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Exciton-exciton interaction in transition metal dichalcogenide monolayers and van der Waals heterostructures

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Due to a strong Coulomb interaction, excitons dominate the excitation kinetics in two-dimensional (2D) materials. While Coulomb scattering between electrons has been well studied, the interaction of excitons is more challenging and remains to be explored. As neutral composite bosons consisting of electrons and holes, excitons show nontrivial scattering dynamics. Here, we study exciton-exciton interaction in transition-metal dichalcogenides and related van der Waals heterostructures on microscopic footing. We demonstrate that the crucial criterion for efficient scattering is a large electron/hole mass asymmetry, giving rise to internal charge inhomogeneities of excitons and emphasizing their cobosonic substructure. Furthermore, both exchange and direct exciton-exciton interactions are boosted by enhanced exciton Bohr radii. We also predict an unexpected temperature dependence that is usually associated with phonon-driven scattering, and we reveal an orders of magnitude stronger interaction of interlayer excitons due to their permanent dipole moment. The developed approach can be generalized to arbitrary material systems and will help to study strongly correlated exciton systems, such as moire super lattices.

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I. INTRODUCTION

The emergence of atomically thin two-dimensional (2D) materials, such as graphene and monolayer transition metal dichalcogenides (TMDs), has initiated a new research field offering a platform for the investigation of many-body correlations and quantum phenomena [1–4]. The strong Coulomb interaction in TMD monolayers gives rise to excitons, dominating the optical response, relaxation dynamics, and transport characteristics [5–8]. Excitons are neutral composite bosons (cobosons) consisting of Coulomb-bound electrons and holes. Due to a complex band structure exhibiting multiple valleys, there is a variety of different exciton species in TMDs including bright, momentum, and spin-dark intralayer excitons [9–11], as well as spatially separated interlayer excitons in van der Waals heterostructures [12–15].

Previous theoretical studies have addressed the fundamental many-body processes governing the phonon-driven exciton dynamics in monolayer TMDs [11,16–19] and van der Waals heterostructures [20–22]. In the considered weak-excitation regime, excitons were treated as noninteracting bosons. However, as the excitation density increases, the cobosonic nature of excitons comes to the surface and exciton-exciton scattering becomes increasingly important [23–25]. While scattering between electrons has been treated extensively in literature [26,27], a microscopic treatment of the Coulomb interaction of excitons as neutral cobosonic quasiparticles has proven to be challenging [28–30]. The role of direct and exchange exciton-exciton interactions in TMDs has been previously discussed, but exclusively for bright excitons interacting in a monolayer [25]. In particular, exciton-exciton scattering, incorporating the remarkable intervalley and interlayer excitonic landscape in 2D materials, has so far remained unrevealed.

In this work, we investigate exciton-exciton scattering in TMD monolayers and van der Waals heterostructures based on a microscopic and quantum-mechanic approach. We evaluate the efficiency of the exciton-exciton interaction by calculating the excitation-induced dephasing (EID) of excitonic resonances in the incoherent limit. We resolve the underlying intravalley and intervalley as well as intralayer and interlayer exciton-exciton scattering channels, cf. Fig. 1. We reveal an intriguing temperature and screening dependence of EID and provide microscopic insights into the fundamental nature of scattering between intralayer and interlayer excitons. The latter exhibit a permanent out-of-plane dipole moment, and their interaction can be considered as an efficient dipole-dipole coupling [Fig. 1(a)] resulting in an EID in the range of a few meV. In contrast, intralayer excitons do not have a permanent dipole moment and interact through higher-order electric moments induced by the internal charge inhomogeneity of excitons as cobosonic quasiparticles. Here, we show that the mass asymmetry between electrons and holes, as well as the overlap of Bohr radii, are the key quantities.
determining the exciton-exciton scattering efficiency. The gained microscopic insights are applicable to a broader class of excitonic, multi-valley materials.

II. THEORETICAL MODEL

To investigate exciton-exciton scattering on a microscopic footing in 2D materials, we first define the many-particle Hamilton operator. Following the approach described in Ref. [30], we derive the excitonic Hamilton operator from the conventional electron-electron Hamiltonian by employing an identity operator expansion [31] and rewriting the electron and hole creation and annihilation operators $e^{(t)}$ and $v^{(t)}$ into excitonic operators $p^{(t)}$. We obtain $H = H_0 + H_{	ext{int}}$, where the interaction-free part $H_0$ includes the excitonic energies $\epsilon^e_Q = E^x + \frac{e^2}{2q^2} - \frac{e^2}{2Q^2}, Q$ being the center-of-mass momentum, $M^x$ the valley-dependent exciton mass, $E^x$ the excitonic eigenenergies, and $\alpha = (n, \xi)$. The latter is a compound index including the excitonic state $n = 1, 2, \ldots$ in the valley $\xi = (\xi_x, \xi_y) = \text{KK}, \text{KK'}, \text{K}, \text{K}, \Lambda, \text{K}, \Lambda$, i.e., in this work we consider the hole to be localized around the K point, while the electron lies either around the K, K', or \Lambda point (also often referred to as Q point in literature [32]). Moreover, we focus on spin-allowed transitions [Fig. 2(a)]. In principle, exciton-exciton scattering including spin-dark states is also possible, but we expect this type of scattering to be qualitatively similar to the scattering with momentum-dark states that have been considered in this work.

The eigenenergies $E^x$ and the associated excitonic wave functions $\psi_{\alpha, Q}$ are obtained by solving the Wannier equation [16,20], which is derived within the effective-mass approximation [33]. Thus, the Wannier equation provides reliable excitonic binding energies when the exciton is well localized in momentum space and the parabolic approximation holds [34]. In the case of monolayers, we treat the screened Coulomb potential entering the Wannier equation within the Keldysh approach [35–37] to account for the finite width of the TMD and screening effects. For charge carriers within a heterostructure, we solve the Poisson equation for two aligned homogeneous slabs, resulting in a generalized Keldysh screening [20]. The obtained excitonic eigenenergies can be found in Table I in the Supplementary Material [38] and are in agreement both with DFT studies [39] and experimental observations [40]. In Fig. 2(b), the corresponding center-of-mass-dependent exciton dispersion $\epsilon^e_Q$ is schematically illustrated for monolayer WSe$_2$ showing the $n = 1s$ state of bright KK and momentum-dark KK', K\Lambda excitons. Since the latter are energetically lowest states, we expect that exciton-exciton scattering involving both bright and dark excitons will be efficient even at room temperature.

The second part of the Hamiltonian of interest in this work is the exciton-exciton interaction $H_{\text{int}}$, given by

$$H_{\text{int}} = \frac{1}{2} \sum \mathcal{W}_q^{\alpha\beta\beta'\alpha'} \langle \phi^\dagger_{\alpha, Q+Q'} P_{\beta, Q} P_{\beta', Q'} P_{\alpha', Q'} \rangle,$$

with $\mathcal{W}_q^{\alpha\beta\beta'\alpha'} = \mathcal{W}_q^{\alpha\beta\beta'\alpha'} + 2\mathcal{U}_q^{\alpha\beta\beta'\alpha'}$, and where summation over the excitonic indices $\alpha, \beta, \beta'$ and momenta $Q, Q'$ is implied [30]. The matrix element $\mathcal{W}_q^{\alpha\beta\beta'\alpha'}$ includes direct electron-electron, hole-hole, and electron-hole interactions ($\mathcal{U}_q^{\alpha\beta\beta'\alpha'}$) and exchange interactions ($\mathcal{V}_q^{\alpha\beta\beta'\alpha'}$). In this work, we focus on the most relevant valley conserving exciton-exciton scattering processes ($\alpha = \alpha' \equiv \mu$ and $\beta = \beta' \equiv \nu$) involving a small momentum transfer in the energetically lowest $n = 1s$ state, and therefore intervalley interactions have been omitted in the exciton-exciton Hamiltonian (1). Figure 1(b) illustrates exemplary scattering processes involving only KK states (process I) and including different valleys (process II). The direct part of the monolayer excitonic Coulomb matrix element reads

$$\mathcal{W}^{\text{mono}}_q = W_d D_\mu(q) D_\nu(q),$$

with the screened Coulomb potential $W_d$ and $D_\mu(q) = (F_\mu, \beta^{(\nu, q)} - F_\nu, \beta^{(\mu, q)})$ including the form factors $F_\mu(q) = \sum_{\nu} \varphi_{\mu, q+\nu} \varphi_{\nu, q}$ (see Supplementary Material for details). The latter include the mass ratios $\alpha^e = \frac{m_e^{\mu}}{m_e^{\nu}}, \alpha^h = 1 - \alpha^e$, where $m_e^{\mu(\nu)}$ is the electron (hole) mass in the valley $\mu(\nu) = \text{K}, \Lambda, \text{K'}$. When considering scattering processes within a heterostructure, the form factors...
are weighted differently depending on whether the scattering occurs between interlayer excitons exclusively or between intralayer and interlayer excitons, cf. the Supplemental Material. The exchange contribution to the interaction reads

\[ U_{q}^{\mu\nu}\eta = \frac{1}{2} \left( \delta_{\mu,\nu} \tilde{U}_{q}^{\mu\nu} + \delta_{\mu,\eta} \tilde{U}_{q}^{\nu\mu} \right), \tag{3} \]

with \( \tilde{U}_{q}^{\mu\nu} = \sum_{\eta q_{2}} \hat{W}_{q_{1},q_{2}}^{\mu\nu} G_{\eta}(q_{1},\alpha^{\mu}) G_{\eta}(q_{2},B^{\nu}q) \). Here we introduced \( G_{\eta}(q_{1},\alpha^{\mu}) = \varphi_{\eta,q_{1}}^{*}\varphi_{\mu,q_{1}+q} \) with \( i = 1,2 \) and \( \hat{W}_{q_{1},q_{2}}^{\mu\nu} = \hat{W}_{q_{1}}(q \cdot M_{\mu\eta}(q \cdot M_{\nu}^{*})) \), where \( M_{\eta} \) is the optical matrix element describing the transition probability between the conduction and valence bands in the same valley \( \eta = \mu,\nu \) [33,41]. We obtain \( M_{\eta} \) using \( k \cdot p \) theory [42,43] and deduce

\[ |M_{\eta} \cdot e_{z}|^{2} = M_{\eta}^{\alpha_{\eta}} = \frac{m}{2} (1 \pm \delta_{\eta,K}) \]

for left-handed (\( \alpha_{+} \)) and right-handed (\( \alpha_{-} \)) circularly polarized light in the vicinity of \( \eta = K \). The lattice constant \( a_{0} \), the band gap \( E_{Br} \), and the overlap integrals \( t_{i} = \langle u_{i,\eta}\mid \hat{p}

\langle u_{i,\eta} \rangle \rangle \) with the Bloch factors \( u_{i,\eta} \) are extracted from DFT calculations [32,44]. Note that the exchange interaction is only nonzero when the hole valley of one of the two scattering excitons is identical to the electron valley of the other exciton involved in the scattering process. Figure 3 illustrates the excitonic Coulomb matrix element in a hBN-encapsulated WSe\(_{2}\) monolayer considering different scattering channels with \( \mu = KK \) and \( \nu = KK, KA, KK' \) in real and momentum space. We distinguish between direct \( V \) [Figs. 3(a) and 3(b)] and exchange contributions \( U \) [Figs. 3(c) and 3(d)]. We proceed by discussing these contributions separately, starting with the direct interaction. Since excitons are effectively neutral quasiparticles composed by electrons and holes, the resulting direct interaction potential in real space is reminiscent of the Lennard-Jones potential, cf. Fig. 3(b) [45]. We find that both repulsive or attractive exciton-exciton interactions occur for different exciton species and length scales. Our model predicts that the strength of the direct interaction is determined by the mass ratios of electrons and holes of the involved excitons. This can be seen by performing a Taylor expansion of Eq. (2) for small \( q \) giving

\[ V_{q}^{\mu

\nu} = \sum_{\eta} W_{q_{1}}^{\mu\nu} g_{\eta\nu}^{0} Q_{\eta q_{1}} Q_{\eta}, \]

with \( r_{\eta\nu}^{0} = \langle \mu \rangle \rangle q_{\nu}/\Lambda_{1} \), where \( r_{\eta\nu}^{0} \) is the excitonic Bohr radius. Furthermore, we have introduced the effective excitonic charge

\[ Q_{\mu} = \left( \mu_{\eta_{\mu}}^{m_{\eta_{\mu}}} + \mu_{\eta_{\nu}}^{m_{\eta_{\nu}}} \right) / \left( m_{\eta_{\mu}}^{m_{\eta_{\mu}}} + m_{\eta_{\nu}}^{m_{\eta_{\nu}}} \right). \tag{4} \]

with \( Q_{\mu}/\epsilon = \pm 1 \) determining the sign of the interexcitonic potential and thus dictating the repulsive or attractive nature of the interaction. The latter can be interpreted as a force resulting from the internal charge inhomogeneity of the exciton. In particular, an exciton with a heavy hole will be positively charged in its center, surrounded by a negatively charged shell resulting from the orbiting electron. Considering the effective excitonic charges, the matrix element in the long-range limit is always positive for \( \mu = \nu \), while it becomes negative if the interacting excitons have inverted mass ratios. For example, we find an attractive character at small distances for the KK-\( \Lambda \) and KK-\( \Lambda' \) interaction in Fig. 3(b). While holes are heavier than electrons for KK excitons (\( Q_{\mu} > 0 \)), the opposite is the case for KA and KK’ (\( Q_{\mu} < 0 \)). Moreover, having the hole at the K point and the electron at the \( \Lambda \) point rather than at the \( \Lambda' \) point increases the exciton-exciton interaction by a factor of 10 in momentum space, cf. Fig. 3(a). This is a direct consequence of a larger mass asymmetry, and consequently larger effective charge for K\( \Lambda \) excitons (\( n_{K}^{\Lambda} \approx 0.6 m_{0} \) and \( m_{K}^{\Lambda} \approx 0.6 m_{0} \), vs \( m_{K}^{\Lambda} \approx 0.4 m_{0} \) [32]). Moreover, the direct interaction strongly depends on the exciton Bohr radius (expected distance between electron and hole) as it scales with the quadrupole moments of the excitons.

In contrast to the direct contribution, the exchange interaction \( U \) is nonvanishing at \( q = 0 \) and dominates in the considered momentum range. This behavior has already been established for interacting (bright) excitons in semiconductor quantum wells [46]. Moreover, the interaction is always repulsive and not highly sensitive to changes in electron and hole masses. In particular, the exchange interaction is only weakly reduced in momentum space when KK excitons are scattering with KK’ excitons instead of K\( \Lambda \) excitons, cf. Fig. 3(c). We also note that the exchange contribution can be estimated as \( U_{q} \propto E_{Br} r_{\eta\nu}^{0} / q \) for \( q \ll 1 \), where \( E_{Br} \) is the excitonic binding energy [25,47,48].
Note that the latter is strongly suppressed. The intralayer excitons we consider scattering of KK interlayer excitons with other bright small momenta, we find that qualitatively. By expanding the direct matrix elements for WSe$_2$ layer. The inset in (b) illustrates the screening dependence of the matrix elements.

Fig. 1(a). As a consequence, the exciton-exciton interaction between interlayer excitons in the exemplary MoSe$_2$-WSe$_2$ heterostructure is up to two orders of magnitude larger than in the monolayer WSe$_2$ case, cf. Figs. 3(c) and 3(d). Importantly, the direct interlayer and intralayer matrix elements also differ qualitatively. By expanding the direct matrix elements for small momenta, we find that $\gamma_{\mu\nu\nu\mu}(\omega) \propto W q^3$ vanishes for $q \to 0$, whereas the interlayer element remains nonzero, cf. Figs. 3(a) and 4(a), as well as the Supplemental Material [38], for details.

Based on the derived excitonic Coulomb matrix elements, we now calculate the dephasing of optical polarizations induced by exciton-exciton scattering that is referred to in literature as excitation-induced dephasing (EID) [50–52]. EID is a directly accessible phenomenon in experiments, and becomes manifest as a density-dependent broadening of excitonic transitions. In contrast to another recently published work [52], we evaluate the EID in the incoherent limit, i.e., in the long-time regime [33]. Note that we do not consider optical nonlinearities, but instead focus on the linear regime that is relevant for photoluminescence and transient absorption experiments.

We exploit microscopic access to the EID due to exciton-exciton interactions by evaluating the Heisenberg equation of motion for the excitonic polarization $P_{\mu\nu} = \langle P_{\mu\nu}(Q,\omega) \rangle$ in the light cone, i.e., $Q = 0$. When commuting the exciton-exciton Hamiltonian $H_{\nu\mu}$ with the polarization, exciton-exciton correlations such as $S \propto \langle P^\dagger P \rangle$ need to be considered, which previously have been treated within the Hartree-Fock approximation [30]. Here, we go beyond this and evaluate the equations of motion in second-order Born-Markov approximation [33,50], cf. the Supplemental Material [38]. To linear order in exciton density, we obtain $\dot{P}_{\mu\nu}|_{\nu\mu} = -\gamma_{\mu\nu\nu\mu}(\omega)|_{\nu\mu}$, introducing the excitation-induced dephasing

$$\gamma_{\nu\mu}(T) = \frac{\pi}{h} \sum_{q \in \mathcal{Q} q} |V_{q\nu\mu\nu\mu}(\omega)|^2 N_q(T) \delta(\Delta \epsilon),$$

with the delta function $\Delta \epsilon = \epsilon_{\nu\nu q} - \epsilon_{\nu\nu q} - \epsilon_{\mu\mu q} + \epsilon_{\mu\mu q}$ ensuring the energy conservation for the considered exciton-exciton scattering processes. The appearing temperature-dependent exciton occupation $N_q(T)$ is estimated with an equilibrium Boltzmann distribution, parameterized by the total exciton density $n = \sum_q N_q^0$.

In the following we focus on the EID of bright KK excitons and evaluate Eq. (5) for the state with $Q = 0$. In general, the expression has to be evaluated numerically, but in this particular case, where intravalley scattering ($\mu = \nu = \text{KK}$) is dominant, the temperature and density dependence of EID can be addressed analytically yielding

$$\gamma_0^{\text{KK}}(T) \big|_{\nu = \text{KK}} = \frac{n}{h} \sqrt{\frac{M_{\text{KK}}}{8\pi k_B T}} \int dq |V_{q}^{\text{KK}}|^2 .$$

We note a linear dependence of EID on exciton density $n$ as well as an explicit temperature dependence scaling with $T^{-1/2}$. Normally, temperature dependencies observed in linewidth experiments are attributed to the interaction with phonons [23]. However, our model predicts that the temperature dependent distribution of excitons in momentum space has a direct consequence on the amount of channels available for an energy and momentum conserving exciton-exciton scattering process. This results in an additional temperature-dependent broadening which can be experimentally separated from the phonon broadening by varying density and temperature.

III. EXCITATION-INDUCED DEPHASING IN MONOLAYERS

We exploit Eqs. (2) and (5) to determine the excitation-induced dephasing of bright KK excitons in a hBN-encapsulated WSe$_2$ monolayer. The choice of substrate is motivated by the fact that Auger processes [53–55], not captured by our theoretical model, are shown to be suppressed in hBN-encapsulated monolayers [56]. Here, we focus on the dominant intravalley scattering channels within the K, $\Lambda$, and K' valley, cf. Figs. 1(b) and 2(b). We illustrate the temperature and density dependence of the EID for the WSe$_2$ monolayer in Fig. 5. As confirmed by earlier experiments [23,57] and expected from our theory, the EID increases linearly with exciton density $n$, i.e., $\gamma_{\nu\mu}^{\text{KK}} = \gamma_{\nu\mu\nu\mu}^{\text{KK}} n$ with the slope $\gamma_{\nu\mu}$. However, as demonstrated in Fig. 5(b), the slope of the EID is highly temperature dependent with $\gamma_{\nu\mu}(T) = 2.9 \cdot 10^{-10} (4.9 \cdot 10^{-10}) \mu \text{eV cm}^2/\text{K}$ for $T = 300 \text{ K}$. This behavior is governed by the temperature dependence of the exciton distributions of the bright KK and momentum-dark KA and KK' states [Fig. 5(c)]. For low temperatures ($T < 30 \text{ K}$), KK’ excitons determine the EID, since most excitons reside in this energetically lowest state, see Fig. 2(b) and Table I in the Supplemental Material [38] for the energetic hierarchy of excitonic states in WSe$_2$. At elevated temperatures the EID is dominated by KA excitons reflecting their highest occupation, see Fig. 5(c). Hence, we have addressed the importance of dark excitonic states on the EID. Note that the intervalley scattering channels are expected to be most efficient for tungsten-based TMDs. In molybdenum-based TMDs, in particular MoSe$_2$, where the KK state is the energetically lowest state [10], bright excitons are expected to dominate the EID.
IV. EXCITON-INDUCED DEPHASING IN HETEROSTRUCTURES

Now, we investigate the impact of excitation-induced dephasing on a hBN-encapsulated MoSe$_2$-WSe$_2$ heterostructure. Here, both the EID of the intralayer (X) as well as of the spatially separated interlayer (IX) excitons within the heterostructure are considered. Note that we consider intralayer excitons in the WSe$_2$ layer. According to a recent DFT study [58], KK interlayer excitons reside in the energetically lowest state in the MoSe$_2$-WSe$_2$ heterostructure. However, intervalley interlayer excitons, in particular the K\(\Lambda\) state, can be found at a similar energy scale [59], and might also have an impact on the EID. However, treating the strong hybridisation at the A-point [58,60] is beyond the scope of this work, and thus these states have not been considered here. Qualitatively, the analysis of the density dependence of the intralayer and interlayer EID is similar to the monolayer case, cf. Fig. 6(a). We find a linear density dependence, however with drastically higher slope values of \(\gamma\) as well as intervalley scattering (K\(\Lambda\), KK') at fixed exciton density \(n = 10^{11}\) cm\(^{-2}\). Consequently, exclusively interlayer excitons contribute to the EID at all temperatures. In this particular case, the analytical formula in Eq. (6) can be used to evaluate the EID, predicting a \(T^{-\frac{1}{2}}\) temperature dependence for interlayer excitons, as observed in Fig. 6(b).

Finally, we investigate how the choice of substrate affects the EID. In Fig. 7 the EID is shown as a function of the background dielectric screening \(\epsilon_s\) for two different temperatures. We find a similar behavior for \(T = 50\) K and \(T = 300\) K, namely that the EID in both the monolayer and the heterostructure displays a surprisingly moderate variation due to screening despite the strong screening dependence of the Coulomb potential itself. This reflects the moderate decrease of the (direct) excitonic Coulomb matrix elements with screening, as illustrated by the insets in Figs. 3(d) and 4(b). The background is that a larger screening also gives rise to an enhanced Bohr radius, which increases the form factors \(F\) and \(G\) appearing in the excitonic Coulomb matrix elements, cf. Eqs. (2) and (3), respectively. Hence, there is a competition between a decreased Coulomb potential \(W\)
and an increased Bohr radius resulting in a weak overall screening dependence. Still, we observe a stronger screening dependence in the monolayer case compared to heterostructures. This can be traced back to the exchange interaction that is dominating for monolayers and is more sensitive to screening than the direct contribution, which is crucial for heterostructures. In particular, the direct interaction displays a stronger dependence on the excitonic Bohr radius in the limit \( q \ll 1 (V \propto r_B^2) \) compared to the exchange interaction \( (U \propto E_R r_B^3) \), and hence the compensation between decreased Coulomb potential and increased Bohr radius is weakened when the exchange interaction is dominant.

V. CONCLUSION
We have presented a microscopic and quantum-mechanic approach on exciton-exciton scattering in 2D materials and related van der Waals heterostructures. To evaluate the scattering efficiency, we calculate the excitation-induced dephasing (EID) taking into account intravalley and intervalley as well as intralayer and interlayer exciton-exciton scattering channels. We predict an intriguing temperature and screening dependence, and explain this by shedding light into the fundamental nature of exciton-exciton scattering. Spatially separated interlayer excitons in heterostructures exhibit a permanent dipole moment and their interaction can be considered as an efficient dipole-dipole coupling resulting in an EID of a few meV. In contrast, intralayer excitons are neutral cobosonic quasiparticles. The exciton-exciton scattering efficiency is boosted by a large electron/ hole mass asymmetry and Bohr radii overlap of the excitons. The gained insights can guide future experimental studies on the impact of exciton-exciton scattering on optical properties of multivalley 2D materials.

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Correction: The fourth sentence of the abstract contained an error in wording and has been replaced.