

Controllable fusion of electromagnetic bosons in two-dimensional semiconductors

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We propose a physical principle for implementation of controllable interactions of excitons in two-dimensional semiconductors. The key ingredients are tightly bound biexcitons and in-plane anisotropy of the host structure due to, e.g., a uniaxial strain. We show that anisotropy-induced splitting of the radiative exciton doublet couples the biexciton state to continua of exciton scattering states. As a result, two-body elastic scattering of excitons may be resonantly amplified when energetically tuned close to the biexciton by applying a transverse magnetic field or tuning the coupling with the microcavity photon mode. At the resonance excitonic fields may undergo quantum reaction of fusion. The fusion and a reverse reaction of biexciton disintegration may be used for efficient generation of squeezed light. For “bright” excitons in the absence of a microcavity, we predict giant molecules (Feshbach dimers) which can be obtained from a biexciton via rapid adiabatic sweeping of the magnetic field across the resonance. The molecules possess nontrivial entanglement properties. Our proposal holds promise for the strongly correlated photonics and quantum chemistry of light.

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I. INTRODUCTION

A. Foreword

Semiconductor optics holds great promise for the practical implementation of the emergent quantum technologies [1]. The central issues are entanglement and squeezing [2], and these have put bound exciton pairs into the focus of applied research over the past decades [3–10]. The state of the art embodies entangled photon pairs from biexcitons in nanocrystals [11] and quantum dots (QD’s) [12–14] and the low-threshold biexciton lasing in two-dimensional (2D) heterostructures [15–17].

In contrast to “zero-dimensional” states in QD’s, 2D excitons represent propagating (guided) electromagnetic waves [18], which possess massive dispersion and may undergo two-body quantum scattering due to Coulomb forces between the constituent electrons and holes [19]. The exciton dispersion may be efficiently tailored by photonic engineering of the environment [20], with the ultimate case being the microcavity exciton-polariton with drastically reduced effective mass [21]. At low densities 2D excitons behave as interacting bosons and may accumulate in a single quantum state featuring the phenomena of Bose-Einstein condensation (BEC) and superfluidity. Quantum collective effects associated with BEC and pairing of 2D excitons have been the subject of the experimental [22–28] and theoretical studies [9,19,29–33]. Natural connection of these low-temperature equilibrium phenomena to lasing has been a central problem in polaritonics [34].

For the quantum optical applications, 2D heterostructures have several noteworthy benefits as compared to QD’s.

Delocalized 2D ensembles are less prone to the Auger recombination known to be deleterious for lasers [16]. Many-body states of interacting excitons featuring macroscopic entanglement and squeezing may also outperform the isolated localized pairs in such applications as quantum optical lithography [35], sensing [36], and all-optical quantum computing [37].

Aiming primarily at discussion of the underlying two-body physics, we shall use the collective term “excitons” referring either to “bright” excitons or microcavity polaritons from a single perspective. An exciton is essentially a photon dressed by electronic excitations in a 2D semiconductor medium with direct band gap [38]. We shall not be concerned with the “gray” and “dark” excitons [39]. As such, our excitons are statistically *identical* quasiparticles.

A steppingstone for fundamental research on mixtures of excitons and their molecules, as well as for their practical use, would be implementation and control of the interconversion process,

$$\alpha_{\sigma} + \alpha_{\sigma'} \leftrightarrow X_{\uparrow}X_{\downarrow}, \quad (1)$$

where α_{σ} is either a “bright” exciton ($\alpha = X$) or a microcavity polariton ($\alpha = L$) with spin σ (“ $\uparrow$ ” or “ $\downarrow$ ”) and $X_{\uparrow}X_{\downarrow}$ is a biexciton. For atomic Bose (as well as Fermi) gases, such control has taken the name of Feshbach resonance [40]. Controllable synthesis of atomic molecules has spurred development of ultracold quantum chemistry [41] and “superchemistry” exploiting bosonic stimulation of reactions in the presence of BEC [42–44].

The Feshbach resonance concurrently offers a mechanism to adjust the strength of two-body interactions between particles at will, from increasingly strong repulsion to attraction through unitarity [40]. This is achieved by tuning the energy of the scattering channel of interest (called “open” channel)

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with respect to the energy of the molecule. The scattering channel admitting the molecular state is designed as energetically “closed” by sustaining the corresponding dissociation threshold above the energy of colliding particles in the “open” channel. The Feshbach resonance occurs when the “open” channel crosses the molecular level. Provided the molecule is tightly bound, the energy mismatch between the channels is large, making the *coherent coupling* to the continuum of the “closed” channel inefficient. On the other hand, the very same coupling to the resonant molecular state affects dramatically the particle scattering in the “open” channel. The nature of the coherent coupling depends on the particular setting and will be discussed in more detail below.

Such an additional possibility of tuneable interactions would be of paramount interest in the context of excitons, as it would enable strong photonic nonlinearities at ultralow densities. On general grounds, one would also expect strong interactions and pairing to be accompanied by entanglement and squeezing of light [2]. The latter features have not yet been fully appreciated in the context of ultracold atoms. In contrast, entanglement and squeezing emerge naturally in nonlinear optics of 2D semiconductors, where interactions between excitons provide nonlinear susceptibilities [45–47].

B. Coherent link

The crucial ingredient of a Feshbach resonance is a coherent link between the “open” scattering channel of interest and the “closed” molecular channel. In prototypical atomic Feshbach resonances such a link has been enabled either by the hyperfine interaction [48] or by the photon exchange with an external radiation field [49]. In semiconductors, signatures of a Feshbach resonance have recently been reported for a twisted bilayer 2D heterostructure [50] and attributed to hybridization of exciton-electron scattering states with the intralayer (closed channel) trion state [51]. In this case the coherent link is presumably due to interlayer electron (or hole) tunneling.

For a pair of identical excitons, two possible mechanisms of coherent coupling to a biexciton have been proposed. The first one relies on the so-called giant oscillator strength model [19,52] of a biexciton put into a microcavity: The biexciton may coherently dissociate into an exciton and a microcavity photon [53]. Several theoretical [54–56] and experimental [57–59] studies have been carried out along this direction. The second proposal exploits the dipolar repulsion between the excitons electrically polarized in the transverse direction: The biexciton is thus transformed into a shape resonance [9,10]. Two recent independent experiments [60,61] have reported divergence of the dipolar polariton blueshift consistent with a broad shape resonance [10]. Remarkably, the theory [10] predicts efficient squeezing of the light emitted by polaritons interacting via such a broad resonance. While viability of these proposals may be subjected to debates and further experimental tests, technological relevance of the direction calls for the quest of their possible alternatives.

C. Outline of the paper

In this paper we suggest yet another microscopic mechanism allowing implementation of the coherent coupling to

a biexciton. Our coherent link is due to the natural splitting of the radiative exciton doublet by the electron-hole exchange interaction. This genuinely excitonic mechanism is ubiquitous for a broad variety of 2D semiconductors including traditional quantum wells (QW’s), atomically thin layers of transition metal dichalcogenides (TMD’s) and emerging perovskite-based heterostructures. The coupling can be controlled *in situ* by in-plane structural anisotropy due to, e.g., uniaxial strain.

Tuning the energy of spin-polarized excitons close to a biexciton by a transverse magnetic field results in characteristic resonant behavior of the exciton *s*-wave scattering amplitude. For a broad resonance, this provides fully controllable and increasingly large third-order nonlinear susceptibility [$\chi^{(3)}$] at ultralow photon densities. In microcavities, the fine splitting of the polariton modes and the relative position of the scattering channels can additionally be controlled by a concomitant optical anisotropy of the cavity and the exciton-photon detuning, respectively.

Our estimates of the resonance width indicate that one may expect efficient squeezing of the emitted photons in moderately strained TMD samples. Strong squeezing has previously been predicted for dipolar polaritons [10], although the control over the width and position of the resonance has been limited in that case. The squeezing is immanent to the process (1). One may argue that the coherent interconversion (1) acts similarly to the second-order nonlinear susceptibility [$\chi^{(2)}$] for electromagnetic waves [45,62]. In the left column of Fig. 1 we show ensuing parametric processes of exciton “fusion” and biexciton “disintegration.” These are to be compared with the second-harmonic and difference-frequency generation, respectively, shown in the right column. Fusion (or disintegration) assumes macroscopic population of bosonic modes and occurs on the characteristic timescale $\mathcal{T}_\alpha$ [Eq. (24)]. Unlike $\chi^{(2)}$, the reaction (1) does not require any specific symmetry of the medium with respect to the inversion because the molecule $X_\uparrow X_\downarrow$ corresponds to a scalar field: a *bound pair* of polarization waves.

For “bright” excitons in the absence of a microcavity, we additionally predict giant Feshbach molecules: *quantum halos*. The halos may be obtained from a biexciton via *rapid adiabatic passage* across the resonance. Alternatively, one may think of controllable synthesis of spin-singlet biexcitons from the polarized excitons. Biexciton synthesis (dissociation) is achieved through the interconversion process (1) for two particles, where one has $\sigma = \sigma' = \uparrow$, and is accompanied by a buildup (dissolution) of entanglement in the polarization of the emitted photons. This should be contrasted with the process $X_\uparrow + X_\downarrow \leftrightarrow X_\uparrow X_\downarrow$ (potentially offered by the shape resonance [9], although with limited control), where the degree of entanglement remains constant.

Our consideration opens a new direction in the application-oriented quest of strongly correlated photons and the quantum chemistry of light.

II. THEORETICAL MODEL

A. Single-boson Hamiltonians

We adopt the generic picture of an exciton as an evanescent electromagnetic wave propagating in the structure plane [18,19,38]. For a free-standing monolayer (or a QW) there is

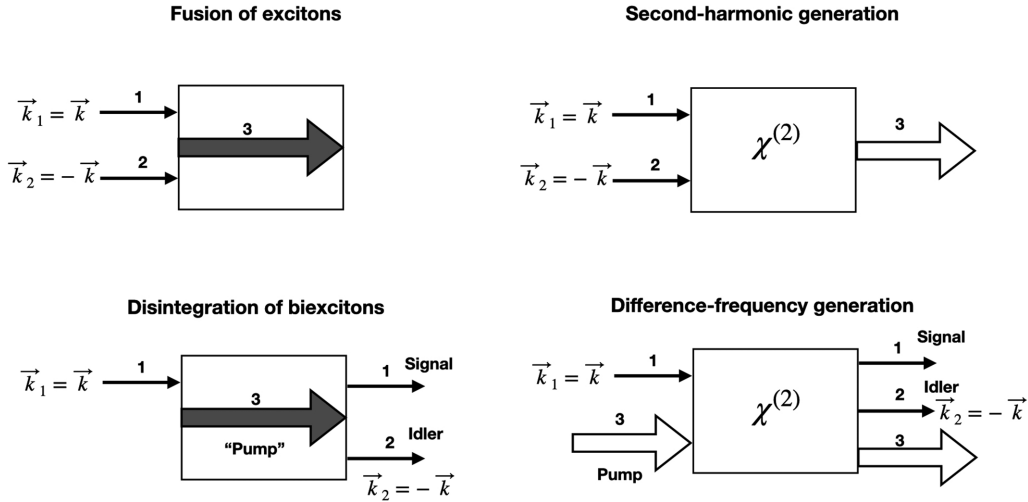


FIG. 1. The parametric processes of exciton “fusion” and biexciton “disintegration” (left column) due to the resonant reaction (1). These are to be compared with the conventional second-harmonic and difference-frequency generation due to the second-order susceptibility $\chi^{(2)}$ (right column) [45]. Energy and in-plane momentum conservation are assumed for the fields (enumerated arrows). Unlike an ordinary second-harmonic polarization field (white arrows), the biexciton (gray arrows) is a scalar field and does not emit light at the second-harmonic frequency. Nevertheless, provided a biexciton field “3” with $\mathbf{k}_3 = 0$ is already present in the 2D medium, the electromagnetic field “1” with the in-plane momentum $\mathbf{k}_1 = \mathbf{k}$ would stimulate coherent disintegration of the biexcitons into a pair of polarization fields (free excitons) with $\mathbf{k}_1 = \mathbf{k}$ and $\mathbf{k}_2 = -\mathbf{k}$ (“signal” and “idler,” respectively). Both “signal” and “idler” fields would be squeezed.

rapid radiative decay of excitons with low momenta $\mathbf{k}$ inside the light cone [63]. The radiative exciton lifetime τ_X may be enhanced by placing the semiconductor onto a substrate [20] or into a microcavity [64]. The dual view of an exciton as a bound electron-hole excitation and an electromagnetic wave then extends to the whole range of in-plane momenta. The cavity polariton in this picture would represent the ultimate case where strong light-matter coupling within the light cone is achieved by placing the 2D semiconductor at an antinode of the microcavity photon mode [21].

In the course of an optical transition the photon spin $\hat{s}$ is transferred to the band electron (hole) in-plane orbital motion in the conduction (valence) band [65]. The same orbital momentum is responsible for the Zeeman-like interaction of an exciton with a static magnetic field $\mathbf{B}$. The three components of an expectation value $\langle \hat{s} \rangle$ are the Stokes parameters encoding the photon polarization [66]. In an unperturbed crystal the bright exciton states with $s_z = +1$ and $s_z = -1$ (hereinafter denoted as $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively) form a degenerate doublet at $\mathbf{k} = 0$. Under the time reversal one has $\hat{s}_z \rightarrow -\hat{s}_z$, whereas $\hat{s}_{x,y} \rightarrow \hat{s}_{x,y}$. Since, on the other hand, $\mathbf{B} \rightarrow -\mathbf{B}$, it follows that the exciton spin $\hat{s}$ may couple only to the transverse component of $\mathbf{B}$. In the electron-hole picture this constraint corresponds to the mere fact that the 2D band orbital momentum does not possess an in-plane component [67–69].

Experimental [70–72] and theoretical [73–76] studies of the optical orientation and alignment of excitons have shown that an effective in-plane magnetic field Ω_α may be induced by uniaxial deformation of the host lattice. Microscopically, the strain would act on the exciton spin via the electron-hole exchange interaction [77]. In the basis of the circularly polarized states $|\uparrow\rangle$ and $|\downarrow\rangle$ the Hamiltonian of an exciton under the combined action of the transverse magnetic field and the

in-plane strain reads

$$\hat{H}_\alpha = \frac{\hbar^2 \hat{p}^2}{2m_\alpha} + \frac{\delta_\alpha(B)}{2} - \hbar \omega_\alpha \cdot \hat{s}, \quad (2)$$

where $\hat{p}$ is the momentum operator, m_α is the boson effective mass,

$$\omega_\alpha = \Omega_{\alpha,x} \mathbf{n}_x + \Omega_{\alpha,y} \mathbf{n}_y + \frac{\mu_B g_\alpha}{\hbar} B \mathbf{n}_z, \quad (3)$$

and the boson spin operator may be expressed as

$$\hat{s} = \hat{\sigma}_x \mathbf{n}_x + \hat{\sigma}_y \mathbf{n}_y + \hat{\sigma}_z \mathbf{n}_z, \quad (4)$$

with $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$ being the Pauli matrices. We assume that the semiconductor band structure is such that the radiative doublet is isolated from various satellite states (e.g., “dark” excitons) [78]. Virtual transitions of the excitons to such states then may be accounted for by background renormalization of the relevant quantities [81].

The label α distinguishes between the “bright” exciton ($\alpha = X$) and the lower-polariton ($\alpha = L$) models. For the “bright” excitons, the term $\delta_X(B)$ describes the diamagnetic shift [82,83] and g_X is the exciton g factor which governs the Zeeman splitting in the transverse magnetic field B . In TMD monolayers one has $g_X \sim 4$ [69,83]. For polaritons, we shall assume large vacuum Rabi splitting $\hbar \Omega_R(B)$ as compared to the detuning $\delta_\pm = \delta_0 - \delta_X(B)/2 \pm \mu_B g_X B$ between the microcavity and the exciton modes, i.e., $\hbar \Omega_R(B) \gg |\delta_\pm|$. All polariton parameters vary along the dispersion curve and approach their bare excitonic values at high momenta. At the bottom of the dispersion one has $\delta_L(B) = \delta_X(B)/2 + \delta_0 - \hbar \Omega_R(B)$ and $g_L = X_0^2 g_X$ with $X_0^2 = 1/2[1 + (1 + \hbar^2 \Omega_R^2 / \delta_\pm^2)^{-1/2}] \approx 1/2$ being the Hopfield coefficient X_p^2 evaluated at $\mathbf{p} = 0$ [82].

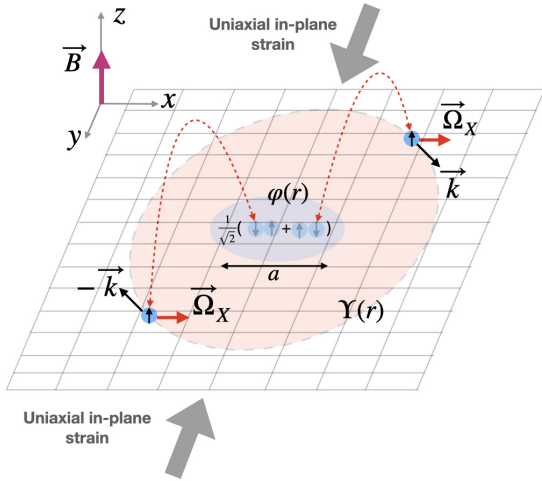


FIG. 2. Schematic view of a synthetic excitonic molecule [Eq. (28)] obtained in a strained 2D semiconductor by sweeping the transverse magnetic field $\mathbf{B}$ across the biexciton resonance. Uniaxial strain applied along the y direction induces an effective magnetic field Ω_X oriented along the x axis. In contrast to $\mathbf{B}$, the field Ω_X is even under time reversal and couples spin-polarized free-pair states $|\mathbf{k}, \uparrow\rangle |-\mathbf{k}, \uparrow\rangle$ to the spin-entangled biexciton state $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ with the spatial part $\varphi(r)$ (blue area) having microscopic size a . Such coupling (depicted by dashed red arrows) acts as a coherent Feshbach link which “dresses” the biexciton by the spin-polarized continuum, the latter forming a quantum halo $\Upsilon(r)$ which extends over the macroscopic area (pink).

A relationship between the effective magnetic field Ω_α and the strain tensor u_{ij} may be established by using a symmetry argument. The scalar product in the Hamiltonian (2) should be invariant under the point symmetries of a 2D crystal. Hence, Ω_α belongs to the same (irreducible) representation as the in-plane coordinates x and y . It follows, that $\Omega_{\alpha,x} = \mathcal{B}_\alpha(u_{xx} - u_{yy})$ and $\Omega_{\alpha,y} = 2\mathcal{B}_\alpha u_{xy}$.

Assuming uniaxial deformation along the direction which constitutes an angle θ with the x axis, the effective magnetic field may be expressed as

$$\Omega_\alpha = -\mathcal{B}_\alpha u [\cos(2\theta)\mathbf{n}_x - \sin(2\theta)\mathbf{n}_y], \quad (5)$$

where $u \ll 1$ is the relative extension of the layer along the chosen direction, and we have assumed that the extension is accompanied by compression along the orthogonal direction by the same (relative) amount. An example of such deformation is sketched in Fig. 2. In general, for $u_{xx} \neq -u_{yy}$ (the area is changed), one would also have an overall shift of the exciton energy proportional to $u_{xx} + u_{yy}$ [76].

The proportionality coefficient $\mathcal{B}_\alpha$ depends on the particular setting under consideration and is governed by the electron-hole exchange. One has $\mathcal{B}_\alpha = \mathcal{B}_\alpha^{(\text{sr})} + \mathcal{B}_\alpha^{(\text{lr})}$, where the first and the second term are due to the short- and long-range parts of the exchange interaction, respectively. For excitons in TMD's, one has $\hbar\mathcal{B}_X^{(\text{sr})}$ in the range 10 to 100 meV [76]. By placing the TMD layer onto a substrate with the amplitude reflection coefficient r_b , one may also activate the long-range part and increase the above estimate by the amount [76],

$$\mathcal{B}_X^{(\text{lr})} = \tau_X^{-1} \frac{2\eta \text{Im}(r_b)}{1 + \text{Re}(r_b)}, \quad (6)$$

with $\eta \sim 1$ –10. For polaritons, the coefficient $\mathcal{B}_L$ may additionally include purely photonic contribution due to an in-plane anisotropy of the microcavity [84,85].

It is worth to point out that the long-range exchange (and the longitudinal-transverse splitting of the cavity mode) also provides the linear (quadratic) in k contributions to the “bright” exciton (cavity polariton) effective magnetic field $\Omega_{X(L)}$ and kinetic energy. Possible effects due to those contributions have been discussed in our previous work [86] and do not affect the conclusions that will be drawn here.

Finally, we notice that none of the above mechanisms requires specific symmetry of the medium with respect to the spatial inversion [76]. In the absence of an inversion center, one may have additional contribution to the effective field Ω_α due to the piezoelectric effect [87].

B. Two-body interactions in the absence of strain

The Coulomb forces between the electrons and holes enable two-body interactions between the excitons. Thus, exchange of the identical fermions results in binding of excitons into biexcitonic molecules [88,89]. By virtue of the optical selection rule discussed above, opposite orientations of the fermionic spins in a biexciton imply the singlet configuration for the associated photons. The orbital wave function of a molecule in the absence of strain ($\Omega_X \equiv 0$) may be conveniently regarded as an $\varepsilon < 0$ solution of the Schrödinger equation,

$$\left[\frac{\hbar^2 \hat{\mathbf{k}}^2}{m_X} + V_{\uparrow\downarrow}^{(X)}(r) \right] \varphi(r) = \varepsilon \varphi(r), \quad (7)$$

where $\hat{\mathbf{k}} = (\hat{\mathbf{p}}_1 - \hat{\mathbf{p}}_2)/2$ is the relative momentum and $V_{\uparrow\downarrow}^{(X)}(r)$ is a static axially symmetric potential describing interaction of two composite bosons [19,81,90]. The potential $V_{\uparrow\downarrow}^{(X)}(r)$ accounts both for the direct and exchange scatterings of the identical fermions, and in the heavy-hole limit approaches the familiar Heitler-London shape with the characteristic dip at short distances. For our analytical estimates we shall use the Gaussian *ansatz*,

$$\varphi(r) = (a\sqrt{\pi})^{-1} e^{-r^2/2a^2} \quad (8)$$

with $a \equiv \hbar/\sqrt{m_X|\varepsilon|}$. We assume $a \sim R_{\uparrow\downarrow}$ with $R_{\uparrow\downarrow}$ being the microscopic range of the potential, i.e., our biexciton is a tightly bound (deep) state. Thus, for TMD monolayers one has a and $|\varepsilon|$ on the order of few nanometers and tens of meV, respectively [5–7]. Studies of an analogous dipositronium problem suggest that excited states of a biexciton do not exist due to a very diffuse structure of a four-particle complex consisting of electrons and holes with equal masses [91].

The excitons with parallel spins interact via the short-range repulsive potentials $V_{\sigma\sigma}^{(X)}(r)$ [92]. The corresponding low-energy s -wave scattering amplitudes may be written as [93]

$$\bar{f}_{\sigma\sigma'}^{(X)}(k) = \frac{\pi}{\ln[k a_{\sigma\sigma'}^{(X)}] - i\pi/2} \quad (9)$$

with $a_{\sigma\sigma'}^{(X)}$'s being the 2D scattering lengths. For the repulsive potentials $V_{\sigma\sigma}^{(X)}(r)$ one has $a_{\sigma\sigma}^{(X)} \sim R_{\sigma\sigma}$, where $R_{\sigma\sigma}$'s are the characteristic microscopic ranges. Such an estimate holds also

for the attractive potential $V_{\uparrow\downarrow}^{(X)}(r)$ under our assumption of tight binding.

Whether one deals with a bound state or a scattering event in the case of attraction depends on the statement of the problem: Relaxation toward a bound state is beyond the elastic scattering considered here. In practice, the reaction $X_{\uparrow} + X_{\downarrow} \rightleftharpoons X_{\uparrow}X_{\downarrow} + \hbar\nu$ due to the potential $V_{\uparrow\downarrow}^{(X)}(r)$ is an uncontrollable (stochastic) process, and the reverse process is of activation (Arrhenius) type [22]. The situation may change for dipolar excitons, where the long-range dipolar repulsion introduces a potential barrier into $V_{\uparrow\downarrow}^{(X)}(r)$, which may transform the bound state into a shape resonance [9]. This may unlock a resonant interconversion process $X_{\uparrow} + X_{\downarrow} \leftrightarrow X_{\uparrow}X_{\downarrow}$, although the degree of control remains limited. We leave the long-range dipolar forces beyond the scope of the present paper as well.

The effective interaction constants are related to the scattering amplitudes by $\bar{g}_{\sigma\sigma'}^{(X)} = -2\hbar^2/m_X \bar{f}_{\sigma\sigma'}^{(X)}(k_c)$, with k_c being the characteristic momentum scale [94]. For a MoS₂ monolayer one may deduce from Eq. (9) (omitting the imaginary part) typical values of $\bar{g}_{\sigma\sigma'}^{(X)}$'s on the order of few tenths of $\mu\text{eV} \times \mu\text{m}^2$. In the relevant limit

$$\sqrt{m_X/\hbar\tau_X} \ll k_c \ll 1/R_{\sigma\sigma'} \quad (10)$$

the three quantities $\bar{g}_{\sigma\sigma'}^{(X)}$, together with the binding energy $|\varepsilon|$ provide complete description of the bare two-body interactions in a dilute exciton gas. Virtual transmutations of the “bright” excitons into remote (in the energy or momentum) satellite states may be regarded as background renormalization of these quantities [81].

For polaritons, we assume the Rabi splitting $\hbar\Omega_R$ being comparable to the biexciton binding energy $|\varepsilon|$. The polariton-polariton interactions at $\Omega_L \equiv 0$ have been a subject of the on-going theoretical [95–97] and experimental [98–101] studies. In most cases the projected potentials $V_{\sigma\sigma'}^{(L)}(\mathbf{k}' - \mathbf{k}) \equiv X_k^2 X_{k'}^2 V_{\sigma\sigma'}^{(X)}(\mathbf{k}' - \mathbf{k})$ may be approximated by some phenomenological constants $g_{\sigma\sigma'}^{(L)}$, on the order of the corresponding effective interaction constants for excitons.

The only exception is the situation where the polariton “ $\uparrow\downarrow$ ” scattering continuum overlaps the biexciton level, i.e.,

$$\delta_L(B) - \delta_X(B) < \varepsilon. \quad (11)$$

By using a toy model with a separable force *in lieu* of the microscopic potential $V_{\uparrow\downarrow}^{(X)}(r)$ we obtain that in this limit the polariton scattering amplitude $\bar{f}_{\uparrow\downarrow}^{(L)}(k)$ is given by Eq. (9) with $X \rightarrow L$ and

$$a_{\uparrow\downarrow}^{(L)} = \sqrt{\frac{m_X}{m_L}} e^{\frac{m_X}{m_L} \nu} a, \quad (12)$$

where $\nu \propto [\varepsilon + \delta_X(B) - \delta_L(B)]/|\varepsilon|$. The corresponding effective interaction reads $g_{\uparrow\downarrow}^{(L)} = -2\hbar^2/m_L \bar{f}_{\uparrow\downarrow}^{(L)}(k)$. Since typically $m_L \ll m_X$ and, by assumption (11), one has $\nu > 0$, we deal with the scattering off a weakly bound state. In 3D such scattering would produce increasingly strong repulsion. Here, in contrast, the scattering amplitude $\bar{f}_{\uparrow\downarrow}^{(L)}(k)$ vanishes.

The weakly bound state occurs under condition (11) as a pole of the scattering amplitude $\bar{f}_{\uparrow\downarrow}^{(L)}(k)$ at $k = i/a_{\uparrow\downarrow}^{(L)}$ and represents a hypothetical polariton molecule $L_{\uparrow}L_{\downarrow}$ [102]. A more involved study [19] has shown, however, that instead of the Arrhenius-type reactions $L_{\uparrow} + L_{\downarrow} \rightleftharpoons L_{\uparrow}L_{\downarrow} + \hbar\nu$, one would rather have an irreversible process $X_{\uparrow}X_{\downarrow} \rightarrow L_{\uparrow} + L_{\downarrow}$, which may be interpreted as autodissociation of a biexciton $X_{\uparrow}X_{\downarrow}$ [103]. Such nonstationary biexciton in a microcavity has been referred to as “bipolariton” [19].

The effective interactions $g_{\sigma\sigma'}^{(\alpha)}$ provide the third-order nonlinear susceptibilities $[\chi^{(3)}]$ for electromagnetic waves [47]. As an example, two-body polariton scattering has been shown to produce degenerate parametric amplification of a signal on coherent pump at specific angle fulfilling momentum conservation (i.e., the phase-matching condition) on the polariton dispersion [104].

III. RESULTS AND DISCUSSION

Consider a system of two identical excitons (either “bright” excitons or cavity polaritons). There are four basis states $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$ whose linear combinations realize the states $S_z = +2, 0, -2$ of the total spin $S_z = s_{z,1} + s_{z,2}$. We notice that since Ω_{α} (the label α standing for X or L , respectively) lies in the structure plane, the sum $\Omega_{\alpha} \cdot \hat{s}_1 + \Omega_{\alpha} \cdot \hat{s}_2$ does not commute with S_z^2 . Hence, the uniaxial deformation may change the spin state of a pair by flipping the spin of either of the two quasiparticles.

This observation implies that, in general, the wave function of the relative motion $\Psi^{(\alpha)}(r)$ would be a superposition of the corresponding three spin states, i.e.,

$$\begin{aligned} \Psi^{(\alpha)}(r) = & |\uparrow\uparrow\rangle \psi_{\uparrow\uparrow}^{(\alpha)}(r) + |\downarrow\downarrow\rangle \psi_{\downarrow\downarrow}^{(\alpha)}(r) \\ & + \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \phi_{\uparrow\downarrow}^{(\alpha)}(r). \end{aligned} \quad (13)$$

The corresponding system of coupled Schrödinger equations may be recast in the form

$$\left(-\frac{\hbar^2}{m_{\alpha}} \nabla_r^2 + \hat{V}_{\alpha} \right) \Psi^{(\alpha)}(r) = E \Psi^{(\alpha)}(r), \quad (14)$$

where

$$\hat{V}_{\alpha} \equiv \begin{bmatrix} V_{\uparrow\uparrow}^{(\alpha)}(r) + \delta_{\alpha}(B) - 2\mu_B g_{\alpha} B & 0 & -\sqrt{2}\hbar\Omega_{\alpha} \cdot \langle \uparrow | \hat{s} | \downarrow \rangle \\ 0 & V_{\downarrow\downarrow}^{(\alpha)}(r) + \delta_{\alpha}(B) + 2\mu_B g_{\alpha} B & -\sqrt{2}\hbar\Omega_{\alpha} \cdot \langle \downarrow | \hat{s} | \uparrow \rangle \\ -\sqrt{2}\hbar\Omega_{\alpha} \cdot \langle \downarrow | \hat{s} | \uparrow \rangle & -\sqrt{2}\hbar\Omega_{\alpha} \cdot \langle \uparrow | \hat{s} | \downarrow \rangle & V_{\uparrow\downarrow}^{(\alpha)}(r) + \delta_{\alpha}(B) \end{bmatrix}. \quad (15)$$

We are interested in a stationary scattering solution of this system near the lowest energy scattering threshold, i.e., $E \rightarrow$

$E_k^{(\alpha)}$ with

$$E_k^{(\alpha)} \equiv \hbar^2 k^2 / m_{\alpha} + \delta_{\alpha}(B) - 2\mu_B g_{\alpha} B, \quad (16)$$

second-quantized many-body Hamiltonian [86,105]

$$\begin{aligned} \hat{H}_\alpha = & \sum_{\mathbf{k}} \left[\frac{\hbar^2 \mathbf{k}^2}{2m_\alpha} + \frac{\delta_\alpha(B)}{2} - \mu_B g_\alpha B \right] \hat{\alpha}_{\uparrow,\mathbf{k}}^\dagger \hat{\alpha}_{\uparrow,\mathbf{k}} + \sum_{\mathbf{K}} \left[\frac{\hbar^2 \mathbf{K}^2}{4m_X} + \varepsilon + \delta_X(B) \right] \hat{C}_{\uparrow\downarrow,\mathbf{K}}^\dagger \hat{C}_{\uparrow\downarrow,\mathbf{K}} \\ & + \frac{\bar{g}_{\uparrow\uparrow}^{(\alpha)}}{2S} \sum_{\mathbf{p},\mathbf{p}',\mathbf{q}} \hat{\alpha}_{\uparrow,\mathbf{p}'+\mathbf{q}}^\dagger \hat{\alpha}_{\uparrow,\mathbf{p}-\mathbf{q}}^\dagger \hat{\alpha}_{\uparrow,\mathbf{p}} \hat{\alpha}_{\uparrow,\mathbf{p}'} \\ & - \hbar \Omega_\alpha \cdot \sum_{\mathbf{k}} [\langle \uparrow \uparrow | \hat{\mathbf{s}} | \downarrow \downarrow \rangle \phi(\mathbf{k}) \hat{C}_{\uparrow\downarrow,\mathbf{K}}^\dagger \hat{\alpha}_{\uparrow,-\mathbf{k}+\mathbf{K}/2}^\dagger \hat{\alpha}_{\uparrow,\mathbf{k}+\mathbf{K}/2}^\dagger + \langle \downarrow \downarrow | \hat{\mathbf{s}} | \uparrow \uparrow \rangle \phi^*(\mathbf{k}) \hat{C}_{\uparrow\downarrow,\mathbf{K}}^\dagger \hat{\alpha}_{\uparrow,-\mathbf{k}+\mathbf{K}/2} \hat{\alpha}_{\uparrow,\mathbf{k}+\mathbf{K}/2}], \end{aligned} \quad (21)$$

that would yield Eq. (14) and the result (19) in the particular limit of two bosons in vacuum. The operator

$$\hat{C}_{\uparrow\downarrow,\mathbf{K}} = \sum_{\mathbf{k}} \phi(\mathbf{k}) \hat{\alpha}_{\uparrow,-\mathbf{k}+\mathbf{K}/2} \hat{\alpha}_{\downarrow,\mathbf{k}+\mathbf{K}/2} \quad (22)$$

describes a biexciton with the center-of-mass wave vector $\mathbf{K}$, $\hat{\alpha}_{\sigma,\mathbf{p}}$'s stand for single bosons and $\phi(\mathbf{k})$ is the Fourier transform of Eq. (8). The coherent interconversion term in the last line of Eq. (21) has the form of $\chi^{(2)}$ nonlinearity in quantum optics [2,62]. It implements the desired process (1) with $\sigma = \sigma' = \uparrow$. Remarkably, this term does not require the absence of spatial inversion symmetry: The biexciton represents a *bound pair* of polarization waves and the matrix element $\hbar \Omega_\alpha \cdot \langle \uparrow \uparrow | \hat{\mathbf{s}} | \downarrow \downarrow \rangle$ is perfectly allowed in centrosymmetric crystals (see Sec. II A).

The process (1) is expected to be particularly efficient in the broad resonance limit $\beta_\alpha \gg \hbar^2 k_c^2 / m_\alpha$. In this limit, the biexciton operator $\hat{C}_{\uparrow\downarrow,\mathbf{K}}$ may be shown to play the role of an *auxiliary* field which describes onset of pair correlations between the bosons $\alpha_\uparrow$ [10]. One may then adiabatically eliminate $\hat{C}_{\uparrow\downarrow,\mathbf{K}}$ from the Hamiltonian (21) to obtain [10]

$$g_{\uparrow\uparrow}^{(\alpha)} = \bar{g}_{\uparrow\uparrow}^{(\alpha)} - \frac{\hbar^2}{m_\alpha} \frac{2\pi\beta_\alpha}{\Delta_\alpha}. \quad (23)$$

The effective interaction $g_{\uparrow\uparrow}^{(\alpha)}$ provides increasingly large and tuneable $\chi^{(3)}$ [106].

Let us discuss further the similarity between the last line in Eq. (21) and the nonlinear susceptibility of the second order. A manifestation of $\chi^{(2)}$ in nonlinear optics is the second-harmonic generation and the corresponding reverse process known as parametric down conversion [45]. Both of these processes exhibit coherent intensity transfers between electromagnetic waves. In the quantum chemistry parlance, this can be seen as the Bose stimulation of the reaction (1) in a macroscopic ensemble [42–44]. In our case, we may naturally think of such processes as of controllable *fusion* of excitons and *disintegration* of biexcitons, respectively (Fig. 1).

Consider first the fusion, schematically shown on the top of the left column in Fig. 1. A pair of lasers generates polarization waves (i.e., free excitons) with in-plane momenta $\mathbf{k}_1 = \mathbf{k}$ and $\mathbf{k}_2 = -\mathbf{k}$. By adjusting the external magnetic field B such as to satisfy the energy conservation $E_k^{(\alpha)} = \varepsilon + \delta_X(B)$ with $E_k^{(\alpha)}$ given by Eq. (16), one unlocks the resonant reaction (1) which coherently transfers the intensities of the incident fields into a biexciton field with $\mathbf{k}_3 = \mathbf{K}$ (gray arrow). The momentum conservation $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$ (phase-matching condition)

implies that thus generated biexcitons form a condensate at $\mathbf{K} = 0$. The biexciton condensate does not produce an output radiation at the second-harmonic energy $E_k^{(\alpha)}$: Instead, it accumulates inside the 2D crystal and decays spontaneously due to leakage of the constituting excitons into the photonic region of their dispersion (“light cone”) [19].

Now, let us switch off one of the incident laser fields (say, the field “2”). One then passes to the disintegration scheme shown in the bottom. The biexcitons with $\mathbf{K} = 0$ being already present in the crystal, the electromagnetic field “1” with the in-plane momentum $\mathbf{k}_1 = \mathbf{k}$ would stimulate their coherent disintegration into a pair of free excitons with $\mathbf{k}_1 = \mathbf{k}$ and $\mathbf{k}_2 = -\mathbf{k}$. The $\mathbf{k}_1 = \mathbf{k}$ exciton would contribute to amplification of the incident laser field (detected as a “signal” at the output) and the $\mathbf{k}_2 = -\mathbf{k}$ exciton would generate an “idler” photon. If one ignores the origin of the “pump” field (“3”), the disintegration process would be fully analogous to the difference-frequency generation depicted in the bottom on the right. Both “signal” and “idler” fields would be squeezed.

We emphasize that the biexciton field behaves as an independent scalar field: As one may see from Eq. (22), it is a weighted superposition of boson pairs characterized by a *single* momentum $\mathbf{K}$ and not just a free pair $\hat{\alpha}_{\uparrow,-\mathbf{k}+\mathbf{K}/2} \hat{\alpha}_{\downarrow,\mathbf{k}+\mathbf{K}/2}$, which would be characterized by a *pair* of momenta. As such, the fusion and disintegration cannot be reduced to the conventional four-wave mixing.

Following the lines of our earlier work on dipolar polaritons [10], one may deduce from Eq. (21) that fusion of bosons $\alpha_\uparrow$ occurs on the characteristic timescale $\mathcal{T}_\alpha = \sqrt{m_\alpha}/2\pi\beta_\alpha n$, which on substitution of β_α from Eq. (20) may be recast as

$$\mathcal{T}_\alpha = (4\pi n a^2)^{-1/2} \Omega_\alpha^{-1}. \quad (24)$$

For a broad resonance, squeezing of electromagnetic waves is observed on this timescale [10]. The squeezing is indicative of strong correlations near resonance. The result (19), on the other hand, offers a way to explore such strong correlations in the ultimate limit of two bosons in vacuum. We delve deeper into this intriguing scenario in the subsequent section.

Naively, one would expect that a broad resonance would be beneficial for fusion and squeezing at low densities. In practice, however, one should compare the timescale $\mathcal{T}_\alpha$ with the boson radiative lifetime τ_α . Faster radiative decay may provide stronger coupling Ω_α (see Sec. II A), but a photon may escape the crystal before the reaction (1) takes place. Also compatibility of a broad resonance with condition (ii) should be discussed with care.

Although the above equations in their generic forms apply both for “bright” excitons ($\alpha = X$) and lower polaritons ($\alpha = L$), the actual results as defined by the respective parameters are very different. Below we discuss these two distinct cases separately and in greater detail.

A. “Bright” excitons in the absence of a microcavity ($\alpha = X$)

We obtain $\Delta_X = \bar{\Delta}_X = \varepsilon + 2\mu_B g_X B$ and

$$a_X = ae^{\gamma/2},$$

so that the exciton scattering amplitude (19) takes the genuine s -wave resonant form. This implies the resonant pairing phenomenology, echoing the physics of a shape resonance suggested previously for dipolar excitons [9] and polaritons [10]. Treating the colliding excitons as impenetrable disks of radius $R_{\uparrow\uparrow}$ and assuming $R_{\uparrow\uparrow} \ll a$ yields the estimate (see Appendix C)

$$\delta\mathcal{X} \sim \left[\frac{\ln R_{\uparrow\uparrow}/a}{\ln kR_{\uparrow\uparrow}} \right]^2. \quad (25)$$

Despite the apparent crudeness of such approximation for $V_{\uparrow\uparrow}^{(X)}(r)$, the result (25) correctly captures the 2D kinematics: The excitons tend to avoid each other at $k \rightarrow 0$, which results in suppression of the coherent coupling to the biexciton.

Condition (ii) implies $|\varepsilon| \gg \beta_X$. This inequality may also be recast in a more transparent form as $(\hbar\Omega_X/\varepsilon)^2 \ll 1$. It is instructive to consider compatibility of this condition with the narrow ($\beta_X \ll \hbar^2 k_c^2/m_X$) vs broad ($\beta_X \gg \hbar^2 k_c^2/m_X$) resonance regimes. By using the definition (20) and assuming $k_c \sim \sqrt{n}$, these regimes may be recast as $(\hbar\Omega_X/\varepsilon)^2 \ll na^2$ and $(\hbar\Omega_X/\varepsilon)^2 \gg na^2$, respectively. Since, generically, $na^2 \lesssim 1$, one can see, that a narrow resonance is always compatible with (ii), whereas a broad resonance would additionally require $na^2 \ll 1$.

Being considered as a complex function of the energy $E = \hbar^2 k^2/m_X$ the resonant part of the exciton scattering amplitude (19) has poles defined by the equation $E = \bar{\Delta}_X - \beta_X \ln(|\varepsilon|e^{-\gamma}/E) - i\pi$. At negative detuning $\bar{\Delta}_X < 0$ there is a single pole that asymptotically approaches the straight line $E = \bar{\Delta}_X$ as $\bar{\Delta}_X \rightarrow -\infty$. By writing $\bar{\Delta}_X(B) = 2\mu_B g_X (B - B_0)$ and considering the energy E as a function of B , we may let $E(0) \approx \varepsilon$. As the magnetic field B exceeds the threshold value

$$B_{\text{th}} = B_0 + \beta_X (2\mu_B g_X)^{-1} [1 + \ln(|\varepsilon|e^{-\gamma}/\beta_X)], \quad (26)$$

a second pole emerges at positive energies (see Fig. 4). This pole is a resonance characterized by the decay rate $\propto \beta_X$. Interestingly, the resonance coexists with the weakly bound state

$$E(B) = -|\varepsilon|e^{-\gamma} e^{-2\mu_B g_X B/\beta_X} \quad (27)$$

at $B \gg B_{\text{th}}$. This should be contrasted to the s -wave Feshbach scattering in 3D [107] and scattering in higher partial-wave channels in 2D [86,105], where the bound state becomes substituted by the resonance.

The wave function of the bound state can be written in the form

$$\Psi(\mathbf{r}) = \Upsilon(\mathbf{r}) |\uparrow\uparrow\rangle + w\varphi(\mathbf{r}) \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad (28)$$

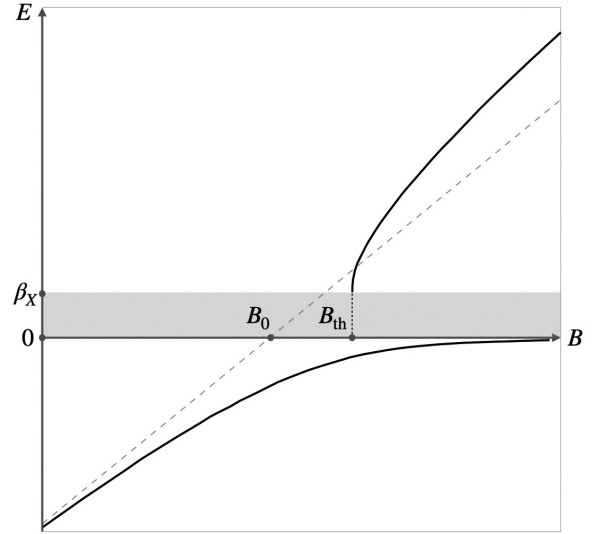


FIG. 4. The poles E of the exciton s -wave scattering amplitude $f_{\uparrow\uparrow,\text{res}}^{(X)}(k)$ as functions of the magnetic field B . The full equation for the pair polarization bubble has been used (see Appendix B). At $B > B_{\text{th}}$ the weakly bound state coexists with a resonance at $E > 0$ (only the real part is shown). The dashed line indicates the asymptote $E(B) = 2\mu_B g_X (B - B_0)$. At $B \gg B_{\text{th}}$ the wave function of the weakly bound state takes the universal form of the quantum halo.

where $\varphi(r)$ is the tightly bound core given by Eq. (8) and $\Upsilon(r)$ is the so-called *quantum halo* which extends well beyond the microscopic range of the potential $V_{\uparrow\uparrow}^{(X)}(r)$ (Fig. 2). By using Eq. (27) and the relation [86] $w^2 = (2\mu_B g_X)^{-1} \partial E / \partial B$, the relative weight of the core w^2 may be expressed as

$$w^2 = \frac{|\varepsilon|}{\beta_X} e^{-\gamma} e^{-2\mu_B g_X B/\beta_X}. \quad (29)$$

One can see that w rapidly approaches zero as B is tuned beyond the threshold B_{th} , so that the contribution of the halo to the state (28) becomes dominant. In the same limit, the halo takes the form

$$\Upsilon(r) = \frac{1}{\sqrt{\pi a_\Upsilon^2}} K_0(r/a_\Upsilon) \quad (30)$$

with $a_\Upsilon \equiv \hbar/\sqrt{m_X E(B)} \rightarrow \infty$ as $E(B) \rightarrow 0$. Equation (30) is universal in the sense that it does not depend on the details of the microscopic interaction potential. In the opposite limit $B \rightarrow 0$, the relative weight w^2 approaches unity: The bound state becomes the bare biexciton.

Let us discuss manifestation of the predicted phenomenology in optical experiments. The most basic quantity is the exciton oscillator strength f_X which defines the radiative decay rate Γ_X . The oscillator strength scales with the coherence area covered by the exciton center-of-mass translational motion [52,108], which for the weakly bound state (30) may be expressed as $f_\Upsilon = f_X |\Upsilon_0|^2$, where Υ_0 is the $\mathbf{p} = 0$ value of the Fourier transform $\Upsilon_{\mathbf{p}} = \sqrt{4\pi a_\Upsilon^2/S/(1 + p^2 a_\Upsilon^2)}$ of Eq. (30). The upper bound on a_Υ is defined by the condition (10) and, ultimately by the quantization area S (the area of the 2D structure). The oscillator strength of an exciton constituting the halo approaches that of a free exciton (plane wave) as

$a_\gamma \rightarrow \sqrt{S/4\pi}$. On the other hand, the oscillator strength of the halo is enhanced with respect to the bare biexciton by the factor $(a_\gamma/a)^2$ [109]. Hence, the emergence of the halo should manifest itself in exponential growth and subsequent saturation of Γ_γ , as B is swept across B_{th} . The sweeping of the magnetic field in this case should be performed adiabatically starting from $B = 0$, which would require sufficiently long lifetime τ_X of the bare exciton, i.e., $\tau_X \gg \hbar/\beta_X$ with β_X being the resonance width given by Eq. (20).

Alternatively, one may think of controllable assembly (synthesis) of a biexciton from a polarized continuum, akin to the Feshbach ramp in ultracold atoms [40]. Interestingly, the three-body recombination, which is known to be a major side effect for synthesis of atomic molecules [40], is absent for excitons. There are three factors that preclude such an inelastic process. First, as we have pointed out above, the exciton halo is formed when the “open” channel is still energetically *below* the resonance. Second, the probability for three excitons to approach each other is suppressed by the Pauli principle for the constituent electrons and holes. Deep bound states of three excitons do not exist (although one cannot exclude trimers of macroscopically large radius [110]). Finally, the level ε is likely to be a unique bound state of the potential $V_{\uparrow\downarrow}^{(X)}(r)$ (see Sec. II B), and the polarized exciton continuum couples directly to this level. These factors hold promise for experimental implementation of synthetic molecules and their practical use, as we discuss below.

The polarization part of the wave function (28) evolves from a product state $|\uparrow\uparrow\rangle$ to a maximally entangled state $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ as the magnetic field is tuned from $B \gg B_{th}$ to 0. To quantify the entanglement of the polarization, we evaluate the *concurrence* [111,112]

$$c[\hat{\rho}] \equiv \inf_{\{p_i, \Phi_i\}} \sum_i p_i \bar{c}[\Phi_i], \quad (31)$$

where the infimum is searched over all possible convex decompositions $\{p_i, \Phi_i\}$ of the mixed state,

$$\hat{\rho} \equiv \int \Psi(r) \Psi^\dagger(r) dr = \sum_i p_i |\Phi_i\rangle \langle \Phi_i| \quad (32)$$

obtained by tracing out the spatial part of the wave function (30). Here

$$\bar{c}[\Phi_i] \equiv |\langle \Phi_i^* | \hat{\sigma}_y \otimes \hat{\sigma}_y | \Phi_i \rangle| \quad (33)$$

are concurrencies of the pure bipartite polarization states $|\Phi_i\rangle$.

Although the density matrix $\hat{\rho}$ depends parametrically on the spatial overlap of the core $\varphi(r)$ and the halo $\Upsilon(r)$, we find that the concurrence $c[\hat{\rho}]$ does not depend on this parameter and, in fact, is identical to that of a pure polarization state

$$|\Phi\rangle \equiv \sqrt{1-w^2} |\uparrow\uparrow\rangle + w \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad (34)$$

which formally may be obtained by dropping the spatial components in Eq. (28). Namely, we find

$$c[\hat{\rho}] = \bar{c}[\Phi] = w^2, \quad (35)$$

where $\bar{c}[\Phi]$ is calculated by using Eq. (33) and the relative weight w^2 depends on the applied magnetic field according to Eq. (29). We provide detailed derivation of the relation (35)

in Appendix D. The auxiliary state $|\Phi\rangle$ then allows one to develop a better feel for the entanglement measure (31) by resorting to the alternative version of Eq. (33) for pure states [111]

$$\bar{c}[\Phi] = \left| \sum_{i=1}^4 \langle e_i | \Phi \rangle^2 \right| \quad (36)$$

with $|e_1\rangle = 1/\sqrt{2}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle)$, $|e_2\rangle = i/\sqrt{2}(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle)$, $|e_3\rangle = i/\sqrt{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$, and $|e_4\rangle = 1/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ being the Bell states. One can see that $\bar{c}[\Phi]$ reaches its maximum value when the vector $|\Phi\rangle$ converges (up to an unimportant phase factor) to the Bell state $|e_3\rangle$.

According to Eq. (35), the concurrence $c[\hat{\rho}]$ varies monotonously from 1 to 0 as the magnetic field is swept in the range $B \in [0, +\infty)$. Hence, similarly to the radiative decay rate Γ_X discussed above, the entanglement may follow adiabatically sufficiently rapid variation of B . The ability to prepare an arbitrarily entangled state via a *rapid adiabatic passage* renders the composite state (28) appealing for the quantum information processing. For instance, controllable generation of the Bell state is known to be a crucial stage in the quantum teleportation algorithm [113]. Detailed proposals of such kind are beyond the scope of the present work and will be given elsewhere.

A qualitatively different scenario may be realized in a scattering experiment whereby pairs of spin- $\uparrow$ excitons undergo elastic collisions governed by the scattering amplitude (19). For example, a spin-polarized gas of excitons may be resonantly pumped at B close to B_{th} and then probed in reflectance (or transmittance) by a weak pulse of the *same* circular polarization. The formula (23) then predicts increasingly large blueshift or redshift of the probe signal depending on whether the energy of colliding bosons is above or below the resonance, respectively. Alternatively, one may examine the spectral shifts of the exciton PL signal and spatial distribution of the PL intensity. Consistent description of such experiments can be carried out starting from the Hamiltonian (21) and proceeding along the lines of the many-body theory previously designed for dipolar excitons [9,10] interacting via a shape resonance in the microscopic potential $V_{\uparrow\downarrow}(r)$. A crucial advantage of the present setting is a possibility to control independently the detuning $\bar{\Delta}_X$ and the width β_X of the resonance.

Let us consider the explicit example of excitons in a monolayer of MoS₂. For a free-standing monolayer the matrix element $|\hbar\Omega_X \cdot \langle \uparrow\downarrow | \delta | \downarrow \rangle|$ would be defined through Eq. (5) by the short-range part of the exchange interaction. Taking the upper estimate for the corresponding parameter [76] $\hbar\mathcal{B}_X^{(sr)} \sim 100$ meV, the relative extension $u \sim 0.01$ and the biexciton binding energy [6] $|\varepsilon| \sim 20$ meV, we obtain the ratio $(\hbar\Omega_X/\varepsilon)^2 \sim 10^{-3}$, so that the resonance is expected to be narrow at densities down to $na^2 \sim 10^{-2}$. An intermediate regime between a narrow and a broad resonance at such low densities could potentially be promising for observation of the halos. However, the resonance width $\beta_X \sim (\hbar\Omega_X)^2/|\varepsilon| \sim 0.05$ meV is much less than the exciton radiative decay rate Γ_X (few meV), which may hinder rapid adiabatic preparation of such states as discussed above. Likewise, the lower bound on the characteristic time $\mathcal{T}_X$ (achieved at $na^2 \sim 1$) is comparable

to the exciton radiative lifetime $\tau_X \sim 0.1$ ps. This precludes fusion and squeezing.

The situation changes qualitatively in the presence of a substrate. The substrate characterized by the amplitude reflection coefficient $r_b = -e^{-i\delta\phi}$ with $\delta\phi \ll 1$ may increase the radiative lifetime τ_X by the huge factor $\delta\phi^{-2}$. Thus, in the experiment [20] the factor $\delta\phi \sim 0.1$ has been achieved. The radiative decay rate Γ_X then becomes smaller than the resonance width (as defined by the short-range exchange), and in magnetic fields on the order of few tens of Tesla [83] one should be able to realize controllable synthesis of biexcitons.

The upper bound on the molecular radius as defined by condition (10) would be $a_r \lesssim 20a$, which would require $na^2 \lesssim 10^{-3}$. In the interval of temperatures 10^{-2} K $\ll T \lesssim 0.1$ K one would have a boltzmannian gas of molecules with their internal states being well approximated by the pure states (30). The polarization density matrix $\hat{\rho}$ [Eq. (32)] in this case might be accessed experimentally by cross correlation polarization measurements in a photon coincidence setup analogous to that employed previously for QD's [12] (see also Appendix E).

Furthermore, by using Eq. (6) and Eq. (24), the ratio of the fusion time to the exciton radiative lifetime may be estimated as

$$\frac{\mathcal{T}_X}{\tau_X} \approx (4\pi na^2)^{-1/2} \frac{\delta\phi}{u} (\zeta/\delta\phi + 2\eta)^{-1},$$

with $\zeta \sim 1$ –10 being the dimensionless product of $\mathcal{B}_X^{(sr)}$ and the radiative lifetime in the absence of substrate, and the parameter η coming from the long-range contribution to the exchange. This estimate shows that the ratio $\mathcal{T}_X/\tau_X \sim 0.1$ may be achieved at densities $na^2 \sim 0.1$. The squeezing may be verified by examining the statistics of emitted photons with balanced homodyne detection [114].

A different strategy might be applied to achieve tuneable $\chi^{(3)}$. One may take advantage of the long-range exchange in the presence of a substrate by choosing $r_b \approx e^{i\pi/2}$ and then trying to reach the regime $\beta_X \sim \Gamma_X$ by increasing the relative deformation u . Although $\mathcal{T}_X$ would substantially exceed τ_X in this case, thus precluding efficient $\chi^{(2)}$ processes, one nevertheless should be able to get the tuneable effective interaction (23) in a scattering experiment described above.

B. Lower polaritons in a planar microcavity ($\alpha = L$)

The configuration of two-particle energy levels fulfilling condition (i) in this case is tentatively sketched in Fig. 5. The scattering amplitude $f_{\uparrow\uparrow}^{(L)}(k)$ given by Eq. (19) refers to the scattering of two spin- $\uparrow$ polaritons at the bottom of the corresponding dispersion ($k \rightarrow 0$). In contrast to excitons without a microcavity, for polaritons we find $\Delta_L = \bar{\Delta}_L + (m_X/m_L)\beta_L e\text{Ei}(-1)$ and

$$a_L = i\sqrt{\frac{m_X}{m_L}} a,$$

the latter quantity now being purely imaginary. The imaginary unit cancels with $i\pi/2$ in the denominator of Eq. (19) and thus eliminates the resonant pole structure. One can also show that for polaritons the effect of the background potential is negligible, so that $\varphi_L = 1$.

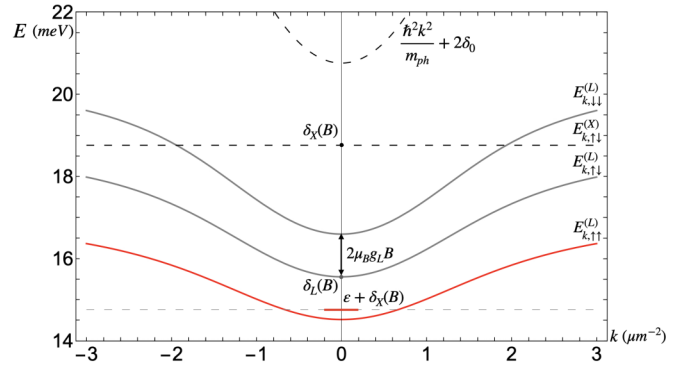


FIG. 5. Configuration of the lower polariton ($\alpha = L$) pair energy levels fulfilling the resonant approximation (i) used to derive the scattering amplitude Eq. (19). The wave vector k stands for the pair relative motion and we have put $K = 0$ (the center-of-mass reference frame). Dashed parabola and horizontal line are the bare two-photon and two-exciton energies, respectively. Short horizontal bar indicates the biexciton energy level. The parameters typical for the GaAs/AlGaAs-based planar microcavities [82] have been used: $m_X = 0.05m_e$ (m_e being the free electron mass), $\hbar\Omega_R = 4$ meV, $|\varepsilon| = 2$ meV, $g_X = 1.35$, $\delta_X(B) = 0.67 \times B$ meV, and we take $B = 14$ T. The two-body scattering process of interest is supposed to take place at the bottom of the lowest energy dispersion line denoted as $E_{k,\uparrow\uparrow}^{(L)}$.

The absence of the pole structure in the scattering amplitude implies the absence of the polariton bound states and resonances. On the other hand, the scattering amplitude still possesses a resonant denominator, which should manifest itself in elastic collisions. To estimate the ratio of the resonance width β_L to the characteristic kinetic energy of polaritons, we first notice that in a mean-field regime the latter is on the order of the corresponding energy for excitons, i.e., one has

$$\hbar^2 k_c^2 / m_L \sim g_{\sigma\sigma}^{(L)} n \sim \hbar^2 n / m_X$$

(see Sec. II B and Appendix A). We believe that such a mean-field estimate is pertinent to the vast majority of experimental cases, where coherent population of polaritons is generated at the bottom of their dispersion [115]. We may then estimate the relevant ratio as

$$\frac{\beta_L}{\hbar^2 k_c^2 / m_L} \sim \frac{m_L}{m_X} \left(\frac{\Omega_L}{\varepsilon} \right)^2 (na^2)^{-1},$$

and conclude that, since, typically, $\Omega_L \sim \Omega_X$, the polariton resonance formally remains narrow down to ultralow densities. However, the energy shift of a probe light pulse in a hypothetical experiment of the type described in Sec. III A would be governed by the interaction constant

$$g_{\uparrow\uparrow,\text{res}}^{(L)} \equiv -\frac{2\hbar^2}{m_L} f_{\uparrow\uparrow,\text{res}}^{(L)} = \frac{\hbar^2}{m_L} \frac{2\pi\beta_L}{\hbar^2 k_c^2 / m_L - \Delta_L}, \quad (37)$$

where we have omitted the logarithm in Eq. (19) assuming that $\Delta_L \sim \hbar^2 k_c^2 / m_L \gg \beta_L$. The result (37) is formally analogous to the effective interaction in the case of a broad resonance given by Eq. (23), with the peculiar difference that now the position of the singularity would also depend on the density n through k_c . The rescaled “resonance width” in the numerator would be comparable with β_X , and may be made

larger than the kinetic energy and the polariton radiative decay rate. Likewise, the polariton fusion time $\mathcal{T}_L$ [Eq. (24)] should be comparable with $\mathcal{T}_X$.

Magneto-optics of microcavities with TMD's being currently at its early stage of development, we consider polaritons in an epitaxial GaAs QW inside a planar GaAs/AlAs-based microcavity [82]. An exemplary configuration of the lower polariton pair energy levels fulfilling the resonant approximation (i) is presented in Fig. 5. One may expect to achieve linear polarization splittings $\hbar\Omega_L$ on the order of 1 meV in such systems under moderate anisotropy [84]. We then obtain $(\hbar\Omega_L)^2/|\varepsilon| \sim 1$ meV for the rescaled “resonance width.” This indeed exceeds the polariton radiative decay rate $\Gamma_L \sim 0.1$ meV by an order of magnitude. The ratio $\mathcal{T}_L/\tau_L$ may also be small at moderate densities $na^2 \sim 0.1$. However, condition (ii) is clearly violated, which means that a proper description of scattering would require going beyond the two-channel model adopted here. We expect that the phenomenology of resonant scattering would still persist at $\hbar\Omega_L \sim \mu_B g_L B$, albeit in a strongly modified form. We postpone the corresponding analysis for future work. We also expect, that in near future either TMD- or perovskite-based settings would provide favorable conditions.

IV. CONCLUSIONS

In summary, we have explored a possibility of controllable interactions of identical excitons (“bright” excitons or microcavity polaritons) in strained 2D semiconductors. The strain induces an effective in-plane magnetic field which couples the spin-polarized two-body scattering continua to a singlet biexciton state, thus acting as a coherent link transforming the biexciton into a scattering resonance. Application of an ordinary transverse magnetic field yields the phenomenology of the Feshbach resonance, wherein the lower-energy “open” scattering channel is tuned across the resonant biexciton level (“closed” channel). For a broad resonance, the two-body interaction of excitons changes from increasingly strong repulsion to attraction, as one crosses the resonance, in full analogy with the control of interactions achieved in ultracold atoms [40]. In contrast to the earlier proposals [9,10,51,53,54] here one has direct access to the width of the resonance through the strain engineering of the host heterostructure. The resonance width defines, in particular, the timescale $\mathcal{T}_\alpha$ [Eq. (24) with $\alpha = X$ or $\alpha = L$ for “bright” excitons or lower polaritons, respectively] characterizing efficiency of squeezing of the output radiation [10]. We expect the effect to be significant in the currently available samples of TMD's.

From the nonlinear optics perspective, the scattering resonance enables tuneable third-order susceptibility $[\chi^{(3)}]$, as well as the parametric processes sharing analogies with the second-harmonic generation and parametric down-conversion. The parametric processes occur for macroscopically populated bosonic modes and may be conveniently regarded as Bose-stimulated reactions of fusion and disintegration. The reactions have the characteristic timescale $\mathcal{T}_\alpha$ and are accompanied by squeezing. Interestingly, neither fusion nor disintegration requires broken inversion symmetry of the medium.

For “bright” excitons in the absence of a microcavity, we find that the scattering amplitude [Eq. (19)] possesses a double-pole structure: in sufficiently strong transverse magnetic field a resonance coexists with a synthetic bound state. The synthetic molecule consists of a singlet biexciton core and a spin-polarized quantum halo which extends far beyond the range of the microscopic interaction potential between the excitons. The halo has giant oscillator strength [52] which is expected to grow exponentially with the applied magnetic field. The spin state of the molecule can be adiabatically tuned from a separable state (halo) to a maximally entangled Bell state (biexciton) by sweeping the magnetic field across the resonance. Our study thus hints explicitly at a connection between the entanglement and squeezing of resonantly paired photons, also anticipated from a general standpoint [2,62], and which yet remains to be explored.

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APPENDIX A: BACKGROUND POLARITON INTERACTIONS

In the ultracold limit, where the de Broglie wavelength of the exciton relative motion $2\pi/k$ greatly exceeds the microscopic range $R_{\sigma\sigma'}$ of the interaction potential $V_{\sigma\sigma'}^{(X)}(r)$, the scattering becomes fully characterized by the 2D scattering length $a_{\sigma\sigma'}^{(X)}$. Simple approximations for $V_{\sigma\sigma'}^{(X)}(r)$ may be used to establish the qualitative dependence of $a_{\sigma\sigma'}^{(X)}$ on $R_{\sigma\sigma'}$ and on the average magnitude of $V_{\sigma\sigma'}^{(X)}(r)$. We shall assume that the Fourier transform $V_{\sigma\sigma'}^{(X)}(\mathbf{k}' - \mathbf{k}) = (2\pi)^{-2} \int V_{\sigma\sigma'}^{(X)}(r) e^{i(\mathbf{k}' - \mathbf{k})\mathbf{r}} d\mathbf{r}$ exists and replace it by the separable force

$$V_{\sigma\sigma'}^{(X)}(\mathbf{k}', \mathbf{k}) = \frac{\hbar^2}{m_X} \lambda_{\sigma\sigma'} e^{-(k'R_{\sigma\sigma'})^2/2} e^{-(kR_{\sigma\sigma'})^2/2}. \quad (\text{A1})$$

By using the Lippmann-Schwinger equation for the two-body T matrix

$$T_{\sigma\sigma'}^{(\alpha)}(E_{\mathbf{k}}^{(\alpha)} + i0) = V_{\sigma\sigma'}^{(\alpha)} + V_{\sigma\sigma'}^{(\alpha)} G_0^{(\alpha)} [E_{\mathbf{k}}^{(\alpha)} + i0] T_{\sigma\sigma'}^{(\alpha)} \quad (\text{A2})$$

with $G_0^{(\alpha)}[E_{\mathbf{k}}^{(\alpha)} + i0]$ being the Green function for the free relative motion at the energy $E_{\mathbf{k}}^{(\alpha)} \equiv \hbar^2 k^2/m_\alpha$ and putting $\alpha = X$ (excitons), one immediately gets Eq. (9) with

$$a_{\sigma\sigma'}^{(X)} = R_{\sigma\sigma'} e^{[\gamma/2 - 1/(2\pi\lambda_{\sigma\sigma'})]}. \quad (\text{A3})$$

The magnitudes $\lambda_{\uparrow\uparrow}$ and $\lambda_{\downarrow\downarrow}$ of the repulsive potentials are not fixed. In the limit $\lambda_{\sigma\sigma} \rightarrow +\infty$ one recovers the well-known result for the scattering off an impenetrable disk of radius $2R_{\sigma\sigma} e^{-\gamma/2}$. In the opposite limit $\lambda_{\sigma\sigma} \rightarrow 0$ one gets the Born approximation $f_{\sigma\sigma}^{(X)}(k) = 2\pi^2 \lambda_{\sigma\sigma}$. The strength of the attractive force $\lambda_{\uparrow\downarrow} < 0$ and its range $R_{\uparrow\downarrow}$ should be chosen such as to get the bound state with energy ε and radius $\sim \hbar/\sqrt{m_X \varepsilon}$. By putting $R_{\uparrow\downarrow} \equiv \hbar/\sqrt{m_X \varepsilon}$ and substituting Eq. (A1) into the Schrodinger Eq. (7) written in the $\mathbf{k}$ space, we obtain

$$\phi(\mathbf{q})(\varepsilon - \varepsilon_q) = \lambda_{\uparrow\downarrow} e^{-\varepsilon_q/2|\varepsilon|} \frac{(2\pi)^2}{S} \sum_{\mathbf{k}} \phi(\mathbf{k}) e^{-\varepsilon_{\mathbf{k}}/2|\varepsilon|},$$

where $\phi(\mathbf{k})$ is the Fourier transform of Eq. (8). This further yields

$$1 = \frac{(2\pi)^2 \lambda_{\uparrow\downarrow}}{S} \sum_{\mathbf{k}} \frac{e^{-\varepsilon_{\mathbf{k}}/|\varepsilon|}}{\varepsilon - \varepsilon_{\mathbf{k}}},$$

so that one obtains

$$\lambda_{\uparrow\downarrow} = [\pi e \text{Ei}(-1)]^{-1} \quad (\text{A4})$$

with $\text{Ei}(x)$ being the exponential integral function.

The polariton interaction potential reads $V_{\sigma\sigma'}^{(L)}(\mathbf{k}', \mathbf{k}) = X_k^2 X_{k'}^2 V_{\sigma\sigma'}^{(X)}(\mathbf{k}', \mathbf{k})$. Consistently, we look for the polariton T

matrix in the form

$$T_{\sigma\sigma'}^{(L)}(\mathbf{k}', \mathbf{k}, E_k^{(L)} + i0) = \frac{\hbar^2}{m_X} t_{\sigma\sigma'}^{(L)}(k) X_{k'}^2 X_k^2 e^{-(k'R_{\sigma\sigma'})^2/2} e^{-(kR_{\sigma\sigma'})^2/2}. \quad (\text{A5})$$

By substituting this *ansatz* into Eq. (A2) with $\alpha = L$ (lower polaritons), we obtain

$$t_{\sigma\sigma'}^{(L)}(k) = \{\lambda_{\sigma\sigma'}^{-1} - \Pi_{\sigma\sigma'}^{(L)}[E_k^{(L)} + i0]\}^{-1}, \quad (\text{A6})$$

where the polarization bubble

$$\Pi_{\sigma\sigma'}^{(L)}[E_k^{(L)} + i0] = \pi \int_0^{E_0} \frac{X_0^4 e^{-E/\varepsilon_{\sigma\sigma'}}}{E_k^{(L)} - m_X/m_L E + i0} dE + \pi \int_{E_0}^{+\infty} \frac{X_{+\infty}^4 e^{-E/\varepsilon_{\sigma\sigma'}}}{E_k^{(L)} - (\hbar\Omega_R + E) + i0} dE \quad (\text{A7})$$

has been split into two parts corresponding to the photonlike and exciton-like regions of the polariton dispersion. Here we have defined $E_0 \equiv \hbar\Omega_R m_L/m_X$ and $\varepsilon_{\sigma\sigma'} \equiv \hbar^2/mR_{\sigma\sigma'}^2$. By evaluating the integrals we find

$$\Pi_{\sigma\sigma'}^{(L)}(E_k^{(L)} + i0) = \pi X_0^4 \frac{m_L}{m_X} \left\{ \ln \left[\frac{E_k^{(L)}}{\hbar\Omega_R - E_k^{(L)}} \right] - i\pi \right\} + \pi X_{+\infty}^4 e^{(\hbar\Omega_R - E_k^{(L)})/\varepsilon_{\sigma\sigma'}} \text{Ei} \left[\frac{E_k^{(L)} - \hbar\Omega_R}{\varepsilon_{\sigma\sigma'}} \right] \quad (\text{A8})$$

for $E_k^{(L)} < \hbar\Omega_R$ and

$$\Pi_{\sigma\sigma'}^{(L)}(E_k^{(L)} + i0) = \pi X_0^4 \frac{m_L}{m_X} \ln \left[\frac{E_k^{(L)}}{\hbar\Omega_R - E_k^{(L)}} \right] + \pi X_{+\infty}^4 e^{(\hbar\Omega_R - E_k^{(L)})/\varepsilon_{\sigma\sigma'}} \left\{ \text{Ei} \left[\frac{E_k^{(L)} - \hbar\Omega_R}{\varepsilon_{\sigma\sigma'}} \right] - i\pi \right\} \quad (\text{A9})$$

for $E_k^{(L)} > \hbar\Omega_R$. The low-energy *polariton* scattering corresponds to $E_k^{(L)} \lesssim \hbar\Omega_R$. For repulsive potentials with $\lambda_{\sigma\sigma} > 0$ one obtains by letting $E_k^{(L)} \rightarrow 0$ in Eq. (A5) and assuming $\varepsilon_{\sigma\sigma'} \gg \hbar\Omega_R$

$$T_{\sigma\sigma}^{(L)} = -\frac{\hbar^2}{m_X} \frac{(2\pi)^{-1} X_0^4}{\ln[k_R a_{\sigma\sigma}^{(L)}]}, \quad (\text{A10})$$

where $k_R = \sqrt{m_L \Omega_R / \hbar}$ and $a_{\sigma\sigma}^{(L)} = \sqrt{m_X/m_L} a_{\sigma\sigma}^{(X)}$ with $a_{\sigma\sigma}^{(X)}$ given by Eq. (A3). This result is in agreement with that obtained in the earlier work [96]. For the attractive potential $\lambda_{\uparrow\downarrow} < 0$ the situation is more subtle. Here $\varepsilon_{\uparrow\downarrow} \equiv |\varepsilon| \sim \hbar\Omega_R$ and one cannot take advantage of the logarithmic expansion of $\text{Ei}(x)$ at $x \rightarrow 0$ in the second term of Eq. (A8) to obtain the formula similar to Eq. (A10). Instead, as $\hbar\Omega_R \rightarrow |\varepsilon|$ and $E_k^{(L)} \rightarrow 0$, this term cancels with the $\lambda_{\uparrow\downarrow}^{-1}$ term in Eq. (A6) and we are left with

$$T_{\uparrow\downarrow}^{(L)}(k) = -\frac{\hbar^2}{m_L} \frac{(2\pi)^{-1}}{\ln[ka_{\uparrow\downarrow}^{(L)}] - i\pi/2}, \quad (\text{A11})$$

where

$$a_{\uparrow\downarrow}^{(L)} = \sqrt{m_X/m_L} \exp \left[\frac{m_X}{m_L} \frac{\hbar\Omega_R - |\varepsilon|}{2\beta_{\uparrow\downarrow}} \right] a, \quad (\text{A12})$$

$\beta_{\uparrow\downarrow} = X_0^4 |\varepsilon| / (1 + \lambda_{\uparrow\downarrow}) \sim |\varepsilon|$ and $a \equiv \hbar / \sqrt{m_X |\varepsilon|}$. The polariton scattering amplitude reads

$$\bar{f}_{\uparrow\downarrow}^{(L)}(k) = \frac{\pi}{\ln[ka_{\uparrow\downarrow}^{(L)}] - i\pi/2}. \quad (\text{A13})$$

Since typically $m_L \ll m_X$, for $\hbar\Omega_R > |\varepsilon|$, i.e., when the discrete level is embedded into the continuum of the polariton scattering states, we obtain the scattering off a weakly bound state. In 3D such scattering would produce increasingly strong repulsive interaction. In 2D, in contrast, the real part of the scattering amplitude vanishes as k^{-1} approaches $a_{\uparrow\downarrow}^{(L)}$. For $\hbar\Omega_R \ll |\varepsilon|$ the expression for $T_{\uparrow\downarrow}^{(L)}$ takes the form of Eq. (A10). In the intermediate region $0 < |\varepsilon| - \hbar\Omega_R \ll |\varepsilon|$ the effective interaction $g_{\uparrow\downarrow}^{(L)} \equiv (2\pi)^2 T_{\uparrow\downarrow}^{(L)}$ is positive and somewhat larger than the corresponding interaction constants in the nominally repulsive channels $g_{\sigma\sigma}^{(L)} \equiv (2\pi)^2 T_{\sigma\sigma}^{(L)}$. Within our simple model we do not find the phenomenology of the

resonant scattering in the bare interaction of polaritons with opposite spins.

APPENDIX B: RESONANT SCATTERING AMPLITUDE

The resonant part of the boson scattering amplitude reads

$$f_{\uparrow\uparrow,\text{res}}^{(\alpha)}(k) = -\frac{2m_\alpha|\Omega_{\uparrow\downarrow}^{(\alpha)}|^2}{\hbar^2} \frac{\pi^2|\langle\varphi|\bar{\psi}_{\uparrow\uparrow,k}^{(\alpha)}\rangle|^2}{\hbar^2k^2/m_\alpha - \bar{\Delta}_\alpha - \Pi_\alpha[E_k^{(\alpha)} + i0]}, \quad (\text{B1})$$

where $\bar{\Delta}_\alpha$ is the bare detuning governed by the external magnetic field, and we have introduced the notation $\Omega_{\uparrow\downarrow}^{(\alpha)} \equiv \hbar\Omega_\alpha \cdot \langle\uparrow|\hat{s}|\downarrow\rangle$. The key elements of Eq. (B1) are the polarization

bubble

$$\Pi_\alpha(E_k^{(\alpha)} + i0) = \int \frac{2|\Omega_{\uparrow\downarrow}^{(\alpha)}|^2|\langle\mathbf{q}|\varphi\rangle|^2}{E_k^{(\alpha)} - E_q^{(\alpha)} + i0} d\mathbf{q} \quad (\text{B2})$$

and the overlap of the background stationary scattering state $\bar{\psi}_{\uparrow\uparrow,k}^{(\alpha)}(\mathbf{r})$ with the bare molecule $\varphi(\mathbf{r})$.

Let us evaluate Eq. (B1) for the lower polaritons ($\alpha = L$). As in the case of background polariton interactions (see above), the integration in the bubble $\Pi_L(E_k^{(L)} + i0)$ may be split into two parts corresponding to the photonlike and exciton-like regions of the polariton dispersion:

$$\Pi_L(y + i0) = \frac{2|\Omega_{\uparrow\downarrow}^{(L)}|^2}{E_a^{(L)}} \left[\int_0^{\frac{\hbar\Omega_R}{E_a^{(L)}}} \frac{e^{-x}}{y - x + i0} dx + \int_{\frac{\hbar\Omega_R}{E_a^{(L)}}}^\infty \frac{e^{-x}}{y - \frac{m_L}{m_X}x - \frac{\hbar\Omega_R}{E_a^{(L)}}} dx \right], \quad (\text{B3})$$

where $E_a^{(L)} \equiv \hbar^2/m_L a^2$ and $y \equiv E_k^{(L)}/E_a^{(L)}$. By our assumption, $\hbar\Omega_R \sim |\varepsilon| \sim \hbar^2/m_X a^2$, and we can write $\hbar\Omega_R/E_a^{(L)} \approx m_L/m_X \equiv \sigma \ll 1$. We then notice that $y \ll \sigma$ and obtain

$$\begin{aligned} \Pi_L(y + i0) &= \frac{2|\Omega_{\uparrow\downarrow}^{(L)}|^2}{E_a^{(L)}} \left\{ e^{-y}[\text{Ei}(y) - \text{Ei}(-\sigma + y) - i\pi] + \frac{e^{1-y/\sigma}}{\sigma} \text{Ei}(-1 - \sigma + y/\sigma) \right\} \\ &= \frac{2|\Omega_{\uparrow\downarrow}^{(L)}|^2}{E_a^{(X)}} e\text{Ei}(-1) + \frac{2|\Omega_{\uparrow\downarrow}^{(L)}|^2}{E_a^{(L)}} \ln \left(\frac{E_k^{(L)}}{E_a^{(X)}} \right). \end{aligned} \quad (\text{B4})$$

By substituting this result into Eq. (B1) we find

$$f_{\uparrow\uparrow,\text{res}}^{(L)}(k) = \frac{\pi\mathcal{G}_L}{(-\hbar^2k^2/m_L + \Delta_L)/2\beta_L + \ln(ka_L) - i\pi/2}, \quad (\text{B5})$$

where $\beta_L \equiv 2m_L a^2 |\Omega_{\uparrow\downarrow}^{(L)}|^2/\hbar^2$, $\Delta_L \equiv \bar{\Delta}_L + \sigma^{-1}\beta_L e\text{Ei}(-1)$, $a_L \equiv ia/\sqrt{\sigma}$ and $\mathcal{G}_L \equiv \pi/a^2 |\langle\varphi|\bar{\psi}_{\uparrow\uparrow,k}^{(L)}\rangle|^2$. According to Eq. (A5), the background polariton scattering amplitude $\bar{f}_{\uparrow\uparrow}^{(L)}(k) \equiv -(2\pi)^2 m_L/2\hbar^2 T_{\uparrow\uparrow}^{(L)}(k)$ is proportional to $\sigma = m_L/m_X \ll 1$. Hence, we may let $\bar{\psi}_{\uparrow\uparrow,k}^{(L)}(\mathbf{r}) = e^{ik\cdot\mathbf{r}}/2\pi$ and obtain $\mathcal{G}_L = 1$.

APPENDIX C: DISTORSION OF THE EXCITON CONTINUUM DUE TO THE BACKGROUND SCATTERING

Let us now evaluate the parameter

$$\mathcal{G}_X \equiv \pi/a^2 |\langle\varphi|\bar{\psi}_{\uparrow\uparrow,k}^{(X)}\rangle|^2, \quad (\text{C1})$$

which accounts for the distortion of the exciton continuum due to the background potential $V_{\uparrow\uparrow}^{(X)}(\mathbf{r})$. To this end, we decompose the stationary scattering state $\bar{\psi}_{\uparrow\uparrow,k}^{(X)}(\mathbf{r})$ into the partial waves,

$$\bar{\psi}_{\uparrow\uparrow,k}^{(X)}(\mathbf{r}) = \frac{1}{2\pi} \sum_{m=-\infty}^{+\infty} i^m \bar{\psi}_{\uparrow\uparrow,m,k}^{(X)}(r) e^{im\varphi},$$

and take the impenetrable disk *ansatz* for the s wave ($m = 0$):

$$\begin{aligned} \bar{\psi}_{\uparrow\uparrow,0,k}^{(X)}(r) &\equiv 0, \quad r \leq R_{\uparrow\uparrow} \\ \bar{\psi}_{\uparrow\uparrow,0,k}^{(X)}(r) &= \frac{1}{2} [H_0^-(kr) + (1 + i\bar{f}_{\uparrow\uparrow}^{(X)}(k))H_0^+(kr)], \quad r > R_{\uparrow\uparrow}, \end{aligned}$$

where $H_0^\pm(kr)$ are the Hankel functions and the background scattering amplitude $\bar{f}_{\uparrow\uparrow}^{(X)}(k)$ is given by Eq. (9) with $a_{\uparrow\uparrow}^{(X)} \equiv R_{\uparrow\uparrow}$. By using the Gaussian biexciton wave function [Eq. (8)] and assuming $R_{\uparrow\uparrow} \ll a$, we obtain in the limit $k \rightarrow 0$:

$$\langle\varphi|\bar{\psi}_{\uparrow\uparrow,k}^{(X)}\rangle \approx \frac{a}{\sqrt{\pi}} \frac{\ln \left[\frac{R_{\uparrow\uparrow} e^{\gamma/2}}{2a} \right]}{\ln \left[\frac{kR_{\uparrow\uparrow} e^{\gamma}}{2} \right]},$$

which on sending $R_{\uparrow\uparrow}/a \rightarrow 0$ yields Eq. (25) for $\mathcal{G}_X$.

APPENDIX D: ENTANGLEMENT DEGREE OF THE MOLECULAR POLARIZATION

By tracing out the spatial parts of the wave function (30), we obtain the polarization density matrix

$$\hat{\rho} = \begin{pmatrix} \langle\Upsilon|\Upsilon\rangle & \frac{w}{\sqrt{2}} \langle\varphi|\Upsilon\rangle & \frac{w}{\sqrt{2}} \langle\varphi|\Upsilon\rangle & 0 \\ \frac{w}{\sqrt{2}} \langle\Upsilon|\varphi\rangle & \frac{w^2}{2} \langle\varphi|\varphi\rangle & \frac{w^2}{2} \langle\varphi|\varphi\rangle & 0 \\ \frac{w}{\sqrt{2}} \langle\Upsilon|\varphi\rangle & \frac{w^2}{2} \langle\varphi|\varphi\rangle & \frac{w^2}{2} \langle\varphi|\varphi\rangle & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (\text{D1})$$

written in the ‘‘computational’’ basis $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$. We have used the notations $\Upsilon(r) = \langle\mathbf{r}|\Upsilon\rangle$ and $\varphi(r) = \langle\mathbf{r}|\varphi\rangle$. One has

$$\langle\Upsilon|\Upsilon\rangle = 1 - w^2 \quad (\text{D2})$$

and $\langle\varphi|\varphi\rangle = 1$, so that the mixed state (D1) is fully characterized by two parameters: the relative weight of the core w^2 and the overlap integral $\langle\varphi|\Upsilon\rangle$. Surprisingly, as we show below, the latter drops from the final result for the entanglement measure.

Let us evaluate Eq. (31) by following the analytical prescription [111,112] based on the methods of linear algebra. To this end, we diagonalize $\hat{\rho}$ and build an auxiliary symmetric matrix $\hat{\tau}$ with the elements

$$\tau_{+-} \equiv \sqrt{\lambda_+ \lambda_-} \langle -|\hat{\sigma}_y \otimes \hat{\sigma}_y|+ \rangle, \quad (\text{D3})$$

where

$$\lambda_{\pm} = \frac{1}{2}[1 \pm \sqrt{(1-2w^2)^2 + 4w^2 \langle\varphi|\Upsilon\rangle}] \quad (\text{D4})$$

are the nonzero eigenvalues of $\hat{\rho}$ and

$$|\pm\rangle = \frac{1}{\sqrt{2 + v_{\pm}^2}} \begin{pmatrix} v_{\pm} \\ 1 \\ 1 \\ 0 \end{pmatrix} \quad (\text{D5})$$

are the corresponding (normalized) eigenvectors, with

$$v_{\pm} \equiv \frac{1 - 2w^2 \pm \sqrt{(1-2w^2)^2 + 4w^2 \langle\varphi|\Upsilon\rangle}}{\sqrt{2w \langle\varphi|\Upsilon\rangle}}. \quad (\text{D6})$$

We then compute the singular values of $\hat{\tau}$ as square roots of the eigenvalues of the positive hermitian matrix $\hat{\tau}\hat{\tau}^\dagger$. The unique nonzero singular value reads

$$\mathcal{L} = 2 \left(\frac{\lambda_+}{2 + v_+^2} + \frac{\lambda_-}{2 + v_-^2} \right), \quad (\text{D7})$$

which, on substitution of Eq. (D4) and Eq. (D6), yields the formula

$$c[\hat{\rho}] \equiv \mathcal{L} = w^2 \quad (\text{D8})$$

for the concurrence of the mixed state $\hat{\rho}$. The absence of the overlap integral $\langle\varphi|\Upsilon\rangle$ in this final result is surprising and calls for further investigation.

APPENDIX E: BOLTZMANNIAN GAS OF MOLECULES

At low molecular densities ($na_y^2 \ll 1$) the polarization density matrix $\hat{\rho}$ defined by Eq. (32) may be reconstructed by performing cross correlation polarization measurements in a photon coincidence setup analogous to that employed previously for QD's [12]. Indeed, assuming the center-of-mass motion of the molecules being uncorrelated with their internal state [represented by the pure state $\Psi(\mathbf{r})$], the total density matrix for a grand-canonical ensemble may be written in a

factorized form

$$\hat{\rho}_{\text{GC}} = \frac{e^{\mu\hat{N}/k_B T}}{Z_{\text{GC}}} (e^{-\hat{\mathbf{K}}^2 \lambda_T^2})^{\otimes N} \otimes \hat{\rho}^{\otimes N} \quad (\text{E1})$$

with

$$Z_{\text{GC}} = \sum_N \frac{e^{\mu\hat{N}/k_B T}}{N!} (\text{Tr}[e^{-\hat{\mathbf{K}}^2 \lambda_T^2}])^N \quad (\text{E2})$$

being the grand-canonical partition function and the thermal de Broglie wavelength of a molecule $\lambda_T \equiv \sqrt{\hbar^2/4mk_B T}$ satisfying the condition

$$a_y \ll \lambda_T \ll n^{-1/2}. \quad (\text{E3})$$

A two-photon coincidence count randomly picks out a pair from the total flux and projects its polarization state onto a specific measurement state $|\psi_v\rangle$ set by the corresponding optical elements (polarizers and quarter- and half-wave plates). The average number of such coincidences n_v should include projection of the grand-canonical ensemble (E1) onto a single pair polarization state $\hat{\rho}$ and consecutive averaging over the total number of molecules N , as well as over their center-of-mass positions $\mathbf{R}_i$. Formally, such a procedure may be written as

$$n_v = \mathcal{N} \langle \psi_v | \sum_N \langle \mathbf{R}_1, \dots, \mathbf{R}_N | \hat{\mathcal{P}}^\dagger \hat{\rho}_{\text{GC}} \hat{\mathcal{P}} | \mathbf{R}_1, \dots, \mathbf{R}_N \rangle | \psi_v \rangle, \quad (\text{E4})$$

where

$$\hat{\mathcal{P}} \equiv \frac{1}{N} \sum_{i=1}^N \sum_{\sigma, \sigma'} |\sigma \sigma'\rangle_i \langle \sigma' \sigma| \quad (\text{E5})$$

is the required projector, $\mathcal{N}$ is a constant which depends on the photoluminescence yield and detector efficiency, and $v = 1, \dots, 16$ labels a particular measurement state within (what would be) a tomographically complete set of measurements [116]. By substituting Eq. (E1) into Eq. (E4), one obtains

$$n_v = \mathcal{N} \langle \psi_v | \hat{\rho} | \psi_v \rangle. \quad (\text{E6})$$

Hence, the single-molecule density matrix $\hat{\rho}$ does indeed constitute a legitimate observable under the conditions formulated above.

Whereas the polarization state of a bare biexciton $|e_3\rangle$ is prescribed by the quantum statistics, thermal fluctuations of the relative phase in the orbital part of Eq. (30) may reduce the degree of entanglement. The relative phase would enter the overlap $\langle\varphi|\Upsilon\rangle$ in Eq. (D1), but it does not appear in the final result (35) for the concurrence. By virtue of the convexity property [111], the latter thus should be regarded as an upper bound for the result one would obtain on the basis of the experimental measurements. This bound is reached progressively, as one increases the ratio $\hbar\Omega_X/k_B T$.

For a quantum degenerate gas, the description in terms of a pure state (30) is no longer adequate and one should proceed from a many-body solution of the Hamiltonian (21).

[1] P. Lodahl, S. Mahmoodian, and S. Stobbe, Interfacing single photons and single quantum dots with photonic nanostructures, *Rev. Mod. Phys.* **87**, 347 (2015).

[2] M. O. Scully and M. S. Zubairy, *Quantum Optics* (Cambridge University Press, Cambridge, UK, 1997).

- [3] R. C. Miller, D. A. Kleinman, A. C. Gossard, and O. Munteanu, Biexcitons in GaAs quantum wells, *Phys. Rev. B* **25**, 6545 (1982).
- [4] E. J. Sie, A. J. Frenzel, Y.-H. Lee, J. Kong, and N. Gedik, Intervalley biexcitons and many-body effects in monolayer MoS₂, *Phys. Rev. B* **92**, 125417 (2015).
- [5] Y. You, X.-X. Zhang, T. C. Berkelbach, M. S. Hybertsen, D. R. Reichman, and T. F. Heinz, Observation of biexcitons in monolayer WSe₂, *Nat. Phys.* **11**, 477 (2015).
- [6] K. Hao, J. F. Specht, P. Nagler, L. Xu, K. Tran, A. Singh, C. K. Dass, C. Schüller, T. Korn, M. Richter, A. Knorr, X. Li, and G. Moody, Neutral and charged inter-valley biexcitons in monolayer MoSe₂, *Nat. Commun.* **8**, 15552 (2017).
- [7] Z. Li, T. Wang, Z. Lu, C. Jin, Y. Chen, Y. Meng, Z. Lian, T. Taniguchi, K. Watanabe, S. Zhang, D. Smirnov, and Su-Fei Shi, Revealing the biexciton and trion-exciton complexes in BN encapsulated WSe₂, *Nat. Commun.* **9**, 3719 (2018).
- [8] F. Thouin, S. Neutzner, D. Cortecchia, V. A. Dragomir, C. Soci, T. Salim, Y. M. Lam, R. Leonelli, A. Petrozza, A. R. S. Kandada, and C. Silva, Stable biexcitons in two-dimensional metal-halide perovskites with strong dynamic lattice disorder, *Phys. Rev. Mater.* **2**, 034001 (2018).
- [9] S. V. Andreev, Resonant pairing of excitons in semiconductor heterostructures, *Phys. Rev. B* **94**, 140501(R) (2016).
- [10] S. V. Andreev, Dipolar polaritons squeezed at unitarity, *Phys. Rev. B* **101**, 125129 (2020).
- [11] P. Tamarat, L. Hou, J.-B. Trebbia, A. Swarnkar, L. Biadala, Y. Louyer, M. I. Bodnarchuk, M. V. Kovalenko, J. Even, and B. Lounis, The dark exciton ground state promotes photon-pair emission in individual perovskite nanocrystals, *Nat. Commun.* **11**, 6001 (2020).
- [12] R. M. Stevenson, R. J. Young, P. Atkinson, K. Cooper, D. A. Ritchie, and A. J. Shields, A semiconductor source of triggered entangled photon pairs, *Nature (London)* **439**, 179 (2006).
- [13] C. L. Salter, R. M. Stevenson, I. Farrer, C. A. Nicoll, D. A. Ritchie, and A. J. Shields, An entangled-light-emitting diode, *Nature (London)* **465**, 594 (2010).
- [14] A. Dousse, J. Suffczynski, A. Beveratos, O. Krebs, A. Lemaître, I. Sagnes, J. Bloch, P. Voisin, and P. Senellart, Ultra-bright source of entangled photon pairs, *Nature (London)* **466**, 217 (2010).
- [15] T. Kondo, T. Azuma, T. Yuasa, and R. Ito, Biexciton lasing in the layered perovskite-type material (C₆H₁₃NH₃)₂PbI₄, *Solid State Commun.* **105**, 253 (1998).
- [16] J. Q. Grim, S. Christodoulou, F. Di Stasio, R. Krahne, R. Cingolani, L. Manna, and I. Moreels, Continuous-wave biexciton lasing at room temperature using solution-processed quantum wells, *Nat. Nanotechnol.* **9**, 891 (2014).
- [17] E. P. Booker, M. B. Price, P. J. Budden, H. Abolins, Y. del Valle-Inclan Redondo, L. Eyre, I. Nasrallah, R. T. Phillips, R. H. Friend, F. Deschler, and N. C. Greenham, Vertical cavity biexciton lasing in 2D dodecylammonium lead iodide perovskites, *Adv. Opt. Mater.* **6**, 1800616 (2018).
- [18] F. De Fornel, *Evanescent Waves: From Newtonian Optics to Atomic Optics* (Springer Science & Business Media, New York, 2001), Vol. 73.
- [19] A. L. Ivanov, H. Haug, and L.V. Keldysh, Optics of excitonic molecules in semiconductors and semiconductor microstructures, *Phys. Rep.* **296**, 237 (1998).
- [20] H. H. Fang, B. Han, C. Robert, M. A. Semina, D. Lagarde, E. Courtade, T. Taniguchi, K. Watanabe, T. Amand, B. Urbaszek, M. M. Glazov, and X. Marie, Control of the exciton radiative lifetime in van der Waals heterostructures, *Phys. Rev. Lett.* **123**, 067401 (2019).
- [21] C. Weisbuch, M. Nishioka, A. Ishikawa, and Y. Arakawa, Observation of the coupled exciton-photon mode splitting in a semiconductor quantum microcavity, *Phys. Rev. Lett.* **69**, 3314 (1992).
- [22] J. C. Kim and J. P. Wolfe, Bose-Einstein statistics of an excitonic gas in two dimensions: Excitons and biexcitons in a GaAs quantum well, *Phys. Rev. B* **57**, 9861 (1998).
- [23] A. A. High, J. R. Leonard, A. T. Hammack, M. M. Fogler, L. V. Butov, A. V. Kavokin, K. L. Campman, and A. C. Gossard, Spontaneous coherence in a cold exciton gas, *Nature (London)* **483**, 584 (2012).
- [24] A. V. Gorbunov and V. B. Timofeev, Phase diagram of the Bose condensation of dipolar excitons in GaAs/AlGaAs quantum-well heterostructures, *JETP Lett.* **96**, 138 (2012).
- [25] S. Misra, M. Stern, A. Joshua, V. Umansky, and I. Bar-Joseph, Experimental study of the exciton gas-liquid transition in coupled quantum wells, *Phys. Rev. Lett.* **120**, 047402 (2018).
- [26] R. Anankine, M. Beian, S. Dang, M. Alloing, E. Cambril, K. Merghem, C. G. Carbonell, A. Lemaître, and F. Dubin, Quantized vortices and four-component superfluidity of semiconductor excitons, *Phys. Rev. Lett.* **118**, 127402 (2017).
- [27] F. Katsch and A. Knorr, Optical preparation and coherent control of ultrafast nonlinear quantum superpositions in exciton gases: A case study for atomically thin semiconductors, *Phys. Rev. X* **10**, 041039 (2020).
- [28] L. Sigl, F. Sigger, F. Kronowetter, J. Kiemle, J. Klein, K. Watanabe, T. Taniguchi, J. J. Finley, U. Wurstbauer, and A. W. Holleitner, Signatures of a degenerate many-body state of interlayer excitons in a van der Waals heterostack, *Phys. Rev. Res.* **2**, 042044(R) (2020).
- [29] E. Hanamura and H. Haug, Condensation effects of excitons, *Phys. Rep.* **33**, 209 (1977).
- [30] P. Nozières and D. Saint James, Particle vs. pair condensation in attractive Bose liquids, *J. Phys. France* **43**, 1133 (1982).
- [31] G. Röpke, A. Schnell, P. Schuck, and P. Nozières, Four-particle condensate in strongly coupled fermion systems, *Phys. Rev. Lett.* **80**, 3177 (1998).
- [32] Y. E. Lozovik, O. L. Berman, and M. Willander, Superfluidity of indirect excitons and biexcitons in coupled quantum wells and superlattices, *J. Phys.: Condens. Matter* **14**, 12457 (2002).
- [33] R. Hanai, P. B. Littlewood, and Y. Ohashi, Dynamical instability of a driven-dissipative electron-hole condensate in the BCS-BEC crossover region, *Phys. Rev. B* **96**, 125206 (2017).
- [34] A. Chiocchetta, A. Gambassi, and I. Carusotto, Laser operation and Bose-Einstein condensation: Analogies and differences, in *Universal Themes of Bose-Einstein Condensation*, edited by N. P. Proukakis, D. W. Snoke, and P. B. E. Littlewood (Cambridge University Press, Cambridge, UK, 2017), pp. 409–423.
- [35] A. N. Boto, P. Kok, D. S. Abrams, S. L. Braunstein, C. P. Williams, and J. P. Dowling, Quantum interferometric optical

- lithography: Exploiting entanglement to beat the diffraction limit, *Phys. Rev. Lett.* **85**, 2733 (2000).
- [36] J. P. Dowling, Quantum optical metrology—The lowdown on high-N00N states, *Contemp. Phys.* **49**, 125 (2008).
- [37] T. Kashiwazaki, T. Yamashima, N. Takanashi, A. Inoue, T. Umeki, and A. Furusawa, Fabrication of low-loss quasi-single-mode PPLN waveguide and its application to a modularized broadband high-level squeezer, *Appl. Phys. Lett.* **119**, 251104 (2021).
- [38] V. M. Agranovich and V. Ginzburg, *Crystal Optics with Spatial Dispersion, and Excitons*, Springer Series in Solid-State Sciences (Springer, Berlin, 1984), Vol. 42.
- [39] C. Robert, T. Amand, F. Cadiz, D. Lagarde, E. Courtade, M. Manca, T. Taniguchi, K. Watanabe, B. Urbaszek, and X. Marie, Fine structure and lifetime of dark excitons in transition metal dichalcogenide monolayers, *Phys. Rev. B* **96**, 155423 (2017).
- [40] C. Chin, R. Grimm, P. Julienne, and E. Tiesinga, Feshbach resonances in ultracold gases, *Rev. Mod. Phys.* **82**, 1225 (2010).
- [41] M. T. Bell and T. P. Softley, Ultracold molecules and ultracold chemistry, *Mol. Phys.* **107**, 99 (2009).
- [42] D. J. Heinzen, R. Wynar, P. D. Drummond, and K. V. Kheruntsyan, Superchemistry: Dynamics of coupled atomic and molecular Bose-Einstein condensates, *Phys. Rev. Lett.* **84**, 5029 (2000).
- [43] M. G. Moore and A. Vardi, Bose-enhanced chemistry: Amplification of selectivity in the dissociation of molecular Bose-Einstein condensates, *Phys. Rev. Lett.* **88**, 160402 (2002).
- [44] Z. Zhang, S. Nagata, K.-X. Yao, and C. Chin, Many-body chemical reactions in a quantum degenerate gas, *Nat. Phys.* **19**, 1466 (2023).
- [45] R. W. Boyd, The nonlinear optical susceptibility, in *Nonlinear Optics*, 3rd ed., edited by R. W. Boyd (Academic Press, Burlington, 2008), pp. 1–67.
- [46] R. Takayama, N. H. Kwong, I. Rumyantsev, M. Kuwata-Gonokami, and R. Binder, T-matrix analysis of biexcitonic correlations in the nonlinear optical response of semiconductor quantum wells, *Eur. Phys. J. B* **25**, 445 (2002).
- [47] S. Schumacher, N. H. Kwong, and R. Binder, Influence of exciton-exciton correlations on the polarization characteristics of polariton amplification in semiconductor microcavities, *Phys. Rev. B* **76**, 245324 (2007).
- [48] E. Timmermans, P. Tommasini, M. Hussein, and A. Kerman, Feshbach resonances in atomic Bose-Einstein condensates, *Phys. Rep.* **315**, 199 (1999).
- [49] P. O. Fedichev, Yu. Kagan, G. V. Shlyapnikov, and J. T. M. Walraven, Influence of nearly resonant light on the scattering length in low-temperature atomic gases, *Phys. Rev. Lett.* **77**, 2913 (1996).
- [50] I. Schwartz, Y. Shimazaki, C. Kuhlenskamp, K. Watanabe, T. Taniguchi, M. Kroner, and A. Imamoğlu, Electrically tunable Feshbach resonances in twisted bilayer semiconductors, *Science* **374**, 336 (2021).
- [51] C. Kuhlenskamp, M. Knap, M. Wagner, R. Schmidt, and A. Imamoğlu, Tunable Feshbach resonances and their spectral signatures in bilayer semiconductors, *Phys. Rev. Lett.* **129**, 037401 (2022).
- [52] E. I. Rashba and G. E. Gurgenishvili, Edge absorption theory in semiconductors, *Sov. Phys. Solid State* **4**, 759 (1962).
- [53] I. Carusotto, T. Volz, and A. Imamoğlu, Feshbach blockade: Single-photon nonlinear optics using resonantly enhanced cavity polariton scattering from biexciton states, *Europhys. Lett.* **90**, 37001 (2010).
- [54] M. Wouters, Resonant polariton-polariton scattering in semiconductor microcavities, *Phys. Rev. B* **76**, 045319 (2007).
- [55] M. A. Bastarrachea-Magnani, A. Camacho-Guardian, M. Wouters, and G. M. Bruun, Strong interactions and biexcitons in a polariton mixture, *Phys. Rev. B* **100**, 195301 (2019).
- [56] E. V. Denning, A. Knorr, F. Katsch, and M. Richter, Bichromatic four-wave mixing and quadrature-squeezing from biexcitons in atomically thin semiconductor microcavities, *Phys. Rev. B* **106**, 195307 (2022).
- [57] M. Navadeh-Toupchi, N. Takemura, M. D. Anderson, D. Y. Oberli, and M. T. Portella-Oberli, Polaritonic cross Feshbach resonance, *Phys. Rev. Lett.* **122**, 047402 (2019).
- [58] N. Takemura, S. Trebaol, M. Wouters, M. T. Portella-Oberli, and B. Deveaud, Polaritonic Feshbach resonance, *Nat. Phys.* **10**, 500 (2014).
- [59] N. Takemura, M. D. Anderson, M. Navadeh-Toupchi, D. Y. Oberli, M. T. Portella-Oberli, and B. Deveaud, Spin anisotropic interactions of lower polaritons in the vicinity of polaritonic Feshbach resonance, *Phys. Rev. B* **95**, 205303 (2017).
- [60] I. Rosenberg, D. Liran, Y. Mazuz-Harpaz, K. West, L. Pfeiffer, and R. Rapaport, Strongly interacting dipolar-polaritons, *Sci. Adv.* **4**, eaat8880 (2018).
- [61] B. Datta, M. Khatoniar, P. Deshmukh, F. Thouin, R. Bushati, S. De Liberato, S. K. Cohen, and V. M. Menon, Highly nonlinear dipolar exciton-polaritons in bilayer MoS₂, *Nat. Commun.* **13**, 6341 (2022).
- [62] L. Mandel and E. Wolf, Some quantum effects in nonlinear optics, *Optical Coherence and Quantum Optics* (Cambridge University Press, Cambridge, UK, 1995), pp. 1069–1108.
- [63] E. Hanamura, Rapid radiative decay and enhanced optical nonlinearity of excitons in a quantum well, *Phys. Rev. B* **38**, 1228 (1988).
- [64] N. S. Voronova, I. L. Kurbakov, and Yu. E. Lozovik, Bose condensation of long-living direct excitons in an off-resonant cavity, *Phys. Rev. Lett.* **121**, 235702 (2018).
- [65] F. Meier and B. P. Zakharchenya, *Optical Orientation* (North-Holland, Amsterdam, 1984).
- [66] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Interscience, New York, 1965).
- [67] G. Sallen, L. Bouet, X. Marie, G. Wang, C. R. Zhu, W. P. Han, Y. Lu, P. H. Tan, T. Amand, B. L. Liu, and B. Urbaszek, Robust optical emission polarization in MoS₂ monolayers through selective valley excitation, *Phys. Rev. B* **86**, 081301(R) (2012).
- [68] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nat. Nanotechnol.* **7**, 490 (2012).
- [69] A. Srivastava, M. Sidler, A. V. Allain, D. S. Lembke, A. Kis, and A. Imamoğlu, Valley Zeeman effect in elementary optical excitations of monolayer WSe₂, *Nat. Phys.* **11**, 141 (2015).
- [70] T. Koda and D. W. Langer, Splitting of exciton lines in wurtzite-type II-VI crystals by uniaxial stress, *Phys. Rev. Lett.* **20**, 50 (1968).

- [71] O. Akimoto and H. Hasegawa, Strain-induced splitting and polarization of excitons due to exchange interaction, *Phys. Rev. Lett.* **20**, 916 (1968).
- [72] C. Gourdon and P. Lavallard, Fine structure of heavy excitons in GaAs/AlAs superlattices, *Phys. Rev. B* **46**, 4644 (1992).
- [73] G. L. Bir, G. E. Pikus, L. G. Suslina, and D. L. Fedorov, Excitonic piezoreflection in cubic crystals of zinc sulfide, *Fiz. Tverd. Tela* **12**, 1187 (1970).
- [74] G. L. Bir, G. E. Pikus, L. G. Suslina, and D. L. Fedorov, Exchange interaction and piezooptics of excitons in cubic crystals of ZnS, *Fiz. Tverd. Tela* **12**, 3218 (1970).
- [75] G. E. Pikus and F. G. Pikus, The mechanism of heavy and light hole mixing in GaAs/AlAs superlattices, *Solid State Commun.* **89**, 319 (1994).
- [76] M. M. Glazov, F. Dirnberger, V. M. Menon, T. Taniguchi, K. Watanabe, D. Bougeard, J. D. Ziegler, and A. Chernikov, Exciton fine structure splitting and linearly polarized emission in strained transition-metal dichalcogenide monolayers, *Phys. Rev. B* **106**, 125303 (2022).
- [77] G. E. Pikus and G. L. Bir, Exchange interaction in excitons in semiconductors, *Sov. Phys. JETP* **33**, 195 (1970).
- [78] Beyond the bosonic model (2), the exciton spin relaxation may also occur via sequential fermionic spin-flips involving the dark exciton as an intermediate state [79]. The short-range electron-hole exchange suppresses such processes. In TMD's these are further suppressed due to the valleys in the absence of an inversion center [68,80].
- [79] T. Amand and X. Marie, Exciton spin dynamics in semiconductor quantum wells, in *Spin Physics in Semiconductors*, edited by M. I. Dyakonov (Springer International Publishing, Cham, 2017), pp. 69–103.
- [80] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Control of valley polarization in monolayer MoS₂ by optical helicity, *Nat. Nanotechnol.* **7**, 494 (2012).
- [81] M. I. Sheboul and W. Ekardt, Theory of biexcitons using the boson formalism: The ground state binding energy, *Physica Status Solidi (b)* **73**, 165 (1976).
- [82] B. Piętko, D. Zygunt, M. Król, M. R. Molas, A. A. L. Nicolet, F. Morier-Genoud, J. Szczytko, J. Łusakowski, P. Zięba, I. Tralle, P. Stepnicki, M. Matuszewski, M. Potemski, and B. Deveaud, Magnetic field tuning of exciton-polaritons in a semiconductor microcavity, *Phys. Rev. B* **91**, 075309 (2015).
- [83] A. V. Stier, N. P. Wilson, K. A. Velizhanin, J. Kono, X. Xu, and S. A. Crooker, Magnetooptics of exciton Rydberg states in a monolayer semiconductor, *Phys. Rev. Lett.* **120**, 057405 (2018).
- [84] G. Panzarini, L. C. Andreani, A. Armitage, D. Baxter, M. S. Skolnick, V. N. Astratov, J. S. Roberts, A. V. Kavokin, M. R. Vladimirova, and M. A. Kaliteevski, Exciton-light coupling in single and coupled semiconductor microcavities: Polariton dispersion and polarization splitting, *Phys. Rev. B* **59**, 5082 (1999).
- [85] O. Bleu, D. D. Solnyshkov, and G. Malpuech, Optical valley Hall effect based on transitional metal dichalcogenide cavity polaritons, *Phys. Rev. B* **96**, 165432 (2017).
- [86] S. V. Andreev, Pairing of electromagnetic bosons under spin-orbit coupling, *Phys. Rev. B* **106**, 155157 (2022).
- [87] Y. Peng, M. Que, J. Tao, X. Wang, J. Lu, G. Hu, B. Wan, Q. Xu, and C. Pan, Progress in piezotronic and piezo-phototronic effect of 2D materials, *2D Mater.* **5**, 042003 (2018).
- [88] S. A. Moskalenko, The theory of Mott exciton in alkali-halide crystals, *Zh. Opt. Spektrosk.* **5**, 147 (1958).
- [89] F. Čulík, Exciton-exciton “collisions” in crystals, *Czech. J. Phys.* **16**, 194 (1966).
- [90] E. Hanamura, Theory of many Wannier excitons. I, *J. Phys. Soc. Jpn.* **37**, 1545 (1974).
- [91] A. J. C. Varandas, J. da Providência, M. Brajczewska, and J. P. da Providência, On dipositronium and molecular hydrogen: similarities and differences, *Eur. Phys. J. D* **69**, 114 (2015).
- [92] Repulsive vs attractive characters of the potentials $V_{\uparrow\uparrow}^{(X)}(r)$, $V_{\downarrow\downarrow}^{(X)}(r)$, and $V_{\uparrow\downarrow}^{(X)}(r)$, respectively, have been confirmed by numerous experiments on dense ensembles, where the short-range correlations produce observable shifts of the exciton PL lines [79].
- [93] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Oxford, 1969).
- [94] Here one should put $k_c = \sqrt{2m_X k_B T}/\hbar$ for a classical gas of excitons at $T > T_{\text{BKT}}$ and $k_c = \sqrt{2m_X \mu}/\hbar \sim \sqrt{n}$ for a quasi-condensate characterized by a positive chemical potential μ at $T < T_{\text{BKT}}$, where T_{BKT} is the Berezinskii-Kosterlitz-Thouless transition temperature [117]. Note also the difference between a genuine binary mixture and our spin-1 system of electromagnetic bosons, where the odd-wave inter-species scattering is forbidden [86].
- [95] T. Byrnes, G. V. Kolmakov, R. Y. Kezerashvili, and Y. Yamamoto, Effective interaction and condensation of dipolaritons in coupled quantum wells, *Phys. Rev. B* **90**, 125314 (2014).
- [96] O. Bleu, G. Li, J. Levinsen, and M. M. Parish, Polariton interactions in microcavities with atomically thin semiconductor layers, *Phys. Rev. Res.* **2**, 043185 (2020).
- [97] H. Hu, H. Deng, and Xia-Ji Liu, Two-dimensional exciton-polariton interactions beyond the Born approximation, *Phys. Rev. A* **106**, 063303 (2022).
- [98] A. Delteil, T. Fink, A. Schade, S. Höfling, C. Schneider, and A. İmamoğlu, Towards polariton blockade of confined exciton-polaritons, *Nat. Mater.* **18**, 219 (2019).
- [99] E. Estrecho, T. Gao, N. Bobrovska, D. Comber-Todd, M. D. Fraser, M. Steger, K. West, L. N. Pfeiffer, J. Levinsen, M. M. Parish, T. C. H. Liew, M. Matuszewski, D. W. Snoke, A. G. Truscott, and E. A. Ostrovskaya, Direct measurement of polariton-polariton interaction strength in the Thomas-Fermi regime of exciton-polariton condensation, *Phys. Rev. B* **100**, 035306 (2019).
- [100] P. Stepanov, A. Vashisht, M. Klaas, N. Lundt, S. Tongay, M. Blei, S. Höfling, T. Volz, A. Minguzzi, J. Renard, C. Schneider, and M. Richard, Exciton-exciton interaction beyond the hydrogenic picture in a MoSe₂ monolayer in the strong light-matter coupling regime, *Phys. Rev. Lett.* **126**, 167401 (2021).
- [101] D. W. Snoke, V. Hartwell, J. Beaumariage, S. Mukherjee, Y. Yoon, D. M. Myers, M. Steger, Z. Sun, K. A. Nelson, and L. N. Pfeiffer, Reanalysis of experimental determinations of polariton-polariton interactions in microcavities, *Phys. Rev. B* **107**, 165302 (2023).
- [102] G. C. La Rocca, F. Bassani, and V. M. Agranovich, Biexcitons and dark states in semiconductor microcavities, *J. Opt. Soc. Am. B* **15**, 652 (1998).

- [103] A. Maruani and D. S. Chemla, Active nonlinear spectroscopy of biexcitons in semiconductors: Propagation effects and Fano interferences, *Phys. Rev. B* **23**, 841 (1981).
- [104] P. G. Savvidis, J. J. Baumberg, R. M. Stevenson, M. S. Skolnick, D. M. Whittaker, and J. S. Roberts, Angle-resonant stimulated polariton amplifier, *Phys. Rev. Lett.* **84**, 1547 (2000).
- [105] S. V. Andreev, Pairing of fermions under spin-orbit coupling in two dimensions, *Phys. Rev. B* **106**, 214523 (2022).
- [106] The average kinetic energy of the relative motion in the denominator of Eq. (23) cancels in the case of massive, parabolic dispersion assumed here.
- [107] V. Gurarie and L. Radzihovsky, Resonantly paired fermionic superfluids, *Ann. Phys.* **322**, 2 (2007).
- [108] R. J. Elliott, Intensity of optical absorption by excitons, *Phys. Rev.* **108**, 1384 (1957).
- [109] This estimate does not account for the extrusion of the average boson momenta beyond the light cone due to the tight binding in real space [118]. However, this additional effect is of secondary importance here.
- [110] T. Ren and I. Aleiner, Three-boson bound states in two dimensions, *Phys. Rev. B* **95**, 045401 (2017).
- [111] F. Mintert, A. R. R. Carvalho, M. Kuś, and A. Buchleitner, Measures and dynamics of entangled states, *Phys. Rep.* **415**, 207 (2005).
- [112] W. K. Wootters, Entanglement of formation of an arbitrary state of two qubits, *Phys. Rev. Lett.* **80**, 2245 (1998).
- [113] M. Riebe, H. Häffner, C. F. Roos, W. Hänsel, J. Benhelm, G. P. T. Lancaster, T. W. Körber, C. Becher, F. Schmidt-Kaler, D. F. V. James, and R. Blatt, Deterministic quantum teleportation with atoms, *Nature (London)* **429**, 734 (2004).
- [114] G. Breitenbach, S. Schiller, and J. Mlynek, Measurement of the quantum states of squeezed light, *Nature (London)* **387**, 471 (1997).
- [115] An alternative thermal estimate $\hbar^2 k_c^2 / m_L \sim T_{\text{BKT}}$, with $T_{\text{BKT}} \sim \hbar^2 n / m_L$, may be orders of magnitude larger in the case of polaritons.
- [116] D. F. V. James, P. G. Kwiat, W. J. Munro, and A. G. White, Measurement of qubits, *Phys. Rev. A* **64**, 052312 (2001).
- [117] O. I. Utesov, M. I. Baglay, and S. V. Andreev, Effective interactions in a quantum Bose-Bose mixture, *Phys. Rev. A* **97**, 053617 (2018).
- [118] D. S. Citrin, Long radiative lifetimes of biexcitons in GaAs/Al_xGa_{1-x}As quantum wells, *Phys. Rev. B* **50**, 17655 (1994).