf{Q}}^{\xi, \xi', s, s'} = \frac{1}{\mathcal{A}} \sum_{\mathbf{Q}, S} |C_{\mathbf{Q}, S}^{\xi, \xi', s, s'}|^2 N_{\mathbf{Q}}^{\xi, \xi', S}. \quad (23)$$

Here, $C_{\mathbf{Q}, S}^{\xi, \xi', s, s'}$ are the excitonic spin eigenfunctions solving Eq. (D1), cf. Appendix D.

The aim of this work is to present and quantify this new many-body Rashba spin-flip mechanism, which arises as a further effect on top of all other known spin-flip effects. Hence, we leave the analysis of the interplay of Rashba single spin-flip mechanisms with other Coulomb-scattering mechanisms such as double spin-flip intervalley exchange [10,11] or spin-conserving intervalley Coulomb scattering such as Dexter coupling [6,69] for future work. However, the theory can be straightforwardly extended to account for these mechanisms as well, similar to the exciton-phonon interaction described above. Also, for a full picture, density-dependent mechanisms such as Auger scattering [70,71] need to be considered. In this contribution however, we stay in linear order of the exciton density N .

In the following, we examine the local-electric-field-induced phonon-assisted spin relaxation in one example atomically thin semiconductor, a monolayer MoSe₂.

V. SPIN RELAXATION IN MONOLAYER MoSe₂

We start the analysis with a monolayer MoSe₂ on a sapphire substrate, where the momentum-direct spin-dark exciton is energetically located at approximately 1.45 meV [14,72] above the optically addressable spin-bright exciton. This small bright-dark splitting is a direct consequence of excitonic effects, as the bare conduction band splitting is on the order of 20 meV [45]. Within the used effective-mass approach, this implies a short-range intervalley exchange blue shift [9,63] of the spin-bright momentum-direct, i.e., intravalley K - K A_{1s} exciton of 5.5 meV, from which we can obtain an upper estimate of the short-range intervalley exchange blue shift of the spin-bright momentum-indirect, i.e., intervalley K - K' exciton of 9.8 meV [73–75] following the procedure in Ref. [69]. Note, that in our simulations we assume a fixed bright-dark splitting, which is experimentally known from h-BN-encapsulated MoSe₂ monolayer samples [14,72], irrespective of the chosen substrate material, which might not always be valid. Here, *ab initio* calculations [76], which properly take into account substrate effects with meV precision, are needed. However, the average environmental dielectric constants $\frac{1}{2}(\epsilon_1 + \epsilon_2)$ for h-BN encapsulation ($\epsilon_1 = \epsilon_2 = 4.8$ [58]) and sapphire substrates ($\epsilon_1 = \sqrt{11.6 \cdot 9.4}$ [61] and $\epsilon_2 = 1$) are almost equal, so that we expect a similar net screening and, hence, a similar Coulomb exchange interaction in both cases. Note that, on a SiO₂ substrate, monolayer MoSe₂ preserves its bright ground state [77]. In Fig. 8, we depict the energies at zero center-of-mass momentum of the four considered exciton species.

Due to the small bright-dark splitting of the K - K excitons allowing efficient spin hybridization, a monolayer MoSe₂ is a promising candidate for efficient excitonic Rashba spin relaxation induced by out-of-plane electric fields. In our case, the electric field is a local field $E_{z, \mathbf{q}}^{\text{loc}}$ self-consistently induced by the spatial asymmetries of the dielectric environment of the

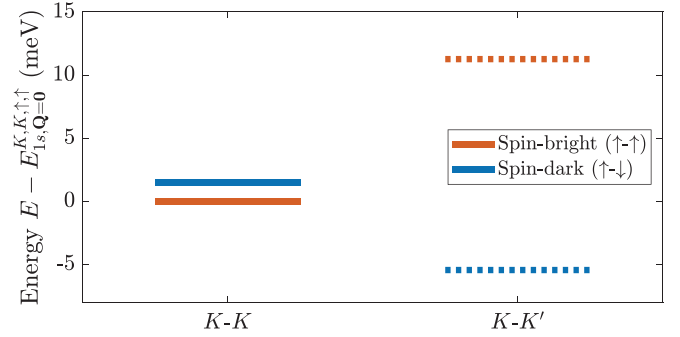


FIG. 8. Energies at zero COM $\mathbf{Q} = \mathbf{0}$ for the four considered exciton configurations of a MoSe₂ monolayer on a sapphire substrate.

MoSe₂ monolayer sandwiched between vacuum and a SiO₂ substrate, cf. Eq. (10).

In Fig. 9, we depict the full momentum-dependent exciton dispersions of the lowest spin-bright and spin-dark excitons

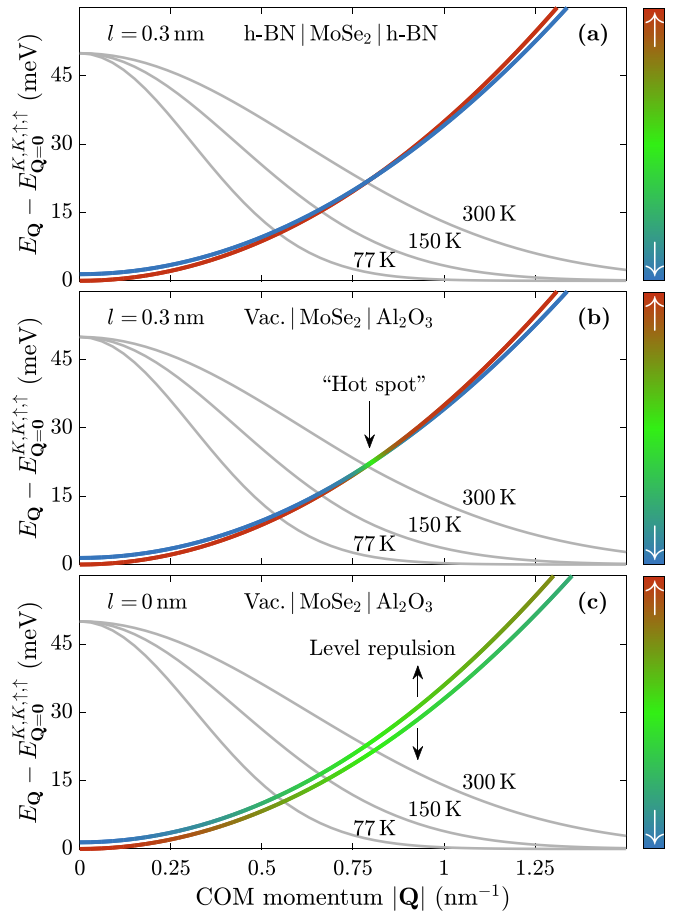


FIG. 9. Dispersions of the spin-bright $E_{\mathbf{Q}}^{K, K, \uparrow, \uparrow}$ (red solid line) and spin-dark $E_{\mathbf{Q}}^{K, K, \uparrow, \downarrow}$ (blue solid line) excitons at the K valley in a MoSe₂ monolayer encapsulated in h-BN with $l = 0.3$ nm (a), and on a sapphire substrate for $l = 0.3$ nm (b) and $l = 0$ nm (c), cf. also Fig. 11. The green color gradient denotes the degree of the electron spin hybridization via a local electric field. Grey solid lines denote Boltzmann distributions of the spin-bright excitonic occupation at various temperatures.

at the K valley, where the green color gradient denotes the degree of the spin hybridization of the electronic part of the excitons. Due to the slightly smaller exciton mass of the spin-bright exciton and the small bright-dark splitting, a hybridization “hot spot” [27] around a COM momentum of 0.8 nm^{-1} occurs. At this region, the initially nonhybridized bands, cf. Fig. 9(a) (h-BN-encapsulated MoSe₂ monolayer, symmetric dielectric environment) cross, which translates into an anticrossing, i.e., level-repulsion behavior, as soon as a spin-hybridizing electric field is present, cf. Fig. 9(b) (MoSe₂ monolayer on a sapphire substrate with $l = 0.3 \text{ nm}$, asymmetric dielectric environment), which increases with increasing local electric field, cf. Fig. 9(c) (MoSe₂ monolayer on a sapphire substrate with $l = 0 \text{ nm}$). The grey solid lines denote Boltzmann distributions at various temperatures, which are important for the interpretation of the exciton dynamics later on.

In the numerical simulations, we take into account spin-bright and spin-dark intra- ($N_Q^{K,K,\uparrow,\uparrow}$, $N_Q^{K,K,\uparrow,\downarrow}$) and intervalley ($N_Q^{K,K',\uparrow,\uparrow}$, $N_Q^{K,K',\uparrow,\downarrow}$) excitonic occupations, cf. also Figs. 8 and 11, in a spin-hybrid description, cf. Eq. (22). We neglect any hole spin flips, as they are suppressed due to the large A-B splitting. We note, that Rashba coupling between distinct valleys K and K' (intervalley spin hybridization) is also strongly suppressed, cf. the discussion to Fig. 2, and therefore neglected. However, intervalley phonon-assisted spin flips are still possible due to the softening of the spin selection rules of the exciton-phonon scattering via intravalley spin hybridization.

As the initial condition for our numerical simulations, we assume a normalized spin-bright excitonic occupation at the K valley within the light cone:

$$N_Q^{K,K,\uparrow,\uparrow}(t=0) = \delta_{Q,0}, \quad (24)$$

which roughly approximates the situation after optically exciting the A_{1s} excitonic transition at the K valley with σ_+ -light.

In Fig. 10, we display the momentum-integrated excitonic occupations $N^{\xi,\xi',s,s'}$ from Eq. (23), which are obtained by projecting the spin-hybrid solutions of Eq. (22) into the old spin basis, for a MoSe₂ monolayer encapsulated in h-BN yielding a zero local field $E_{z,q}^{\text{loc}} = 0$ at $T = 77 \text{ K}$, Fig. 10(a), and for a MoSe₂ monolayer on a sapphire substrate yielding a nonzero local field $E_{z,q}^{\text{loc}} \neq 0$ at increasing temperatures, Figs. 10(b)–10(d). We do not apply any external fields, i.e., $E_z^{\text{ext}} = 0$ always holds. We note, that the total exciton density $N = \sum_{\xi,\xi',s,s'} N^{\xi,\xi',s,s'}$ is always conserved. At initial time, the optically addressable, momentum-direct spin-bright excitonic occupation is populated (orange solid line), which reflects our initial conditions in Eq. (24).

First, we consider the zero-electric-field case in a symmetric dielectric structure [$E_{z,q}^{\text{loc}} = 0$, Eq. (18)] depicted in Fig. 10(a). Here, the spin-bright excitonic intravalley occupation $N^{K,K,\uparrow,\uparrow}$ scatters into the spin-bright intervalley occupation $N^{K,K',\uparrow,\uparrow}$ (orange dotted line) via spin-conserving phonon-assisted intervalley scattering $N^{K,K,\uparrow,\uparrow} \rightarrow N^{K,K',\uparrow,\uparrow}$, cf. process (1) in Fig. 11(a) within 6 ps at 77 K. Spin-dark excitonic occupations remain zero.

Next, in Fig. 10(b), we allow for a nonzero local electric field $E_{z,q}^{\text{loc}} \neq 0$ in Eq. (18), which emerges due

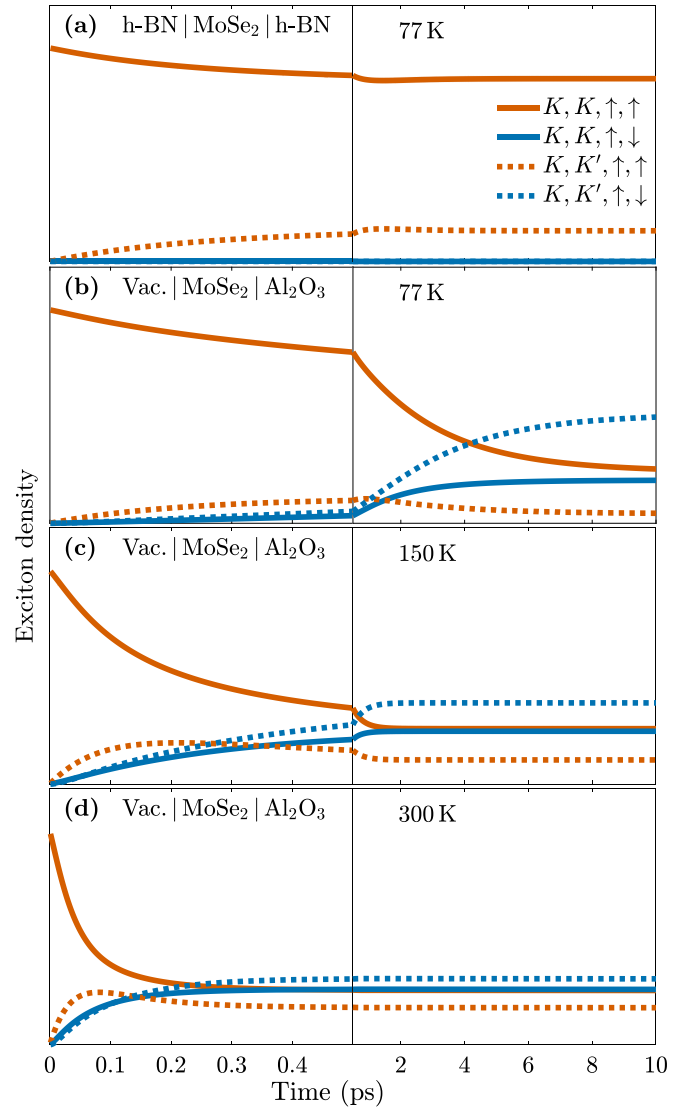


FIG. 10. Dynamics of the total excitonic occupations $N^{\xi,\xi',s,s'}$ from Eq. (23) for a MoSe₂ monolayer encapsulated in h-BN (a) with $\epsilon_1 = \epsilon_2 = 4.8$ [58] and on a sapphire substrate (b), (c), (d) with $\epsilon_1 = \sqrt{11.6 \times 9.4}$ [61] and $\epsilon_2 = 1$ with $l = 0.3 \text{ nm}$ at various temperatures.

to the asymmetric dielectric structure. This way, next to spin-conserving intervalley scattering, phonon-assisted single spin-nonconserving intravalley scattering into $N^{K,K,\uparrow,\downarrow}$ (blue solid line) within 6 ps is activated, cf. process (3) in Fig. 11(b). Additionally, spin-dark intervalley occupations $N^{K,K',\uparrow,\downarrow}$ (blue dotted line) emerge via two paths: On the one hand, it involves two two-step processes. The first two-step process occurs via intervalley spin-conserving scattering into $N^{K,K',\uparrow,\uparrow}$, cf. process (1) in Fig. 11(a), and a subsequent intravalley spin-nonconserving scattering into $N^{K,K',\uparrow,\downarrow}$, cf. process (4) in Fig. 11(b). The second occurring two-step process involves intravalley spin-nonconserving scattering first, cf. process (3) in Fig. 11(b), and intervalley spin-conserving scattering afterwards, cf. process (2) in Fig. 11(a). On the other hand, spin-nonconserving intervalley scattering from $N^{K,K,\uparrow,\uparrow}$ into $N^{K,K',\uparrow,\downarrow}$ also occurs as a one-step process due

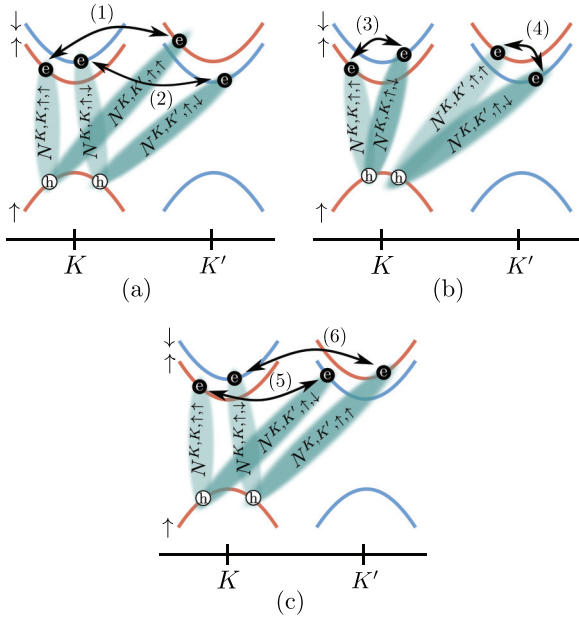


FIG. 11. Phonon-assisted spin-conserving intervalley scattering (a), spin-nonconserving intravalley scattering (b) and spin-nonconserving intervalley scattering (c) in a MoSe₂ monolayer.

to the combined action of valley-momentum phonons and spin hybridization, cf. process (5) in Fig. 11(c). However, even though both scattering paths contribute, the first path is significantly more efficient. Similarly, process (6) in Fig. 11(c) is also of minor importance.

Overall, the spin-dark excitonic occupations $N^{K,K,\uparrow,\downarrow}$ and $N^{K,K',\uparrow,\downarrow}$ rise on a similar time scale as the spin-conserving intervalley scattering, cf. Fig. 10(a), until an overall equilibrium after 8 ps is reached. The reason for this comparably fast equilibration is the small excitonic bright-dark splitting of 1.45 meV, which renders spin hybridization and therefore spin relaxation very efficient. Note that, comparing the zero-field case in Fig. 10(a) to the nonzero-field case in Fig. 10(b) at an equal temperature of 77 K, the efficiency of the spin-conserving intervalley scattering channel, cf. process (1) in Fig. 11(a), does not change in the presence of a spin-hybridizing local field, as the ratio between $N^{K,K,\uparrow,\uparrow}$ and $N^{K,K',\uparrow,\uparrow}$ is approximately preserved.

At higher temperatures such as 150 K in Fig. 10(c) and 300 K in Fig. 10(d), the overall spin-conserving intervalley and spin-nonconserving intra- as well as intervalley scattering dramatically increases: At 150 K an overall equilibrium is reached after 1 ps, which speeds up to 0.2 ps at 300 K. This overall speed-up occurs due to thermal activation of phonons and a thermalization of excitonic occupations. The former increases the induced absorption and emission from and into the phonon bath at increasing temperature and the latter results in a temperature-dependent broadening of the (Boltzmann) distribution in momentum space $\mathbf{Q}$, cf. grey solid lines in Fig. 9. The latter phenomenon is especially responsible for a speed-up of the spin relaxation, as excitonic states at larger center-of-mass momenta $\mathbf{Q}$ become increasingly populated, where the spin relaxation is more efficient due to the momentum-dependent spin coupling and, most importantly,

TABLE I. Spin relaxation times for spin flips of intravalley excitons for MoSe₂ and MoS₂ monolayers on a sapphire and SiO₂ substrate. The spin relaxation times are obtained by extracting the risetime of spin-dark intravalley occupations at the K valley from numerical simulations.

	77 K	150 K	300 K
MoSe ₂ on Al ₂ O ₃ ($l = 0.3$ nm)	1.9 ps	0.28 ps	76 fs
MoSe ₂ on Al ₂ O ₃ ($l = 0$ nm)	0.37 ps	62 fs	14 fs
MoSe ₂ on SiO ₂ ($l = 0.3$ nm)	2.6 ps	0.35 ps	99 fs
MoSe ₂ on SiO ₂ ($l = 0$ nm)	0.57 ps	77 fs	16 fs
MoS ₂ on Al ₂ O ₃ ($l = 0.3$ nm)	14 ns	4.5 ns	0.58 ns
MoS ₂ on Al ₂ O ₃ ($l = 0$ nm)	0.17 ns	50 ps	10 ps

due to an increasing probability of scattering via the “hot spot”, cf. Fig. 9. In Table I, we depict the explicit spin relaxation times, which are obtained by extracting the risetime of the spin-dark intravalley occupations at the K valley from the numerical simulations in Fig. 10.

However, care should be taken in comparing specific numbers to distinct experiments, as a specific dielectric environment has been chosen for the calculation. Also, the bright-dark splitting and van der Waals distance plays a critical role. To illustrate this, we have also performed numerical simulations for vanishing van der Waals distances and a MoS₂ monolayer for the same and distinct selected dielectric environments. The extracted spin relaxation times are displayed in Table I and show a dramatic decrease by decreasing van der Waals distance, which is expected, cf. Fig. 5. For a MoS₂ monolayer within the conditions in Fig. 10, the spin relaxation times are 14 ns at 77 K, which speed up to 0.58 ns at 300 K. Compared to a MoSe₂ monolayer, they are orders of magnitude slower, which is a direct consequence of the larger bright-dark splitting of 14 meV [14] compared to 1.45 meV in MoSe₂ rendering the spin hybridization much less efficient. Other monolayer materials such as WSe₂ or WSe₂ behave similar, as their bright-dark splitting is even larger (40–55 meV [77–80]). In these materials, other spin relaxation mechanisms such as spin-nonconserving scattering via chiral phonons [32–34] are expected to dominate over a Rashba PSOI induced by spatial asymmetries of the dielectric environment. To clarify the role of chiral phonons [32–34] compared Rashba PSOI in monolayer MoSe₂, future work may shed more light on this issue. However, in TMDC heterostructures such as MoSe₂/MoS₂ bilayers, intraexciton fields due to charge-separated interlayer exciton densities can induce a significant many-body Rashba effect [22]. Moreover, for a quantitative comparison to real-world experiments, double spin flips [8–10], which depend on the specific material [11,69], have to be additionally considered in the analysis. Thus, the exact choice of the material and dielectric environment conditions determine, which spin relaxation mechanism is dominant.

VI. CONCLUSION

In this work, we established a Rashba single spin-flip mechanism due to local out-of-plane electric fields

self-consistently induced by spatial asymmetries in the dielectric environment in atomically thin semiconductors. We developed an excitonic many-body description, explicitly calculated the local electric fields for a given dielectric environment and quantified the Rashba coupling strength. For a monolayer MoSe₂, we demonstrated very efficient spin relaxation on a sub-picosecond (150 K) to a hundred-femtosecond (300 K) time scale via a phonon-assisted single electron spin-flip channel.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: DERIVATION OF THE MANY-PARTICLE RASHBA HAMILTONIAN

Spin-orbit Hamiltonian H_{BR} in “first quantization”, cf. Eq. (1) from the main text [19]:

$$H_{\text{BR}} = -\frac{\alpha_{\text{BR}}}{\hbar} \boldsymbol{\sigma} \cdot (\mathbf{E}(\mathbf{r}, z) \times \mathbf{p}). \quad (\text{A1})$$

The second-quantized Hamiltonian $\hat{H}_{\text{BR}}$ is obtained via an expansion in Bloch wave functions:

$$\psi_{\mathbf{k},\lambda}^s(\mathbf{r}, z) = \frac{1}{\sqrt{\mathcal{A}}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{\lambda,\mathbf{k}}(\mathbf{r}) \zeta(z) \chi_s, \quad (\text{A2})$$

and reads

$$\hat{H}_{\text{BR}} = \sum_{\substack{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2, \\ s_1, s_2}} S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} \hat{a}_{\mathbf{k}_1, \lambda_1}^{\dagger s_1} \hat{a}_{\mathbf{k}_2, \lambda_2}^{s_2}, \quad (\text{A3})$$

where the Rashba matrix element is given by

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = \int d^3r \psi_{\mathbf{k}_1, \lambda_1}^{*s_1}(\mathbf{r}) H_{\text{BR}} \psi_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}). \quad (\text{A4})$$

With the wave functions from Eq. (A2), it follows:

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = -\frac{\alpha_{\text{BR}}}{\hbar} \frac{1}{\mathcal{A}} \int d^2r dz e^{-i\mathbf{k}_1 \cdot \mathbf{r}} u_{\mathbf{k}_1, \lambda_1}^{*s_1}(\mathbf{r}) \zeta^*(z) \chi_{s_1}^* \hat{E}_z(\mathbf{r}, z) (\sigma_y p_x - \sigma_x p_y) e^{i\mathbf{k}_2 \cdot \mathbf{r}} u_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}) \zeta(z) \chi_{s_2}, \quad (\text{A5})$$

with the Rashba coupling constant α_{BR} in units of $[\alpha_{\text{BR}}] = e \text{ nm}^2$. Writing the electric field in Fourier representation $\hat{E}_z(\mathbf{r}, z) = \frac{1}{\mathcal{A}} \sum_{\mathbf{q}, \mathbf{G}} e^{i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} \hat{E}_{z, \mathbf{q}+\mathbf{G}}(z)$ [81], where $\mathbf{q}$ is a crystal momentum within the first Brillouin zone and $\mathbf{G}$ is a reciprocal lattice vector, and identifying the quantum-confined electric field as

$$\hat{E}_{z, \mathbf{q}} = \frac{1}{\mathcal{A}} \int dz \hat{E}_{z, \mathbf{q}}(z) |\zeta(z)|^2, \quad (\text{A6})$$

yields

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = -\frac{\alpha_{\text{BR}}}{\hbar} \sum_{\mathbf{q}, \mathbf{G}} \frac{1}{\mathcal{A}} \hat{E}_{z, \mathbf{q}+\mathbf{G}} \int d^2r e^{i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} e^{-i\mathbf{k}_1 \cdot \mathbf{r}} u_{\mathbf{k}_1, \lambda_1}^{*s_1}(\mathbf{r}) \chi_{s_1}^* (\sigma_y p_x - \sigma_x p_y) \chi_{s_2} e^{i\mathbf{k}_2 \cdot \mathbf{r}} u_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}). \quad (\text{A7})$$

Letting the momentum operator act on the Bloch wave function yields

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = -\frac{\alpha_{\text{BR}}}{\hbar} \sum_{\mathbf{q}, \mathbf{G}} \frac{1}{\mathcal{A}} \hat{E}_{z, \mathbf{q}+\mathbf{G}} \int d^2r e^{-i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{q} - \mathbf{G}) \cdot \mathbf{r}} u_{\mathbf{k}_1, \lambda_1}^{*s_1}(\mathbf{r}) \chi_{s_1}^* (\sigma_y (\hbar k_{2,x} + p_x) - \sigma_x (\hbar k_{2,y} + p_y)) \chi_{s_2} u_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}). \quad (\text{A8})$$

Expanding the integral over the unit cells leads to

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = -\frac{\alpha_{\text{BR}}}{\hbar} \sum_{\mathbf{q}, \mathbf{G}} \frac{1}{\mathcal{A}} \hat{E}_{z, \mathbf{q}+\mathbf{G}} \sum_{\mathbf{R}} e^{-i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{q} - \mathbf{G}) \cdot \mathbf{R}} \int_{\mathcal{A}_{\text{UC}}} d^2r e^{-i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{q} - \mathbf{G}) \cdot \mathbf{r}} u_{\mathbf{k}_1, \lambda_1}^{*s_1}(\mathbf{r}) \chi_{s_1}^* (\sigma_y (\hbar k_{2,x} + p_x) - \sigma_x (\hbar k_{2,y} + p_y)) \chi_{s_2} u_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}). \quad (\text{A9})$$

The lattice sum yields

$$\sum_{\mathbf{R}} e^{-i(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{q}) \cdot \mathbf{R}} = N \delta_{\mathbf{k}_1, \mathbf{k}_2 + \mathbf{q}}, \quad (\text{A10})$$

where N is the total number of unit cells. Note, that $e^{i\mathbf{G} \cdot \mathbf{R}} = 1$. Considering further the action of the Pauli matrices on the spin eigenfunctions:

$$\sigma_x \chi_s = \chi_{\bar{s}}, \quad \sigma_y \chi_s = i(\delta_{s,\uparrow} - \delta_{s,\downarrow}) \chi_{\bar{s}}, \quad (\text{A11})$$

yields

$$S_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2} = -\frac{\alpha_{\text{BR}}}{\hbar} \sum_{\mathbf{q}, \mathbf{G}} \hat{E}_{z, \mathbf{q}+\mathbf{G}} \delta_{\mathbf{k}_1, \mathbf{k}_2+\mathbf{q}} \delta_{s_1, s_2} \frac{1}{\mathcal{A}_{\text{UC}}} \int_{\mathcal{A}_{\text{UC}}} d^2r e^{i\mathbf{G}\cdot\mathbf{r}} u_{\mathbf{k}_2+\mathbf{q}, \lambda_1}^{*s_1}(\mathbf{r}) (i(\delta_{s, \uparrow} - \delta_{s, \downarrow})(\hbar k_{2,x} + p_x) - (\hbar k_{2,y} + p_y)) u_{\mathbf{k}_2, \lambda_2}^{s_2}(\mathbf{r}). \quad (\text{A12})$$

Identifying the momentum matrix element as

$$\mathbf{p}_{\mathbf{k}_1, \mathbf{k}_2, \lambda_1, \lambda_2}^{s_1, s_2}(\mathbf{G}) = \frac{1}{\mathcal{A}_{\text{UC}}} \int_{\mathcal{A}_{\text{UC}}} u_{\lambda_1, \mathbf{k}_1}^{*s_1}(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} (\hbar \mathbf{k}_2 + \mathbf{p}) u_{\lambda_2, \mathbf{k}_2}^{s_2}(\mathbf{r}), \quad (\text{A13})$$

expanding over the band extrema with $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{K}^\xi$ and $\mathbf{q} \rightarrow \mathbf{q} + \mathbf{K}^{\xi'}$ and neglecting Umklapp processes with $\mathbf{G} \neq \mathbf{0}$ yields Eq. (2) in the main text.

APPENDIX B: CALCULATION OF THE LOCAL ELECTRIC FIELD

Starting point is the generalized Poisson equation for the Coulomb potential $\hat{\phi}(\mathbf{r})$ [82,83]:

$$\nabla \cdot (\epsilon(\mathbf{r}) \nabla \hat{\phi}(\mathbf{r})) = -\hat{\rho}(\mathbf{r}), \quad (\text{B1})$$

where $\epsilon(\mathbf{r})$ is the spatially dependent dielectric function of the background and $\hat{\rho}(\mathbf{r})$ is the active charge density. Redefining $\mathbf{r} \equiv (\mathbf{r}, z)$ and applying a Fourier transformation for the in-plane coordinates leads to

$$-|\mathbf{q}|^2 \hat{\phi}_{\mathbf{q}}(z) + \frac{1}{\epsilon_{\parallel}(z)} \partial_z (\epsilon_{\perp}(z) \partial_z \hat{\phi}_{\mathbf{q}}(z)) = -\frac{1}{\epsilon_{\parallel}(z)} \hat{\rho}_{\mathbf{q}}(z), \quad (\text{B2})$$

where we explicitly take into account distinct in-plane ($\epsilon_{\parallel}$) and out-of-plane ($\epsilon_{\perp}$) dielectric functions. In Eq. (B1) the inhomogeneity is caused by the operator-valued charge density from Eq. (7) in the main text. We reformulate the Poisson equation for the Green's function $G_{\mathbf{q}}(z, z')$, defined by $\hat{\phi}_{\mathbf{q}}(z) = \int_{-\infty}^{\infty} dz' G_{\mathbf{q}}(z, z') \hat{\rho}_{\mathbf{q}}(z')$:

$$-|\mathbf{q}|^2 G_{\mathbf{q}}(z, z') + \frac{1}{\epsilon_{\parallel}(z)} \partial_z (\epsilon_{\perp}(z) \partial_z G_{\mathbf{q}}(z, z')) = -\frac{1}{\epsilon_{\parallel}(z)} \delta(z - z'). \quad (\text{B3})$$

By defining the Poisson equation piecewise in a geometry of five dielectric slabs (we assume a small interlayer gap l (van der Waals distance) between the TMDC monolayer and substrate and superstrate [49,50], cf. Fig. 1 in the main text), where the inhomogeneity is located in the middle layer at $i = s$:

$$-|\mathbf{q}|^2 G_{i,j,\mathbf{q}}(z, z') + \partial_z^2 G_{i,j,\mathbf{q}}(z, z') = -\frac{1}{\epsilon_i} \delta(z - z') \delta_{i,j}^{i,s}, \quad (\text{B4})$$

where i, j denote the corresponding slab, and employing the electrostatic boundary conditions: $\mathbf{n} \times \mathbf{E}_i^{\parallel} = \mathbf{n} \times \mathbf{E}_j^{\parallel}$ and $\mathbf{n} \cdot \mathbf{D}_i^{\parallel} = \mathbf{n} \cdot \mathbf{D}_j^{\parallel}$ [84], which translate into

$$\begin{aligned} G_{1,j,\mathbf{q}}(-\infty, z') &= G_{n,j,\mathbf{q}}(\infty, z') = 0, \\ G_{i,j,\mathbf{q}}(z_i, z') &= G_{i+1,j,\mathbf{q}}(z_i, z'), \\ \epsilon_i \partial_z G_{i,j,\mathbf{q}}(z, z') \Big|_{z=z_i} &= \epsilon_{i+1} \partial_z G_{i+1,j,\mathbf{q}}(z, z') \Big|_{z=z_i}, \end{aligned} \quad (\text{B5})$$

the Green's function $G_{\mathbf{q}}(z, z') \equiv G_{s,s,\mathbf{q}}(z, z')$ can be solved for

$$\begin{aligned} G_{\mathbf{q}}(z, z') &= \frac{1}{2\epsilon_0 \epsilon_s |\mathbf{q}|} e^{-\bar{\epsilon}_s |\mathbf{q}| |z-z'|} + \frac{1}{2\epsilon_0 \epsilon_s |\mathbf{q}| f_{\mathbf{q}}} ((\epsilon_s - \epsilon_2 + e^{l|\mathbf{q}|} - \epsilon_{s,+} \epsilon_2 - e^{-l|\mathbf{q}|})(\epsilon_{1,+} \epsilon_s - e^{l|\mathbf{q}|} - \epsilon_{1,-} \epsilon_{s,+} e^{-l|\mathbf{q}|}) e^{-\bar{\epsilon}_s d |\mathbf{q}|} \\ &\quad \times (e^{\bar{\epsilon}_s |\mathbf{q}| (z-z')} + e^{-\bar{\epsilon}_s |\mathbf{q}| (z-z')}) + (\epsilon_s - \epsilon_2 + e^{l|\mathbf{q}|} - \epsilon_{s,+} \epsilon_2 - e^{-l|\mathbf{q}|})(\epsilon_{1,+} \epsilon_{s,+} e^{l|\mathbf{q}|} - \epsilon_{1,-} \epsilon_{s,-} e^{-l|\mathbf{q}|}) e^{\bar{\epsilon}_s |\mathbf{q}| (z+z')} \\ &\quad + (\epsilon_{s,+} \epsilon_2 + e^{l|\mathbf{q}|} - \epsilon_{s,-} \epsilon_2 - e^{-l|\mathbf{q}|})(\epsilon_{1,+} \epsilon_s - e^{l|\mathbf{q}|} - \epsilon_{1,-} \epsilon_{s,+} e^{-l|\mathbf{q}|}) e^{-\bar{\epsilon}_s |\mathbf{q}| (z+z')}), \end{aligned} \quad (\text{B6})$$

where we used the abbreviations

$$\epsilon_{i,\pm} = \epsilon_i \pm 1, \quad \epsilon_i = \sqrt{\epsilon_{\parallel,i} \epsilon_{\perp,i}}, \quad \bar{\epsilon}_i = \sqrt{\frac{\epsilon_{\parallel,i}}{\epsilon_{\perp,i}}}. \quad (\text{B7})$$

The electric field $\hat{E}_{z,\mathbf{q}}(z)$, which is generated by the Coulomb potential $\hat{\phi}_{\mathbf{q}}(z)$, is then obtained by

$$\hat{E}_{z,\mathbf{q}}(z) = -\partial_z \hat{\phi}_{\mathbf{q}}(z) = -\partial_z \int dz' G_{\mathbf{q}}(z, z') \hat{\rho}_{\mathbf{q}}(z'), \quad (\text{B8})$$

which yields the quantum-confined electric field $\hat{E}_{z,\mathbf{q}}$:

$$\hat{E}_{z,\mathbf{q}} = \frac{1}{\mathcal{A}} \int dz |\zeta(z)|^2 \hat{E}_{z,\mathbf{q}}(z) = -\frac{1}{\mathcal{A}} \int dz |\zeta(z)|^2 \partial_z \int dz' G_{\mathbf{q}}(z, z') \hat{\rho}_{\mathbf{q}}(z'), \quad (\text{B9})$$

cf. also Eq. (6) in the main text. By separating the z dependence of the charge density $\hat{\rho}_{\mathbf{q}}(z) \equiv -e|\zeta(z)|^2\hat{\rho}_{\mathbf{q}}$, we can identify a classical quantum-confined electric field $E_{z,\mathbf{q}}^{\text{loc}}$ via $\hat{E}_{z,\mathbf{q}} \equiv E_{z,\mathbf{q}}^{\text{loc}}\hat{\rho}_{\mathbf{q}}$:

$$E_{z,\mathbf{q}}^{\text{loc}} = \frac{e}{\mathcal{A}} \int dz |\zeta(z)|^2 \partial_z \int dz' G_{\mathbf{q}}(z, z') |\zeta(z')|^2. \quad (\text{B10})$$

By performing the z derivative and employing confinement wave functions $\zeta(z)$ of the form

$$\zeta(z) = \sqrt{\frac{2}{d}} \cos\left(\frac{\pi}{d}z\right), \quad -\frac{d}{2} \leq z \leq \frac{d}{2}, \quad (\text{B11})$$

the z and z' integrals in Eq. (B10) can be performed, which yields

$$E_{z,\mathbf{q}}^{\text{loc}} = \frac{e}{\mathcal{A}2\epsilon_0\epsilon_{s,\perp}} \frac{g_{\mathbf{q}}}{f_{\mathbf{q}}}, \quad (\text{B12})$$

cf. Eq. (10) in the main text, where

$$g_{\mathbf{q}} = ((\epsilon_{s,-}\epsilon_{2,+}e^{l|\mathbf{q}|} - \epsilon_{s,+}\epsilon_{2,-}e^{-l|\mathbf{q}|})(\epsilon_{1,+}\epsilon_{s,+}e^{l|\mathbf{q}|} - \epsilon_{1,-}\epsilon_{s,-}e^{-l|\mathbf{q}|}) \\ - (\epsilon_{s,+}\epsilon_{2,+}e^{l|\mathbf{q}|} - \epsilon_{s,-}\epsilon_{2,-}e^{-l|\mathbf{q}|})(\epsilon_{1,+}\epsilon_{s,-}e^{l|\mathbf{q}|} - \epsilon_{1,-}\epsilon_{s,+}e^{-l|\mathbf{q}|})) \left(\frac{8\pi^2 \sinh\left(\frac{\bar{\epsilon}_s|\mathbf{q}|d}{2}\right)}{\bar{\epsilon}_s|\mathbf{q}|d(4\pi^2 + (\bar{\epsilon}_s|\mathbf{q}|d)^2)} \right)^2, \quad (\text{B13})$$

and

$$f_{\mathbf{q}} = -\epsilon_{s,-}\epsilon_{s,-}(\epsilon_{1,+}\epsilon_{2,+}e^{-\bar{\epsilon}_s d|\mathbf{q}|}e^{2l|\mathbf{q}|} - \epsilon_{1,-}\epsilon_{2,-}e^{\bar{\epsilon}_s d|\mathbf{q}|}e^{-2l|\mathbf{q}|}) - 2\epsilon_{s,+}\epsilon_{s,-}(\epsilon_1\epsilon_2 - 1)(e^{\bar{\epsilon}_s d|\mathbf{q}|} - e^{-\bar{\epsilon}_s d|\mathbf{q}|}) \\ + \epsilon_{s,+}\epsilon_{s,+}(\epsilon_{1,+}\epsilon_{2,+}e^{\bar{\epsilon}_s d|\mathbf{q}|}e^{2l|\mathbf{q}|} - \epsilon_{1,-}\epsilon_{2,-}e^{-\bar{\epsilon}_s d|\mathbf{q}|}e^{-2l|\mathbf{q}|}). \quad (\text{B14})$$

APPENDIX C: DEVELOPMENT OF THE EXCITONIC PSOI HAMILTONIAN

The many-body Rashba Hamiltonian in low-wave-number approximation restricted to intraband processes reads, cf. Eq. (13) in the main text:

$$\hat{H}_{\text{BR}} = \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q}, \\ \xi, \xi', s, s'}} E_{z,\mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{v}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{v}_{\mathbf{k}'}^{\xi',s'} \hat{v}_{\mathbf{k}}^{\xi,s} + S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{c}_{\mathbf{k}'}^{\xi',s'} \hat{c}_{\mathbf{k}}^{\xi,s} \\ + S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{c}_{\mathbf{k}'}^{\xi',s'} \hat{v}_{\mathbf{k}}^{\xi,s} + S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{v}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{v}_{\mathbf{k}'}^{\xi',s'} \hat{c}_{\mathbf{k}}^{\xi,s}) + \sum_{\mathbf{k}, \mathbf{q}, \xi, s} E_{z,\mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}}^{\dagger\xi,\bar{s}} \hat{v}_{\mathbf{k}}^{\xi,s} + S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}}^{\xi,s}), \quad (\text{C1})$$

In excitonic normal ordering, we obtain

$$\hat{H}_{\text{BR}} = \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q}, \\ \xi, \xi', s, s'}} E_{z,\mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}'}^{\dagger\xi,\bar{s}} \hat{v}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{v}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} + S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{c}_{\mathbf{k}'}^{\xi',s'} \hat{c}_{\mathbf{k}}^{\xi,s}) \\ - \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q}, \\ \xi, \xi', s, s'}} E_{z,\mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{c}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'} \hat{c}_{\mathbf{k}'}^{\xi',s'} \hat{v}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} + S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}'}^{\xi',s'} \hat{v}_{\mathbf{k}'-\mathbf{q}}^{\xi',s'}) \\ + \sum_{\substack{\mathbf{k}, \mathbf{k}', \\ \xi, \xi', s, s'}} E_{z,0}^{\text{loc}} (S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}}^{\xi,s} - S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}}^{\dagger\xi,\bar{s}}) + \sum_{\mathbf{k}, \mathbf{q}, \xi, s} E_{z,\mathbf{q}}^{\text{loc}} S_{\mathbf{k}}^{v,\xi,\bar{s},s} (\hat{v}_{\mathbf{k}+\mathbf{q}}^{\xi,s} \hat{v}_{\mathbf{k}+\mathbf{q}}^{\dagger\xi,\bar{s}} + \hat{v}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}}^{\dagger\xi,\bar{s}}) \\ + \sum_{\mathbf{k}, \mathbf{q}, \xi, s} E_{z,\mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{c,\xi,\bar{s},s} \hat{c}_{\mathbf{k}}^{\dagger\xi,\bar{s}} \hat{c}_{\mathbf{k}}^{\xi,s} - S_{\mathbf{k}}^{v,\xi,\bar{s},s} \hat{v}_{\mathbf{k}}^{\xi,s} \hat{v}_{\mathbf{k}}^{\dagger\xi,\bar{s}}). \quad (\text{C2})$$

In the following, we neglect the first line in Eq. (C2), since we aim for a density-independent description. In the third line of Eq. (C2), the $E_{z,0}^{\text{loc}}$ -contributions, i.e., the spatially independent Hartree contributions due to a filled valence band, do not contribute, since they cancel out with the $\mathbf{q} = \mathbf{0}$ -contributions of the electron-ion interaction (not shown here). Moreover, the second terms in the brackets in the fourth (valence-band self-energy from the many-body term $\hat{v}^{\dagger}\hat{v}^{\dagger}\hat{v}\hat{v}$) and fifth (valence-band self-energy from the one-body term $\hat{v}^{\dagger}\hat{v}$) line in Eq. (C2) cancel. Note that, in contrast to the many-body Coulomb interaction, the one-body contributions due to self-interacting fields in the last line in Eq. (C2) do not vanish in the calculation of the quantum kinetics, since they encode spin-flip processes and are not just proportional to the particle-density operator $\hat{N} = \hat{a}_{\lambda,\mathbf{k}}^{\dagger\xi,s} \hat{a}_{\lambda,\mathbf{k}}^{\xi,s}$. Applying the unit-operator method [64,85] in the third, fourth and fifth lines of Eq. (C2) in lowest order,

$\mathbb{1} = \sum_{\mathbf{k}, \xi, s} \hat{c}_{\mathbf{k}}^{\dagger \xi, s} \hat{c}_{\mathbf{k}}^{\xi, s} + \sum_{\mathbf{k}, \xi, s} \hat{v}_{\mathbf{k}}^{\xi, s} \hat{v}_{\mathbf{k}}^{\dagger \xi, s} + \mathcal{O}(Na_B^2)^2$, we arrive at

$$\begin{aligned} \hat{H}_{\text{BR}} = & - \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q}, \\ \xi, \xi', s, s'}} E_{z, \mathbf{q}}^{\text{loc}} (S_{\mathbf{k}}^{v, \xi, \bar{s}, s} \hat{P}_{\mathbf{k}, \mathbf{k}'+\mathbf{q}}^{\dagger \xi, \xi', s, s'} \hat{P}_{\mathbf{k}-\mathbf{q}, \mathbf{k}'}^{\xi, \xi', \bar{s}, s'} + S_{\mathbf{k}'}^{c, \xi', \bar{s}', s'} \hat{P}_{\mathbf{k}, \mathbf{k}'+\mathbf{q}}^{\dagger \xi, \xi', s, s'} \hat{P}_{\mathbf{k}-\mathbf{q}, \mathbf{k}'}^{\xi, \xi', s, s'}) \\ & - S_{\mathbf{k}}^{v, \xi, \bar{s}, s} \hat{P}_{\mathbf{k}+\mathbf{q}, \mathbf{k}'}^{\dagger \xi, \xi', s, s'} \hat{P}_{\mathbf{k}, \mathbf{k}'}^{\xi, \xi', \bar{s}, s'} - S_{\mathbf{k}'}^{c, \xi', \bar{s}', s'} \hat{P}_{\mathbf{k}, \mathbf{k}'}^{\dagger \xi, \xi', s, s'} \hat{P}_{\mathbf{k}, \mathbf{k}'}^{\xi, \xi', s, s'}). \end{aligned} \quad (\text{C3})$$

After an expansion in excitonic wave functions [64]

$$\hat{P}_{\mathbf{k}, \mathbf{k}'}^{\xi, \xi', s, s'} = \sum_{\mu} \varphi_{\mu, \alpha_{\xi, \xi'}^s, \mathbf{k} + \beta_{\xi, \xi'}^{s, s'} \mathbf{k}'}^{\xi, \xi', s, s'} \hat{P}_{\mu, \mathbf{k}-\mathbf{k}'}^{\xi, \xi', s, s'}, \quad (\text{C4})$$

where $\varphi_{\mu, \mathbf{q}}^{\xi, \xi', s, s'}$ solves the Wannier equation:

$$\left(\tilde{E}_{\text{gap}}^{\xi, \xi', s, s'} + \frac{\hbar^2 \mathbf{q}^2}{2m_{\text{r}, \xi, \xi'}^{s, s'}} \right) \varphi_{\mu, \mathbf{q}}^{\xi, \xi', s, s'} - \sum_{\mathbf{q}'} V_{\mathbf{q}-\mathbf{q}'} \varphi_{\mu, \mathbf{q}'}^{\xi, \xi', s, s'} = E_{\mu}^{\xi, \xi', s, s'} \varphi_{\mu, \mathbf{q}}^{\xi, \xi', s, s'}, \quad (\text{C5})$$

with renormalized band gap $\tilde{E}_{\text{gap}}^{\xi, \xi'}$, relative momentum $\mathbf{q}$, reduced mass $m_{\text{r}, \xi, \xi'}^{s, s'} = (\frac{1}{m_e^{s, s'}} + \frac{1}{m_h^{s, s'}})^{-1}$ with effective masses of the electron/hole $m_{e/h}^{\xi, s}$, Coulomb potential $V_{\mathbf{q}}$ and excitonic energy $E_{\mu}^{\xi, \xi', s, s'}$ with excitonic quantum number μ , we finally obtain

$$\hat{H}_{\text{BR-X}} = \sum_{\substack{\mu, v, \mathbf{Q}, \\ \xi, \xi', s, s'}} (S_{\mu, v, \mathbf{Q}}^{h, \xi, \xi', s, s'} \hat{P}_{\mu, \mathbf{Q}}^{\dagger \xi, \xi', \bar{s}, s'} \hat{P}_{v, \mathbf{Q}}^{\xi, \xi', s, s'} - S_{\mu, v, \mathbf{Q}}^{e, \xi, \xi', s, s'} \hat{P}_{\mu, \mathbf{Q}}^{\dagger \xi, \xi', s, s'} \hat{P}_{v, \mathbf{Q}}^{\xi, \xi', s, s'}), \quad (\text{C6})$$

cf. Eq. (14) in the main text, with matrix elements

$$S_{\mu, v, \mathbf{Q}}^{h, \xi, \xi', s, s'} = \sum_{\mathbf{q}, \mathbf{q}'} \alpha_{\text{BR}, v}^{\xi} (i(\delta_{\bar{s}, \uparrow} - \delta_{\bar{s}, \downarrow})q_x - q_y) E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}} (\varphi_{\mu, \mathbf{q}+\beta_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{* \xi, \xi', \bar{s}, s'} - \varphi_{\mu, \mathbf{q}'+\beta_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{* \xi, \xi', \bar{s}, s'}) \varphi_{v, \mathbf{q}'+\beta_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{\xi, \xi', s, s'}, \quad (\text{C7})$$

$$S_{\mu, v, \mathbf{Q}}^{e, \xi, \xi', s, s'} = - \sum_{\mathbf{q}, \mathbf{q}'} \alpha_{\text{BR}, c}^{\xi} (i(\delta_{s', \uparrow} - \delta_{s', \downarrow})q_x - q_y) E_{z, \mathbf{q}-\mathbf{q}'}^{\text{loc}} (\varphi_{\mu, \mathbf{q}-\alpha_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{* \xi, \xi', s, s'} - \varphi_{\mu, \mathbf{q}-\alpha_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{* \xi, \xi', s, s'}) \varphi_{v, \mathbf{q}-\alpha_{\xi, \xi'}^{s, s'} \mathbf{Q}}^{\xi, \xi', s, s'}, \quad (\text{C8})$$

cf. Eq. (15) and Eq. (16) in the main text.

APPENDIX D: EXCITONIC SPIN EIGENVALUE EQUATION

The excitonic spin eigenvalue equation reads [22]:

$$E_{\mu, \mathbf{Q}}^{\xi, \xi', s_1, s_2} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s_1, s_2} + S_{\mu, v, \mathbf{Q}}^{h, \xi, \xi', \bar{s}_1, \bar{s}_2} \delta_{\mu, v} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', \bar{s}_1, \bar{s}_2} - S_{\mu, v, \mathbf{Q}}^{e, \xi, \xi', s_1, \bar{s}_2} \delta_{\mu, v} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s_1, \bar{s}_2} = E_{\mu, \mathbf{Q}}^{\xi, \xi', S} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s_1, s_2}, \quad (\text{D1})$$

where $E_{\mu, \mathbf{Q}}^{S, \xi, \xi'}$ is the spin-diagonal exciton dispersion with respect to the excitonic spin-diagonal quantum number S and $C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s_1, s_2}$ is the spin-diagonal eigenfunction. Note, that we neglected possible interactions between distinct excitonic states $\mu \neq v$ in Eq. (D1), as we are only interested in the dynamics of the lowest-lying $\mu = 1s$ exciton. However, such interactions, which have been shown to hybridize s - p excitons [20,21], can be straightforwardly included. At zero electric field (or zero momentum), the excitonic spin-diagonal quantum number S corresponds to the uncoupled spins of the exciton, i.e., if $E_{z, \mathbf{q}} \rightarrow 0$ (or $\mathbf{Q} \rightarrow \mathbf{0}$), then $S \rightarrow \{(\uparrow, \uparrow), (\uparrow, \downarrow), (\downarrow, \uparrow), (\downarrow, \downarrow)\}$.

The excitonic transitions are transformed as follows:

$$\hat{P}_{\mu, \mathbf{Q}}^{\xi, \xi', s, s'} = \sum_S C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s, s'} \hat{P}_{\mu, \mathbf{Q}}^{\xi, \xi', S}, \quad (\text{D2})$$

with

$$\sum_S C_{\mu, \mathbf{Q}, S}^{* \xi, \xi', s, s'} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s'', s'''} = \delta_{s, s''} \delta_{s', s'''}, \quad \sum_{s, s'} C_{\mu, \mathbf{Q}, S}^{* \xi, \xi', s, s'} C_{\mu, \mathbf{Q}, S}^{\xi, \xi', s, s'} = \delta_{S, S'}, \quad (\text{D3})$$

which enables a formulation of the excitonic theory in the spin-diagonal basis S .

APPENDIX E: PARAMETERS

All parameters are known from first-principle calculations or taken from literature. No additional fitting parameters have been introduced.

In Table II, we display the parameters, which are not related to phonon scattering, used in all numerical simulations.

For the numerical evaluation of the Wannier equation in Eq. (C5), which provides the excitonic binding energies and wave functions $\varphi_{\mu, \mathbf{q}}^{\xi, \xi', s, s'}$ necessary to estimate the excitonic energy landscape and the Rashba-, cf. Eq. (15) and Eq. (16), and exciton-phonon coupling elements, cf. Ref. [22], we use the analytical dielectric function from Ref. [90], which is fitted

TABLE II. Parameters used in the simulations.

Quantity	MoSe ₂	MoS ₂
Bright-dark splitting $E_{1s, \mathbf{Q}=0}^{K, K, \uparrow, \uparrow} - E_{1s, \mathbf{Q}=0}^{K, K, \uparrow, \downarrow}$ (meV)	-1.45 [14,72]	14 [14]
Effective spin-up electron mass $m_e^{K, \uparrow}/m_0$ [45]	0.495	0.435
Effective spin-down electron mass $m_e^{K, \downarrow}/m_0$ [45]	0.57	0.465
Effective spin-up hole mass $m_h^{K, \uparrow}/m_0$ [45]	0.595	0.54
Rashba coupling constant for electrons $\alpha_{BR}^{e, K}$ (e nm ²) [86]	0.011	0.003
Rashba coupling constant for holes $\alpha_{BR}^{h, K}$ (e nm ²) [86]	0.0422	0.041
Monolayer width d (nm) [87]	0.6527	0.618
Static out-of-plane dielectric constant $\epsilon_{\perp, 0}$ [59]	7.2	6.2
Static bulk dielectric constant $\epsilon_{\text{bulk}, 0} = \sqrt{\epsilon_{\text{bulk}, \parallel, 0} \epsilon_{\text{bulk}, \perp, 0}}$ [59]	12.05	10.47
Plasmon peak energy $\hbar\omega_{\text{pl}}$ (eV) [88]	22.0	22.5
Thomas-Fermi parameter α_{TF} (fit to <i>ab initio</i> results [89])	1.9	1.5
Calculated 1s excitonic binding energies with $l = 0.3$ nm [49,50] (meV)		
Spin-bright, SiO ₂ substrate	-441	-478
Spin-dark, SiO ₂ substrate	-455	-486
Spin-bright, Al ₂ O ₃ substrate	-341	-367
Spin-dark, Al ₂ O ₃ substrate	-355	-375
Spin-bright, h-BN encapsulated	-325	-349
Spin-dark, h-BN encapsulated	-339	-357

to *ab initio* calculations from the Computational Materials Repository [89], and the screened Coulomb potential $V_{\mathbf{q}} = \frac{e^2}{\mathcal{A}} \int d\mathbf{z} d\mathbf{z}' |\zeta(\mathbf{z})|^2 G_{\mathbf{q}}(\mathbf{z}, \mathbf{z}') |\zeta(\mathbf{z}')|^2$ with the Green's function from Eq. (B6) in the isotropic limit with $\epsilon_s \rightarrow \epsilon_{s, \mathbf{q}}$, where $\epsilon_{s, \mathbf{q}}$ is the bulk dielectric function of the analytic model from Ref. [90].

All relevant parameters for the exciton-phonon interaction such as electron-phonon interaction potentials, phonon dispersions, and phonon modes are taken from *ab initio* calculations in Refs. [67,68] and are not displayed in Table

II for better readability. For intravalley scattering, we take into account A', TO, LA, and TA modes and for intervalley scattering we take into account A', LO, TO, LA, and TA modes [91]. The electron-phonon interaction potentials in deformation-potential approximation from Refs. [67,68] for acoustic phonons are rescaled by a factor of $\frac{1}{\sqrt{2}}$ to properly consider the fact, that piezoelectric coupling, which is naturally included in the effective electron-phonon interaction potentials from Refs. [67,68], is ineffective for exciton-phonon interaction [92].

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