Theory of Exciton-Phonon Coupling

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The effects of the electron-phonon interaction on optical excitations can be understood in terms of exciton-phonon coupling, and require a careful treatment in low-dimensional materials with strongly bound excitons or strong electron-hole interaction in general. Through phonon absorption and emission processes, the optically accessible excitons are scattered otherwise optically dark finite-momentum exciton states. We derive a practical expression for the phonon-induced term of the exciton self-energy (denoted as the exciton-phonon self-energy) that gives the temperature dependence of the optical transition energies and their lifetime broadening resulting from the exciton’s interaction with the phonons. We illustrate this theory on a two-dimensional model, and show that our expression for the exciton-phonon self-energy differs qualitatively from previous expressions found in the literature that neglect the exciton binding or electron-hole correlations.

A wealth of two-dimensional and nanocrystalline materials with interesting optical properties have been studied in recent years, including transition-metal dichalcogenides, layered heterostructures and halide perovskites. In these systems, the optical excitations lead to the formation of strongly bound electron-hole pair states known as excitons. Many of their useful opto-electronic properties (e.g., photocurrent generation, single-photon emission, etc.) depend on the scattering dynamics and diffusion of the excitons. This dynamics is governed by several processes: the interaction of excitons with defects, the exciton-exciton interaction, and the exciton-phonon interaction. In particular, exciton-phonon coupling effects can be identified by their distinctive temperature dependence, whether in the exciton mean free path, lifetimes or emission spectra.

The exciton-phonon coupling mechanism originates from a combined action of the electron-hole and the electron-phonon interactions, both of which can be described from first principles. On the one hand, the electron-hole interaction underlies the formation of excitons, and can be addressed with the Bethe-Salpeter equation (BSE) within the ab initio GW-BSE method. This method solves the interacting two-particle problem for an electron and a hole, and yields the exciton energies and wavefunctions, which allow to predict the optical absorption spectra of materials. The electron-phonon interaction, on the other hand, has largely been studied within density functional perturbation theory (DFPT), which provides an ab initio description of the phonon energy spectrum and coupling potential. This framework has been used to study the effect of phonons on the band structure and carrier mobility as a function of temperature. Going beyond DFT, electron-electron correlation effects to the electron self-energy may further be included at the GW level from ab initio using the GWPT method in computing the electron-phonon interaction.

Describing the dynamics of photoexcited states from first principles is a challenging task. Simulations of hot electrons were achieved by retaining the electron-phonon interaction only, with the rationale that electrons far from the band edges would scatter freely without forming bound excitons. It is necessary, however, to include the electron-hole interaction to predict the lifetime of absorption and emission states when they originate from bound excitons.

An early attempt to compute the temperature-dependent broadening and renormalization of exciton states was based on a one-particle picture of the electron-phonon coupling. This scheme has been used to compute the absorption spectrum of h-BN and MoS₂ at finite temperature. In this approach, the electron-phonon renormalization and broadening of the band structure is computed before solving the BSE. This method does not, however, describe correctly the process where excitons scatter into finite-momentum bound states, which is necessary to enforce energy conservation. Alternatively, the supercell BSE technique does account for the phonon-mediated interaction between optical excitons and a limited number of finite-momentum excitons commensurate to the supercell size. It does so only within a static approximations, which is valid for non-polar materials. This approach predicts the exciton energy renormalization as a function of temperature, but makes no prediction on the scattering lifetime of the excitons. Recent methods formally achieved a proper description of exciton dynamics with exciton-phonon scattering amplitude deduced from Fermi’s golden rule using exciton-phonon coupling matrix elements. This approach enforces energy conservation, and is consistent with the theory presented in this paper, as well as other methods derived from many-body perturbation theory. Another effect of phonons on the exciton binding energies comes from the lattice screening, and this has been recently computed from first principles.

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In this work, we develop a general theory of the exciton-phonon coupling that is amenable to first-principles calculation. The central object is the exciton-phonon self-energy (i.e., the contribution to the exciton self-energy due to exciton-phonon interaction; there are of course contributions due to other excitations in a system), which yields the energy renormalization of the exciton states, as well as their scattering lifetime due to phonons. We apply this theory to a tight-binding model in two dimensions and discuss how it differs from other methods. This paper is organized as follows. Section I reviews the theory of electron-hole and electron-phonon interactions. Section II presents the extension of the one-particle theory to the exciton-phonon coupling, and the main equations for the phonon-induced temperature-dependent exciton lifetimes and energies. In Sec. III, we apply this scheme to a 2D tight-binding model, and discuss the consequences of electron-hole interactions on the scattering dynamics of two-dimensional systems. The main findings are summarized in Sec. IV. Several mathematical details of the derivation can be found in supplemental materials50.

I. ELECTRON-HOLE AND ELECTRON-PHONON INTERACTIONS

As a starting point for the treatment of electron-hole and electron-phonon interactions, we consider a mean-field fixed-ions Hamiltonian for the electrons \( H_0 = \hat{T}_k + V_{\text{SCF}}(r) \), where \( \hat{T}_k \) is the kinetic energy operator, and \( V_{\text{SCF}}(r) \) is the self-consistent field potential. Within the density functional theory (DFT) framework, \( V_{\text{SCF}} \) includes the potential of the ions, the Hartree potential and the exchange-correlation potential. Solving the one-particle Hamiltonian yields the set of unperturbed wavefunctions \( \phi_i(r) \) and energies \( \epsilon_i \), where the label \( i \) comprises a band index \( (n_i) \), a wavevector \( (\mathbf{k}_i) \), and eventually a spin index \( (\sigma) \).

These quantities are used to construct the time-ordered Green’s function, defined in the one-particle basis and in time as \( G_{ii'}^0(t) = -i \langle \hat{T}_k c_i(t) c_i^\dagger(0) \rangle_{ii'} \), where \( c_i^\dagger \) and \( c_i \) are the electron creation and annihilation operators, \( \hat{T}_k \) is Wick’s time-ordering operator, and “0” indicates here that the expectation value is taken over a ground state that is not perturbed by the phonons. The creation and annihilation operators follow the commutation relations

\[
\{ c_i, c_j^\dagger \} = c_i c_j^\dagger + c_j c_i^\dagger = \delta_{ii'}
\]

and \( \{ c_i, c_j \} = \{ c_i^\dagger, c_j^\dagger \} = 0 \). In terms of frequencies, the one-particle Green’s function writes as

\[
G_{ii'}^0(\omega) = \frac{1}{\omega - \epsilon_i \pm i\eta} \delta_{ii'}
\]

where \( \pm \eta \) is an real infinitesimal number with the same sign as \( \epsilon_i \), the eigenvalue measured with respect to the chemical potential.

The electronic energies and wavefunctions that define the starting point need not be obtained from DFT; they may also be obtained from a model Hamiltonian or from a many-body scheme. It is required however to have an effective Hamiltonian that depends implicitly on the atomic coordinates and that can be differentiated with respect to these coordinates to obtain the dynamical matrix and the electron-phonon coupling elements. Such a Hamiltonian, for example, may be constructed from the self-energy computed in the \( GW \) formalism33,51,52.

A. Electron-hole interaction

A class of neutral excitations of an insulating system is composed of an electron being promoted into the conduction bands and leaving a hole in the valence bands. If the Coulomb attraction between the electron and the hole is sufficiently strong, they may form a bound exciton, that is, a bound state whose excitation energy is smaller than the fundamental band gap. The procedure to compute the exciton spectrum from the BSE is described in Ref. 24.

The starting point to describe excitons is the set of independent (or non-interacting) electron-hole pairs, typically with quasiparticle energies from a \( GW \) calculation in the \( ab \) \textit{initio} \( GW \)-BSE approach. The corresponding propagator for these fictitious excitations is

\[
L_{vc'}^0(\omega) = \frac{1}{\omega - (\epsilon_v - \epsilon_c) + i\eta} \delta_{cc'} \delta_{vv'}
\]

where \( v \) and \( c \) refer to the labeling of occupied (valence band) and unoccupied (conduction band) states which involve both band and K-point indices. We call \( L^0 \) the bare electron-hole propagator. It is computed with the fixed-ions Hamiltonian, but the superscript “0” refers to the fact that the electron and hole propagate freely without interacting with one another.

The BSE relates the bare exciton propagator \( L \) to the bare electron-hole propagator \( L^0 \) through the kernel \( K \), as depicted in Fig. 1. The BSE kernel \( K \) is composed of an attractive screened Coulomb interaction between the electron and the hole, and a repulsive Coulomb exchange term. In practice, the BSE is solved by diagonalizing an effective two-particle Hamiltonian,

\[
H_{vc',cv'} = (\epsilon_v - \epsilon_c) \delta_{cc'} \delta_{vv'} + K_{vc,vc'}
\]

FIG. 1. Diagramatic representation of the Bethe-Salpeter equation. The BSE Kernel is expressed as the sum of the bare exchange Coulomb repulsion (single line) and the screened Coulomb attraction (double line) between the electron and the hole.
where $K_{vc,v'c'}$ is the static version of the BSE kernel, and the first term is the sum of the quasiparticle energies of the electron and hole. This Hamiltonian yields the exciton energies $Ω_S$ and electron-hole coefficients $A_{vc}^S$ for each exciton $S$. The resonant part of the bare exciton propagator in the quasiparticle basis can thus be written as

$$L_{vcv'c'}(ω) = \sum_S A_{vc}^S A_{v'c'}^S \omega - Ω_S + iη.$$  \hspace{1cm} (5)

Like the one-particle state indices, the label $S$ comprises a set of discrete quantum numbers as well as the center-of-mass momentum of the exciton ($q_S$) which is the wavevector difference ($k_e - k_h$) between the unoccupied and occupied single-particle orbitals that form the exciton. (The periodicity of the electron dictates that all free electron-hole pairs forming the exciton have the same wavevector difference modulo a reciprocal lattice.) Because of the small momentum carried by photons, only excitons with $q_S \approx 0$ are optically accessible. We will see that finite-momentum excitons ($q_S \neq 0$) are important to describe scattering events by phonons.

Since the $A_{vc}^S$ are eigenfunctions of the two-particle Hamiltonian, they form a complete orthonormal basis for the space spanned by the set of valence and conduction bands used to construct $H^2$. We can use these coefficients to transfer between the $vc$ basis and the $S$ basis. For example, the bare exciton propagator writes

$$L_{SS'}(ω) = \sum_{vc,v'c'} A_{vc}^S A_{v'c'}^S \sum_{vc,v'c'} \frac{1}{ω - Ω_S + iη}.$$ \hspace{1cm} (6)

The absorption spectrum at zero temperature without electron-phonon interaction can be constructed from the exciton energies and electron-hole coefficients. It takes the form

$$e''(ω) = \frac{4π^2e^2}{ω^2} \sum_S \sum_{vc} A_{vc}^S |v| \cdot e |c|^2 δ(ω - Δ + Ω_S)$$ \hspace{1cm} (7)

where $v$ is the velocity operator, $e$ is the photon’s polarization vector, and the summation over exciton states is restricted to zero-momentum excitons. The delta function in Eq. (7) is typically represented as a Lorentzian function with a certain broadening. In most past calculations, this broadening was chosen empirically to reproduce the available experimental data. The absorption line broadening is in fact related to the lifetime of the excitons and, as we show, can be computed from first principles.

B. Lattice dynamics and electron-phonon interaction

The lattice dynamics can be obtained from a self-consistent calculation of the dynamical matrix of the crystal ($Φ$), as detailed in Ref. 27. In real space, the dynamical matrix (or force matrix) corresponds to the second-order derivative of the total energy with respect to the displacement of two atoms: $Φ_{jk}^2(R_j - R_k) = \nabla_{kj} \nabla_{k'j'} E$, where $l$ labels a unit cell of the crystal with lattice vector $R_l$, $κ$ labels an atom in the unit cell, and $j$ labels a Cartesian direction. The phonon frequencies $ω_κ$ and polarization vectors $U_κ^j$ are obtained by diagonalizing the Fourier transform of $Φ$ as

$$M_κω_κ^2 U_κ^j = \sum_{κ',j} Φ_{κ'j}^j(q)U_κ^{j'}$$ \hspace{1cm} (8)

where $M_κ$ is the mass of an atom. The label $n$ for a phonon mode comprises a branch index and a wavevector ($q$ or $q_κ$). The DFPT method allows for the self-consistent calculation of the first-order derivative of the local potential with respect to atomic displacements, $V_{\lambda κj}SCF(r)$. Thanks to the Hellman-Feynman theorem and the $2n + 1$ theorem, only the first-order derivatives of the potential and density need to be computed self-consistently in order to construct the dynamical matrix $S_k$.

The phonon propagator is defined in time as $D_κ(t) = -i(\hat{T}_0 A_κ(t) A_κ(0))_0$, where $A_κ = a_κ^+ + a_κ$ is the sum of a phonon creation and annihilation operator. In frequency space, the phonon propagator writes as

$$D_κ(ω) = \frac{1}{ω - ω_κ + iη} - \frac{1}{ω + ω_κ + iη}.$$ \hspace{1cm} (9)

The electron-phonon interaction stems from the perturbation to the fixed-atoms Hamiltonian created by the phonons. A thorough discussion of the electron-phonon interaction in the context of DFT is presented in Ref. 29 and 51. Expanding the Hamiltonian up to second order in the atomic displacements, the electron-phonon coupling potential writes as

$$V_{\lambda κj} = V_{\lambda κj}^{(1)} + V_{\lambda κj}^{(2)} = \sum_κ \sum_{κ',j} g_{κ κ'}^{(2)} A_κ A_κ' c_κ^+ c_j + \sum_κ \sum_{κ',j} g_{κ κ'}^{(2)} A_κ A_κ' c_κ^+ c_j$$ \hspace{1cm} (10)

with the first-order electron-phonon coupling matrix elements

$$g_{κ κ'}^{(1)}(κ, q) = \sqrt{\frac{h}{2M ω_κ}} \langle φ_{κ + q}| ∇_q V_{SCF}(r) | φ_{κ'} \rangle$$ \hspace{1cm} (11)

and the second-order matrix elements

$$g_{κ κ'}^{(2)}(κ, q, κ, q') = \frac{h}{2M ω_κ ω_κ'} \langle φ_{κ + q + q'}| ∇_q V_{SCF}(r) ∇_{q'} V_{SCF}(r) | φ_{κ} \rangle.$$ \hspace{1cm} (12)

The derivative of the potential with respect to a phonon mode is defined as

$$∇_q V_{SCF}(r) = \sum_{κ j} U_κ^j(q)e_q R_l ∇_{lkj} V_{SCF}(r).$$ \hspace{1cm} (13)

The wavevectors $(κ, q)$ are written explicitly in Eq. (11) and (12), but will be omitted in the remainder of the paper to lighten the notation. Also, to make the units explicit, we use $h = 1$ and the mass $M$, which normalizes the phonon eigenvectors according to $∑_κ M_κ |U_κ^j|^2 = M$. It is useful to assign $M$ the value of the average mass of the atoms of the unit cell, so that the phonon eigenvectors are on the order of unity, and
the factor $1/M$ serves as an expansion parameter. Note that each summation over phonon modes in Eq. (10) is implicitly normalized by $\sqrt{N_q}$, where $N_q$ is the number of wavevectors used to sample the Brillouin zone.

The quantity $g_{ii'\lambda}$ is the electron-phonon coupling matrix element between the one-particle states $i$ and $i'$ via the phonon mode $\lambda$. Because of crystal momentum selection rule, for $g_{ii'\lambda}$ to be non-zero, we must have $k_i = k_{i'} + q_\lambda + G$ where $G$ is a reciprocal lattice vector that is non-zero for an Umklapp process. For $g_{ii'\lambda'}$, at the lowest order of perturbation theory, we must have $k_i = k_{i'}$ and $q_\lambda = -q_{\lambda'}$ for the wavevectors, and $\lambda' = \lambda$ for the branch indices. In practice, the second-order electron-phonon coupling matrix elements $g_{ii'\lambda\lambda'}^{(2)}$ are never computed explicitly. Their contribution to the self-energy is approximated in terms of the first-order electron-phonon coupling matrix elements by making use of the acoustic sum rule and the rigid-ion approximation.$^{35,56}$

C. One-particle propagators

We employ the Matsubara formalism to treat the propagators and self-energies at finite temperature. The propagators are defined on the imaginary time axis $\tau = it$ in the interval $[-\beta, \beta]$ with $\beta = 1/k_BT$, and are made periodic outside of this range. The one-particle propagator $G$ is composed of odd (fermionic) Matsubara frequencies, while the even frequencies compose all bosonic propagators: electron-hole ($L^0$), exciton ($L$), and phonon ($D$).

The interacting Green’s function $G$ can be expanded in powers of the perturbation as

$$G_{ii'}(\tau) = -\sum_{n=0}^{\infty} (-1)^n \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n$$

$$\times \langle T c_i(\tau) c_{i'}^\dagger(0) V_{ep}(\tau_1) \cdots V_{ep}(\tau_n) \rangle_0$$  \hspace{1cm} (14)

and we adopt the convention that in each expectation value $\langle \ldots \rangle$, only distinct and connected diagrams should be retained.$^{57}$ The time-dependent operators are expressed in the interaction picture, that is

$$e_i(\tau) = e^{i\hat{H}_0\tau} c_i(0) e^{-i\hat{H}_0\tau}$$ \hspace{1cm} (15)

with the mean field Hamiltonian $\hat{H}_0 = \sum_i \epsilon_i c_i^\dagger c_i$. Equation (14) can be cast into a Dyson equation for $G$, depicted in Fig. 2, as

$$G_{ii'}(\omega, T) = G_{ii'}^0(\omega) + \sum_{i'i''} G_{ii''}(\omega) \Sigma_{i'i''}(\omega, T) G_{ii'}(\omega, T)$$ \hspace{1cm} (16)

which defines the one-particle electron-phonon self-energy $\Sigma$

The perturbative expansion of $G$ with Eq. (14) yields powers of $V_{ep}^{(1)}$ and $V_{ep}^{(2)}$, where $V_{ep}^{(1)}$ appears an even number of times in each term. The Migdal theorem states that this expansion can be truncated to the lowest power of $1/M$. Since $V_{ep}^{(1)}$ is proportional to $1/\sqrt{M}$ and $V_{ep}^{(2)}$ is proportional to $1/M$.

![Fig. 2. Dyson equation for the one-particle propagator and the electron-phonon self-energy, expressed as the sum of the Fan-Migdal term and the Debye-Waller term.](image)

The self-energy can be cast into a Dyson equation for the one-particle propagator and the electron-phonon self-energy, expressed as the sum of the Fan-Migdal term and the Debye-Waller term. The two terms remain in the self-energy after truncation: the Fan-Migdal (FM) term and the Debye-Waller (DW) term, written as

$$\Sigma_{ii'}(\omega, T) = \Sigma_{ii'}^{FM}(\omega, T) + \Sigma_{ii'}^{DW}(T).$$  \hspace{1cm} (17)

The FM term is dynamic (i.e. complex and frequency-dependent) and stems from the first-order electron-phonon coupling potential. Its analytic expression is

$$\Sigma_{ii'}^{FM}(i\omega_n) = \sum_{i'i''} g_{ii''\lambda} g_{i'i''\lambda}^{(2)} [2N_B(\omega_n) + 1].$$  \hspace{1cm} (19)

The self-energy allows for the mixing of electronic states through the off-diagonal components of the self-energy ($i \neq i'$). This mixing is only possible among states with the same crystal momentum ($k_i = k_{i'}$). If the bands are well-separated in energy, one may use only the diagonal elements of the self-energy to obtain the renormalization of the bands as

$$\epsilon_i + \Delta \epsilon_i(T) = \epsilon_i + \text{Re}\Sigma_i(\epsilon_i, T)$$ \hspace{1cm} (20)

and in general, $\Delta \epsilon_i(0) \neq 0$. Correspondingly, the inverse lifetime of the electronic state is

$$\tau^{-1}_i(T) = 2|\text{Im}\Sigma_i(\epsilon_i, T)|.$$  \hspace{1cm} (21)

In Eq. (20) and (21), the temperature renormalization and lifetime is computed in the on-the-mass-shell limit, that is, by evaluating the self-energy at the bare energy, rather than the renormalized energy. This is the preferred approach for phonon perturbations, as it gives results in good agreement with a self-consistent calculation of the self-energy.$^{38}$
II. EXCITON-PHONON SELF-ENERGY: SELF-ENERGY OF EXCITONS FROM COUPLING TO PHONONS

We seek similar expressions for the exciton energy ($\Omega_\text{exc}$) and lifetime ($\tau_\text{exc}$) due to coupling to phonons that would allow one to compute absorption spectra at zero and finite temperature through Eq. (7). The phonon-induced corrections will be given by the diagonal components of the exciton-phonon self-energy ($\Xi_{\text{SS}}$) to be discussed below, namely,

$$\Omega_\text{exc} + \Delta\Omega_\text{exc}(T) = \Omega_\text{exc} + \text{Re}\Xi_{\text{SS}}(\Omega_\text{exc}, T)$$

(22)

for the exciton energies, and

$$\tau_\text{exc}^{-1}(T) = 2|\text{Im}\Xi_{\text{SS}}(\Omega_\text{exc}, T)|$$

(23)

for the inverse lifetime of the excitons, that is, the absorption line broadening.

The expression for the exciton-phonon self-energy is obtained by considering the interacting exciton propagator ($\Lambda$) defined as

$$\Lambda_{\text{exc}}(\tau) = -\sum_{n=0}^{\infty}(-1)^n\int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n \times \langle T c\gamma(\tau^+)c\gamma(\tau) c\gamma(0)^+=0\rangle \hat{H}_1(\tau_1) \cdots \hat{H}_1(\tau_n)\rangle_0$$

(24)

where $\tau^+$ is a time infinitesimally larger than $\tau$, and the interaction term $\hat{H}_1(\tau)$ is the sum of the static electron-hole interaction kernel $\hat{K}$ and the electron-phonon coupling potential $\hat{V}_{\text{ep}}$. Equation (24) reduces to the BSE if $\hat{V}_{\text{ep}} = 0$.

The exciton-phonon self-energy connects the interacting exciton propagator $\Lambda$ to the bare exciton propagator $L$ (without electron-phonon interaction) in a Dyson-like equation:

$$\Lambda_{\text{SS}}(\omega, T) = L_{\text{SS}}(\omega) + \sum_{S_1S_2} L_{S_1S_2}(\omega) \Xi_{S_1S_2}(\omega, T) \Lambda_{S_2S'}(\omega, T).$$

(25)

In order to express the exciton-phonon self-energy in an analytic form, it is useful to first consider the case without the electron-hole interaction.

A. Independent electron-hole-pair-phonon self-energy

We define $\Lambda^0$ as the electron-hole propagator with the electron-phonon interaction, but without the electron-hole interaction, calling it the independent electron-hole-pair-phonon (IEHPP) propagator, given by

$$\Lambda^0_{\text{exc}}(\tau) = -\sum_{n=0}^{\infty}(-1)^n\int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n \times \langle T c\gamma(\tau^+)c\gamma(\tau) c\gamma(0)^+=0\rangle \hat{V}_{\text{ep}}(\tau_1) \cdots \hat{V}_{\text{ep}}(\tau_n)\rangle_0$$

(26)

The corresponding IEHPP self-energy $\Xi^0$ is defined through the Dyson equation

$$\Lambda^0_{\text{exc}}(\omega, T) = \Xi^0_{\text{exc}}(\omega) + \sum_{\nu\nu'} L_{\text{exc}}(\omega, T) \Xi^0_{\text{exc}}(\omega, T)$$

(27)

which is depicted in Fig. 3.

A detailed derivation of $\Xi^0$ is provided in supplemental materials. Throughout this derivation, we assume the existence of a band gap that does not allow for a significant density of thermal carriers at the temperature of interest, which is typically room temperature, where $E_g > k_B T$.

The different contributions to the IEHPP self-energy are grouped in three terms, according to the topology of the diagrams depicted in Fig. 4.

$$\Xi^0_{\text{exc}}(\omega, T) = \Xi^0_{\text{exc}}^\text{FM}(\omega, T) + \Xi^0_{\text{exc}}^\text{X}(\omega, T) + \Xi^0_{\text{exc}}^\text{DW}(\omega, T).$$

(28)

The Fan-Migdal term is further split in two contributions: the dynamic term (FMD) and the static term (FMs),

$$\Xi^0_{\text{exc}}^\text{FM}(\omega, T) = \Xi^0_{\text{exc}}^\text{FMD}(\omega, T) + \Xi^0_{\text{exc}}^\text{FMs}(\omega, T).$$

(29)

The dynamic FM describes the propagation of an electron-hole pair being temporarily knocked into a different electron-hole state while absorbing/emitting a phonon. Either the hole scatters into another valence state of different momentum, or the electron scatters into another conduction state. Its diagrammatic expression is given by

$$\Xi^0_{\text{exc}}^\text{FM}(i\omega_n) = -\frac{1}{\beta} \sum_{\lambda} D_{\lambda}(i\omega_n) \Lambda^0_{\text{exc}}(i\omega_n + i\omega_n) \times \left[ g_{\gamma'\nu'\lambda} g_{\gamma'\nu'\lambda} \delta_{\gamma\nu\lambda} + g_{\gamma'\nu'\lambda} g_{\gamma'\nu'\lambda} \delta_{\nu\gamma'\lambda} \delta_{\gamma'\nu'\lambda} \right].$$

(30)

Performing the convolution of the bare electron-hole propagator $L^0$ with the phonon propagator $D$, we obtain the analytic expression

$$\Xi^0_{\text{exc}}^\text{FMD}(i\omega_n) = \sum_{\lambda} \sum_{\nu'\nu} g_{\gamma'\nu'\lambda} g_{\gamma'\nu'\lambda} \delta_{\gamma\nu\lambda} \times \left[ N_B(\omega_n) - N_B(\epsilon_\nu' - \epsilon_\nu) \right] \frac{1 + N_B(\epsilon_\nu' - \epsilon_\nu)}{2\omega_n} + \frac{N_B(\omega_n)}{2\omega_n} \frac{1 + N_B(\epsilon_\nu' - \epsilon_\nu)}{2\omega_n}$$

$$+ \sum_{\nu'\nu} g_{\gamma'\nu'\lambda} g_{\gamma'\nu'\lambda} \delta_{\gamma\nu\lambda}$$

$$+ \frac{N_B(\omega_n) - N_B(\epsilon_\nu - \epsilon_\nu)}{2\omega_n} \frac{1 + N_B(\epsilon_\nu - \epsilon_\nu)}{2\omega_n}$$

(31)
term. It is given by

\[
\Sigma_{\text{IEHPP}} = \sum_{\alpha} \frac{1}{\beta} \sum_{\alpha'} \sum_{\nu''} \sum_{\nu'''} D_\alpha (i\omega_n) L_{\alpha'\nu''\nu'''}^0 (i\omega_m) \left( g_{\nu''\nu'''}^{\alpha \alpha'} g_{\nu''\nu'''}^{\nu'''} \right) \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} + g_{\nu''\nu'''}^{\alpha \alpha'} g_{\nu''\nu'''}^{\nu'''} \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

and its analytic expression is

\[
\Sigma_{\text{IEHPP}}^{(\alpha \alpha')} = \sum_{\nu''} \sum_{\nu'''} g_{\nu''\nu'''}^{\alpha \alpha'} g_{\nu''\nu'''}^{\nu'''} \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

where the symbol \( \mathcal{S} \) means that the terms in brackets should be symmetrized with the substitution \( v, c \leftrightarrow v', c' \) and a factor of \( 1/2 \). The static FM term includes transitions that cannot be described as an intermediate electron-hole pair, such as the hole being coupled to a conduction band state or the electron being coupled to a valence band state. These transitions are only virtual, in the sense that they do not conserve energy and do not contribute to the imaginary part of the self-energy.

The next set of diagrams are the phonon exchange (X) term, defined as

\[
\Xi_{\text{X}}^{(\alpha \alpha')} = \sum_{\lambda} g_{\nu''\nu'''}^{\alpha \alpha'} g_{\nu''\nu'''}^{\nu'''} \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

and one can safely assume that \( N_B (\epsilon_c - \epsilon_v, T) \ll N_B (\omega_h, T) \).

The static FM term has the same topology as the dynamic FM term. It is given by

\[
\Xi_{\text{FM}}^{(\alpha \alpha')} = \frac{1}{\beta} \sum_{\nu''} g_{\nu''}^{\alpha \alpha'} g_{\nu''}^{\nu'''} \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

In this process, the electron emits a phonon that is being absorbed later on by the hole, or vice-versa. This term is exclusively off-diagonal, since the electron and the hole exchange momentum and are being scattered into different states. It will be non-zero only when \( k_e = k_c + q_h + \mathbf{G} \) and \( k_v = k_c + q_e + \mathbf{G} \).

Finally, the Debye-Waller contribution to \( \Xi_0 \) is simply the second-order interaction of the electron and the hole with the phonon modes, giving

\[
\Xi_{\text{DW}}^{(\alpha \alpha')} = \frac{1}{\beta} \sum_{\lambda} \left[ g_{\nu''}^{\alpha \alpha'} \delta_{\nu''\nu'''} - g_{\nu''}^{\nu'''} \delta_{\nu''\nu'''} \right] \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

Consider a non-interacting electron-hole excited state with energy \( \epsilon_e - \epsilon_v \). We can show that the diagonal component of the IEHPP self-energy for this state is

\[
\Xi_{\text{IEHPP}}^{(\epsilon_e - \epsilon_v)} = \sum_{\nu''} \sum_{\nu'''} g_{\nu''\nu'''} \delta_{\nu''\nu'''} \delta_{\nu''\nu'''} \right)
\]

This is the expected result. Without the electron-hole interaction, the corrections to the optical excitations are simply given by the electron-phonon interaction corrections to the one-particle energies that make up the transitions. Since the imaginary part of the self-energy has opposite signs for electrons and holes, we also have that

\[
|\text{Im} \Sigma_{\text{IEHPP}}^{(\epsilon_e - \epsilon_v)}| = |\text{Im} \Sigma_{\text{IEHPP}}^{(\epsilon_v - \epsilon_e)}| + |\text{Im} \Sigma_{\text{IEHPP}}^{(\epsilon_e - \epsilon_v)}|.
\]

The broadening of a non-interacting electron-hole transition is thus the sum of the broadenings of the one-particle states.

### B. Exciton-phonon self-energy

The exciton-phonon self-energy \( \Xi \) is obtained by expanding the interacting exciton propagator \( \Lambda \) in the bare exciton basis as

\[
\Lambda_{\text{SS'}}^{(\tau)} = \sum_{n=0}^{\infty} (-1)^n \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n \times \langle T c_{\nu''} (\tau) c_{\nu'''} (0) \bar{V}_{\nu''} (\tau_1) \cdots \bar{V}_{\nu'''} (\tau_n) \rangle_0 + \Lambda_{\text{SS'}}^{\text{non-excitonic}} (\tau)
\]
where the last term regroups all the “non-excitonic” diagrams and will be discussed further below. In this formulation, the electron-hole interaction is already included in \( L \) (the bare exciton propagator without considering coupling of the exciton to phonons), and one needs to expand the perturbation in powers of \( V_{ep} \) only. The solution is thus analogous to the one-particle case, i.e., considering an exciton as a single particle interacting with the phonons. The physical motivation for this formulation is that the two kinds of processes occur on different time scales. The electron-hole interaction is much faster than the electron-phonon interaction, since the plasmon frequency is much larger than the typical phonon frequency.

We define the exciton annihilation operator as

\[ c_S = \sum_{vc} A^S_{vc} c^\dagger_v c_c \]  

with the coefficient \( A^S \) from solving the BSE, and we treat these excitations as bosons. This treatment is not exact, since the Bose commutation relations are not exactly fulfilled by the operators in Eq. \( (40) \). However, in the low exciton density limit\(^9\) we can take

\[ [c_S, c^\dagger_{S'}] = c_c c^\dagger_{S'} - c^\dagger_{S'} c_c = \delta_{SS'} . \]  

The bare exciton propagator is diagonal in the exciton basis and is formally defined as

\[ L_{SS'}(\tau) = - \langle e^{i\vec{k}^2 p} c_S(0) e^{-i\vec{k}^2 p} \rangle_{2p0} \]  

where the subscript \( 2p0 \) refers to the ground state of a Hamiltonian that includes electron-hole interactions through the BSE kernel but does not include electron-phonon interactions. In this picture, the time dependence of the operators is given by

\[ c_S(\tau) = e^{i\vec{k}^2 p} c_S(0) e^{-i\vec{k}^2 p} \]  

with the two-particle Hamiltonian \( \vec{H}^2 p = \sum S \Omega_S c^\dagger_c c_S \). The perturbation terms \( V_{ep} = V^{(1)}_{ep} + V^{(2)}_{ep} \) appearing in Eq. \( (39) \) may be expressed in the exciton basis as

\[ V^{(1)}_{ep} = \sum_{SS'\lambda} g^{(1)}_{SS'\lambda} A^\dagger_{\lambda} c^\dagger_v c^\dagger_c S' \]  

and

\[ V^{(2)}_{ep} = \sum_{SS'\lambda'} g^{(2)}_{SS'\lambda\lambda'} A^\dagger_{\lambda'} A^\dagger_{\lambda} c^\dagger_v c^\dagger_c S' \]  

Here, as defined above, \( A^\dagger_{\lambda} \) is a sum of a phonon creation and annihilation operator, (not to be confused with the electron-hole coefficients \( A^\dagger_{vc} \)). The first- and second-order exciton-phonon coupling matrix elements are the transition amplitude between two exciton states mediated by the electron-phonon coupling potential, e.g.

\[ g_{SS'\lambda} = \langle S' | (\sum \hat{g}_{i\lambda} c^\dagger_i c_p) | S \rangle = \sum_{i\lambda} \langle c^\dagger_i c^\dagger_p | S \rangle g_{i\lambda} \]  

Using Eq. \( (40) \) and \( (1) \) to simplify the expectation values and discarding terms like \( \delta_{SS'} \sum \hat{g}_{v\lambda} \) which produce disconnected diagrams, we arrive at the expressions

\[ g_{SS'\lambda} = \sum_{vc,iv'} A^S_{vc} A^S_{iv'} \left[ \hat{g}_{cc'} \delta_{vi'} - g_{v\lambda} \delta_{c'} \right] \]  

and

\[ g^{(2)}_{SS'\lambda\lambda'} = \sum_{vc,iv'} A^S_{vc} A^S_{iv'} \left[ \hat{g}_{cc'} \delta_{vi'} - g^{(2)}_{v\lambda} \delta_{c'} \right] . \]  

Momentum conservation dictates that \( q_S = q_{S'} + q_{\lambda} \) for \( g_{SS'\lambda} \) to be nonzero, while \( q_{S'} = q_S \) for \( g^{(2)}_{SS'\lambda\lambda'} \). It is worth writing explicitly all the wavevectors in these expressions. For an exciton \( S' \) with center-of-mass momentum \( q_{S'} = Q \) and an exciton \( S \) with center-of-mass momentum \( q_S = q + \mathbf{q} \), the first-order matrix element writes as

\[ g^{(1)}_{SS'\lambda}(Q, \mathbf{q}) = \sum_{vc, k} A^{S\rightarrow Q}_{vc, k} A^{S\rightarrow Q}_{v, k} g_{v\lambda, k}(k + Q, \mathbf{q}) \]  

\[ - \sum_{vv', k} A^{Q,vv,\lambda}_{v', k} A^{Q,vv',\lambda}_{v', k} g_{v\lambda, k}(k, \mathbf{q}) \]  

where \( A^{SQ} \) is the coefficient of the exciton envelope function in \( k \)-space for a hole at \( k \) and an electron at \( k + Q \). We note that \( (Q, \mathbf{q}) \) are not Fourier components of the matrix element; they are momentum information in fact that is contained in the quantum numbers \( S \) and \( S' \). Here we use a somewhat redundant notations to draw out the physics of center-of-mass momentum conservation of the excitons. The second-order matrix elements between two exciton states with the same momentum \( Q \) are

\[ g^{(2)}_{SS'\lambda\lambda'}(Q, \mathbf{q}) = \sum_{vc, iv', k} A^{Q\rightarrow v\lambda}_{vc, k} A^{Q\rightarrow v\lambda}_{v', k} \]  

\[ \times \left[ \hat{g}_{v\lambda, k}(k, \mathbf{q}, -\mathbf{q}) \delta_{vi'} - g^{(2)}_{v\lambda, k}(k, \mathbf{q}, -\mathbf{q}) \delta_{c'} \right] . \]  

Note that the second-order matrix elements do not transfer momentum between the exciton states, even when \( q \neq 0 \).

We may now compute the self-energy from Eq. \( (39) \). Some of the diagrams using quasiparticle (electron/hole) basis for the exciton-phonon self-energy up to second order in electron-phonon coupling are illustrated in Fig. 5. The Debye-Waller diagram coming from the second-order matrix element is

\[ \Xi^{DW}_{SS} = \sum_{\lambda} g^{(2)}_{SS\lambda\lambda} [2 N_p (\Omega_\lambda) + 1] . \]  

This is the same result as for the case without electron-hole interactions, meaning that, using the basis transformation rule of Eq. \( (6) \), we find \( \Xi^{DW}_{SS} = \Sigma^{DW}_{SS} \).

The first-order coupling matrix elements yield the Fano-Migdal term. In the perturbative expansion of \( \Lambda \), the first term of Eq. \( (39) \) produces only the dynamic part of the FM term,
since only this part can be expressed in terms of $g_{SS'}\lambda$. It is given by

$$\Xi_{SS'}^{\text{FM}}(i\omega_n) = -\frac{1}{\beta} \sum_{m\lambda, S''} g_{SS''\lambda} g_{SS'\lambda}^{*} D_{\lambda}(i\omega_n) L_{SS''}(i\omega_n + i\omega_n)$$

with the analytic expression

$$\Xi_{SS'}^{\text{FM}}(i\omega_n) = \sum_{\lambda} \sum_{S''} g_{SS''\lambda} g_{SS'\lambda}^{*} \left[ \frac{N_{B}(\omega_{\lambda}) - N_{B}(\Omega_{S''})}{i\omega_n - \Omega_{S''} + \omega_{\lambda}} + N_{B}(\omega_{\lambda}) + 1 + N_{B}(\Omega_{S''}) \right].$$

We can verify that in the limit where the electron-hole interaction vanishes, that is, when each exciton is composed of a single electronic transition, Eq. (53) reduces to Eq. (31).

In the exciton basis, the phonon exchange term doesn’t need to be added; it is included in the dynamic FM term. This term arises from the cross terms between valence-to-valence and conduction-to-conduction bands coupling when squaring Eq. (47). Since the exciton states mix several electronic transitions across the Brillouin zone, the phonon exchange term does contribute to the diagonal elements of $\Xi$.

All other diagrams of $\Lambda$ in which the scattered state cannot be projected onto the exciton basis are contained in $\Lambda^{\text{non-excitonic}}$. One such diagram is obtained from the static FM term. Therefore, we complete the interacting FM self-energy by adding the static FM term of Eq. (33) so that

$$\Xi_{SS'}^{\text{FM}}(i\omega_n) = \Xi_{SS'}^{\text{FM}}(i\omega_n) + \Xi_{SS'}^{\text{FM}}$$

with $\Xi_{SS'}^{\text{FM}} = \Xi_{SS'}^{\text{FM}}$. Using the non-interacting static FM term here is an approximation. Since the static FM term is composed of virtual transitions across the band gap, the relative error induced by this approximation is at most on the order of $E_{b}^{S}/E_{g}$, where $E_{b}^{S}$ is the binding energy of the exciton.

As formulated, in practical implementation, there will be an additional term in the self-energy, which contributes to $\Lambda^{\text{non-excitonic}}$. Most of the time, the basis of valence and conduction bands used to expand the exciton wavefunctions is not complete; only a subset of the bands are used. Moreover, one typically doesn’t compute all the possible excitons states, but only the first few solutions of the BSE with the lowest eigenvalues. Therefore, there will be a missing contribution to $\Xi_{SS'}^{\text{FM}}$, which we call the completion term, written as $\Xi_{SS'}^{C}$. Since the missing contribution involves high-energy states, this term can be computed by taking these states as free electron-hole pairs. One can construct $\Xi_{SS'}^{C}$ from the expression of $\Xi_{SS'}^{0}$, where the intermediate states $\nu''$ and $c''$ are projected outside of the basis of excitons that were computed. An example of this procedure is given in Sec. III.

Collecting all terms, the final expression for the exciton-phonon self-energy reads

$$\Xi_{SS'}(\omega, T) = \Xi_{SS'}^{\text{FM}}(\omega, T) + \Xi_{SS'}^{\text{FM}}(T) + \Xi_{SS'}^{\text{DW}}(T) + \Xi_{SS'}^{C}(\omega, T).$$

Thus, $\Xi$ contains all the diagrams of $\Xi_{SS'}^{0}$ but with addition of the electron-hole interaction diagrams, as shown in Fig. 5.

Note that $\Xi_{SS'}^{0}$ is complex and frequency-dependent, but its imaginary part is non-zero only at frequencies far from the bare exciton energy, and its real part varies smoothly near the exciton energy. Hence, near the exciton energy ($\Omega_{S}$) we may consider that only the dynamic Fan-Migdal term contributes to the imaginary part of the self-energy, which is

$$\text{Im}\Xi_{SS'}(\omega, T) = -\pi \sum_{\lambda} \sum_{S''} g_{SS''\lambda} g_{SS'\lambda}^{*}$$

$$\times \left[ \frac{N_{B}(\omega_{\lambda}) - N_{B}(\Omega_{S''})}{i\omega_n - \Omega_{S''} + \omega_{\lambda}} + N_{B}(\omega_{\lambda}) + 1 + N_{B}(\Omega_{S''}) \delta(\omega - \Omega_{S''} - \omega_{\lambda}) \right].$$

The temperature renormalization of the exciton energies and their lifetime can finally be computed according to Eqs. (22) and (23).

C. Approximate expressions

Since the excitation energies are usually much larger than the phonon frequencies, it is a safe approximation to use the fact that $N_{B}(\Omega_{S}, T) \ll N_{B}(\omega_{\lambda}, T)$ and write for the diagonal part of the self energy

$$\Xi_{SS'}^{\text{FM}}(\omega, T) = \sum_{\lambda} \sum_{S''} g_{SS''\lambda} g_{SS'\lambda}^{*}$$

$$\times \left[ \frac{N_{B}(\omega_{\lambda}, T)}{\omega - \Omega_{S''} \omega_{\lambda} + i\eta} + \frac{N_{B}(\omega_{\lambda}, T) + 1}{\omega - \Omega_{S''} - \omega_{\lambda} + i\eta} \right].$$

Let us compare the full exciton-phonon self-energy with approximate expressions found in literature. We first define the "uncorrelated exciton" (UE) approximation to the exciton-
phonon self-energy:

$$\Xi_{SS}^{UE} = \sum_{vc} |A_{vc}^s|^2 \Xi_{vcvc}^0 (\varepsilon_v - \varepsilon_c) = \sum_{vc} |A_{vc}^s|^2 \left[ \sum_c (\varepsilon_v - \varepsilon_c) \right]$$

(58)

This approach is equivalent to the one used in previous studies. Several approximations have been made between Eqs. (55) and (58). First, the UE self-energy is constructed using the independent electron-hole-pair-phonon propagator (IEHPP). Then, only the diagonal elements of $\Xi^0$ are used when transforming from the one-particle basis to the exciton basis. Finally, the self-energy is being evaluated at the non-interacting transition energies. The uncorrelated exciton approximation reduces tremendously the computational effort needed to obtain the self-energy, since the knowledge of the finite-momentum exciton states is no longer required. However, it does not yield accurate results for the lifetime of bound excitons, as we show in the next section.

In this approximation, the uncorrelated exciton is just a wavepacket composed of electron-hole pairs that do not interact with each other and hence there is no binding energy. This becomes apparent when looking at the imaginary part of the self-energy. Using Eq. (31), the imaginary part of $\Xi_{SS}^{UE}$ writes as

$$\text{Im}\Xi_{SS}^{UE} = -\pi \sum_{\lambda} \sum_{vc} |A_{vc}^s|^2 \left\{ \sum_{\varepsilon'} |g_{vc\varepsilon'\lambda}|^2 \left[ (N_B(\omega_{\lambda} + f(\varepsilon_{\varepsilon'})) \delta(\varepsilon_v - \varepsilon_c + \omega_{\lambda}) + (N_B(\omega_{\lambda} + 1 - f(\varepsilon_{\varepsilon'})) \delta(\varepsilon_v - \varepsilon_c - \omega_{\lambda}) + \sum_{\varepsilon''} |g_{vc\varepsilon''\lambda}|^2 \left[ (N_B(\omega_{\lambda}) + f(\varepsilon_{\varepsilon''})) \delta(\varepsilon_v - \varepsilon_c + \omega_{\lambda}) + (N_B(\omega_{\lambda}) + 1 - f(\varepsilon_{\varepsilon''})) \delta(\varepsilon_v - \varepsilon_c - \omega_{\lambda}) \right] \right] \right\}$$

(59)

Compare this expression with Eq. (56), where the scattering occurs between exciton states. This very drastic approximation in past studies creates a qualitative difference in the physics of the exciton in the low temperature limit, where $N_B(\omega_{\lambda} + T) \rightarrow 0$. For the lowest bound exciton, from Eq. (56), no states are available for scattering through phonon emission. Hence, the electron-phonon interaction does not contribute to its inverse lifetime. The physical lifetime of this exciton comes from other processes, such as radiative recombination or scattering by impurities. In the UE approximation however, scattering events still occur because the binding energy of the initial and final states are ignored, and the lowest bound exciton has an unphysical lifetime at zero temperature.

For the temperature-dependent energy shift of the excitonic peaks, the accuracy of the UE approximation is unknown at this point. In the following section, we gain some intuition on this matter by computing the self-energy in a model system.

III. APPLICATION TO A MODEL SYSTEM

To illustrate the theory, we present a two-band model in two dimensions, and compute the energy and lifetime of optical excitations as a function of temperature. We use the triangular lattice exciton model proposed by D. Gunlycke and F. Tseng, which mimics the spin-dependent band dispersion of transition metal dichalcogenides near the $K$ and $K'$ valleys, and yields realistic exciton binding energies. The main equations are reported below, and we refer the reader to Ref. 61 for further details of this model.

A. One-particle and two-particle Hamiltonians

The one-particle tight-binding Hamiltonian is $H = \sum_{n\sigma} H_{n\sigma}$ with

$$H_{n\sigma} = \sum_{\mathbf{R}, \delta} t_{n\sigma \delta} c_{n\sigma \mathbf{R}+ \delta}^\dagger c_{n\sigma \mathbf{R}} + \sum_{\mathbf{R}} \varepsilon_n c_{n\sigma \mathbf{R}}^\dagger c_{n\sigma \mathbf{R}}$$

(60)

where $c_{n\sigma \mathbf{R}}^\dagger$ and $c_{n\sigma \mathbf{R}}$ are creation and destruction operators for an electron in the $n^{th}$ orbital on the lattice site $\mathbf{R}$ with spin $\sigma$. 

FIG. 6. a–Two-band model electronic structure for the different spin states $|\uparrow\rangle$ (orange) and $|\downarrow\rangle$ (blue). b–Exciton band structure for the different spin states $|\uparrow\downarrow\rangle$ (orange) and $|\downarrow\uparrow\rangle$ (blue). The filled regions represent the continuum of excited states. c–f–Real space wavefunction $|A^s(\mathbf{R}, \mathbf{Q})\rangle^2$ of the first four optically accessible excitons ($S = 1 - 4, \mathbf{Q} = \Gamma$).
The first term describes the hopping between a site and one of its six closest neighbours, where $\delta$ is the lattice vector from one site to the other. The hopping amplitude is composed of a spatial amplitude $t_n$ and a spin-orbit coupling parameter $\bar{t}_n$ according to

$$t_{n\sigma\delta} = t_n + 4i\sigma\bar{t}_n\sin(K \cdot \delta)$$

where $\sigma = \pm 1/2$ and $K$ is one corner of the 2D hexagonal Brillouin zone. The second term of Eq. (60) is diagonal in lattice site, with $\epsilon_n$ being the on-site parameters. The solutions for the one-particle energies at wavevector $k$ are

$$\epsilon_{n\sigma k} = \epsilon_n + \sum_\delta t_{n\sigma\delta}e^{-ik\cdot\delta}.$$  

(62)

In order for this Hamiltonian to reproduce the main features of typical transition metal dichalcogenides for the valence (v) and conduction (c) band, the parameters are chosen by imposing that the band structure has a band gap $E_g$ located at the $K$ and $K'$ valleys, with band effective masses $m^*$ and a splitting $\Delta$ between different spin bands. The on-site and hopping parameters are thus

$$\epsilon_c = 3t + E_g, \quad \epsilon_v = -3t - \Delta/2, \quad \bar{t}_c = t, \quad \bar{t}_v = -t.$$

with $t = 2\hbar^2/3m^*a^2$ and $a$ is the lattice constant. The resulting band structure is shown in Fig. 6(a) with the parameters $m^* = 0.49, a = 3.13$ Bohr, $E_g = 2.5$ eV, and $\Delta = 425$ meV. Each spin channel admits one valence band and one conduction band. The two spin channels are degenerate for the conduction band, while for the valence band, the splitting of the up and down spins due to spin-orbit coupling reaches a maximum at the $K$ and $K'$ points in the Brillouin zone.

The BSE Hamiltonian, which yields the exciton bands, is made of two terms: the kinetic energy, and the Coulomb interaction between the electron and the hole. Translational symmetry implies that the exciton states possess a well-defined center-of-mass momentum $Q$, and the BSE Hamiltonian writes

$$H_{\sigma Q} = \sum_{k,R} T_{\sigma Q} b_{\sigma R}^\dagger b_{\sigma R} + \sum_{k,R} \left( \epsilon_c - \epsilon_v - V(R) \right) b_{\sigma R}^\dagger b_{\sigma R} + \sum_{Q} \left( \epsilon_c - \epsilon_v - V(R) \right) b_{\sigma R}^\dagger b_{\sigma R}$$

where $b_{\sigma R}^\dagger$ creates an electron at $R_c = R$ with spin $\sigma$, and a hole at $R_h = 0$ with spin $-\sigma$, meaning that no spin-flip occurs in this process. The BSE hopping parameter carries the information on the exciton momentum, and writes

$$T_{\sigma Q \delta} = t_{\nu \sigma \delta} e^{-iQ \cdot \delta/2} - t_{\nu \sigma \delta} e^{-iQ \cdot \bar{\delta}/2}.$$  

(64)

Together, the on-site terms that involve $\epsilon_c$ and $\epsilon_v$ and the hopping term form the kinetic energy component of the excitons. In this model, the Coulomb interaction term is simply taken to be

$$V(R) = \begin{cases} \Delta\nu_0 & (R = 0) \\ \frac{\epsilon^2}{4\pi\varepsilon R} & (R \neq 0) \end{cases}$$  

(65)

where $\varepsilon$ is the dielectric constant of the medium and $\Delta\nu_0$ is the difference between the screened Coulomb interaction and the bare exchange integral at $R = 0$, which we set to $\Delta\nu_0 = 1.6$ eV. Note that, for this model, the spin degrees of freedom do not mix, and at $\Gamma$, both spin channels are equivalent and can be interpreted as singlet exciton states. In what follows, we will assume that the phonons are non-magnetic and cannot flip the spin. The index $\sigma$ will thus be omitted.

Due to the sparse nature of a Hamiltonian with nearest-neighbour hopping, the BSE can be solved efficiently in real space for all $Q$-vectors. Solving the BSE yields the exciton energies $\Omega_{Q\delta}$ and wavefunctions in real space $A^\delta(R,Q)$. Their Fourier transform give the electron-hole coefficients $A^\delta(k,Q)$. Note that, within this model, it is not necessary to specify the one-particle band indices for these coefficients, since there is only a single valence band and conduction band.

The exciton band structure is shown in Fig 6(b). The binding energy of the first four optical excitons is between 100 and 500 meV, and their wavefunction in real space is depicted in Fig. 6(c-f).

**B. Exciton-phonon coupling**

We model the lattice vibration spectrum as a single dispersionless phonon band with frequency $\omega_0$. The electron-phonon coupling strength is also taken to be independent of the phonon wavevector, and we use a single parameter $g$ to represent intra-band coupling ($g_{cc} = g_{vv} = g$; $g_{cv} = 0$). For simplicity of notation, we write the intra-band coupling as $g_{cc} = g_{vv} = g$, and a split-valley hopping parameter $g_{cv}$ as $g_{cv} = 0$. In the present calculation, we set $\omega_0 = 50$ meV and $g = 250$ meV.

The IEHPP self-energy for a hole at $k$ and an electron at $k + \Gamma$ is diagonal in $k$ indices and is given by

$$\Sigma^0_{\Gamma k}(\omega, T) = \sum_q \Sigma^0_{\Gamma k,q}(\omega, T) = \sum_q \frac{|g_c|^2 P_\pm(T)}{\omega - (\epsilon_k + q_\pm \epsilon_{\Gamma}) \pm i\eta} + \frac{|g_v|^2 P_\pm(T)}{\omega - (\epsilon_k - q_\pm \epsilon_{\Gamma}) \pm i\eta}$$

where $P_\pm(T) = N_B(\omega, T) + P_\mp(T) = N_B(\omega, T) + 1$ correspond to phonon absorption and emission channels, respectively, and both channels must be added. In the exciton basis, $\Sigma^0$ is non-diagonal in the indices $S, S'$, but remains diagonal in the wavevector $Q$. Here, we consider only the optical excitons, and we use $\Sigma^0_{\Gamma S}$ to denote the diagonal elements of $\Sigma$. The IEHPP self-energy in the exciton basis is

$$\Sigma^0_{\Gamma S} = \sum_q \sum_q \Sigma^0_{\Gamma k,q}(\omega, T) = \sum_q \sum_k \left| A^\delta(k, \Gamma) \right|^2 \Sigma^0_{\Gamma k,q}(\omega, T)$$

(67)

and we have introduced the symbols $\Sigma^0_{\Gamma k,q}$ and $\Sigma^0_{\Gamma k,q}$ to denote an individual $q$-point’s contribution to the IEHPP self-energy. The exciton-phonon coupling matrix elements are

$$g_{SS'}(Q, q) = \sum_k A^S(k, Q + q) A^{S'}(k, Q) g_c$$

$$- A^S(k, Q + q) A^{S'}(k + q, Q) g_v$$

(68)
and the exciton self-energy is given by

$$\Xi_{T\Sigma}(\omega, T) = \sum_{q} \sum_{S} \frac{|g_{S\delta}(\Gamma, q)|^2 P_{c}(T)}{\omega - \Omega_{q} \pm \omega_{q} + i\eta}. \quad (69)$$

In general, the completion term for the self-energy contains the contribution of the valence and conduction bands excluded from the two-particle basis, as well as the contribution of the exciton states that are not explicitly computed. Within this model, all the electron bands are included in the basis, but only the first $N$ exciton bands are computed. The completion term thus corresponds to the contribution of the remaining exciton states ($S' > N$). We express the completion term in the form

$$\Xi_{T\Sigma}^{C}(\omega, T) = \sum_{q} \left(1 - \frac{\tilde{\xi}_{T\Sigma}(q)}{\tilde{\xi}_{T\Sigma}(q)}\right) \Xi_{T\Sigma,q}^{0}(\omega, T), \quad (70)$$

where we define the partial sum

$$\tilde{\xi}_{T\Sigma}(q) = \sum_{S=1}^{N} |g_{SS}(\Gamma, q)|^2. \quad (71)$$

and the corresponding summation over all exciton states can be obtained with the sum rule

$$\tilde{\xi}_{T\Sigma}(q) = \sum_{S} |g_{SS}(\Gamma, q)|^2 \quad (72)$$

$$= |\epsilon_{c}|^2 + |\epsilon_{v}|^2 - 2\epsilon_{c}\epsilon_{v} \sum_{k} A^{s_{1}}(k + q, \Gamma) A^{s_{2}}(k, \Gamma).$$

The ratio $\tilde{\xi}_{T\Sigma}(q)/\tilde{\xi}_{T\Sigma}(q)$ thus describes how much the first $N$ excitons probe the space of available states at wavevector $q$ for the exciton $\Gamma S$ to couple with.

### C. Results and discussion

Figure 7(a-b) presents the $q$-space convergence of the imaginary part of the exciton-phonon self-energy. The use of a finite value for the infinitesimal parameter $\eta$ eases the convergence with respect to the number of $q$-points, but also introduces an arbitrarily small error in the lifetimes. For the first optical exciton ($S = 1$ in the exciton labeling), the inverse lifetime due to phonons is known to be zero at $T = 0$, since this exciton cannot scatter into a lower energy states by phonon emission. The finite value obtained for $\text{Im}\xi$ with a converged $q$-grid thus indicates the magnitude of the error. A value of $\eta = 10$ meV yields an error smaller than 3 meV for the self-energy, and we use this value for the following computations of $\Xi$. For the second optical exciton state ($S = 2$), we conclude that a $48 \times 48$ $q$-grid is well converged. The temperature-dependent energy shift and the spectral width for the seven lowest exciton states are presented in Fig. 7c. The lowest exciton state, having the largest binding energy, consequently has a longer lifetime than the others at all temperatures.

Figure 8 presents the frequency-dependent self-energy for the second lowest bound exciton. The height of the shaded area represents the completion term, which accounts for a large fraction of the real part of $\Xi$ at all frequencies. Near the $S = 2$ exciton energy ($\Omega_{2} = 2.4$ eV), the imaginary part of $\Xi^\Omega$ doesn’t have any structure, since, without electron-hole interactions, the electron-hole pairs lie above the band gap. However, the presence of bound excitons with finite crystal momentum near $\Gamma$ and $K$ allow the optical excitons to scatter and diffuse, conferring a finite value to the imaginary part of $\Xi$. Just as the electron-hole interaction binds the excitons below the band gap, it also moves the spectral weight of the self-energy towards lower frequencies.

Let us now evaluate the accuracy of previously-used approximate expressions for the real and imaginary parts of the self-energy. The uncorrelated exciton approximation of Eq. (58) corresponds to writing

$$\Xi^{UE}_{T\Sigma} = \sum_{k} |A^{s}(k, \Gamma)|^2 \Xi^{0}_{T\Sigma}(\epsilon_{k} - \epsilon_{\Gamma}). \quad (73)$$

Unlike the full exciton-phonon self-energy, this expression only requires the computation of the exciton’s wave function for the state $\Gamma S$. Figure 9, compares the real and imaginary parts of $\Xi^{UE}$ to those of $\Xi$. The uncorrelated exciton approximation overestimates the inverse lifetime (broadening).
FIG. 8. Real (solid lines) and imaginary part (dashed lines) of the exciton-phonon self-energy with (black) and without (blue) electron-hole interaction. The height of the filled region is the contribution of the completion term to the interacting self-energy.

FIG. 9. Comparison between the exciton-phonon self-energy (black discs) and an approximate expression (blue circles) for the first four bright excitons. a– Energy shift. b– Inverse lifetime.

FIG. 10. Spectral function (imaginary part of the propagator) for the first bright exciton at $T = 0$ computed with the model Hamiltonian at different levels of theory (in all cases, the imaginary part of the self-energy of the particle due to electron-electron interaction is neglected): non-interacting (gray), electron-hole interaction only (orange), electron-phonon interaction only (blue), and both interactions (black).

by an order or magnitude. For the phonon-induced energy shift $\Delta \Omega_S$, the overestimation of the negative shift (renormalization) for the seven lowest optical excitons is about 20% to 40%.

The combined effect of electron-hole and electron-phonon interactions is summarized in Fig. 10, which shows the exciton propagator for the lowest bound exciton as the electron-hole and electron-phonon interactions are switched on separately ($L$, $\Lambda^0$) or simultaneously ($\Lambda$). In all cases, the imaginary part of the self-energy of the particles due to electron-electron interaction is neglected. An artificial broadening parameter ($\eta = 5$ meV) is used to represent the bare exciton propagator ($L$), which would otherwise be infinitely sharp around the exciton energy $\Omega_S$ because of the neglect of the lifetime of the particles due to electron-electron interaction.

The function $L^0(\omega)$ illustrates the spectral decomposition of $L$ into electron-hole pairs. The spiky features in $L^0$ are an artifact of the finite $k$-points sampling used, and the function can be made smooth by using a larger broadening parameter $\eta$. Turning on the electron-phonon interaction broadens these features, as can be seen by comparing $L^0$ with $\Lambda^0$. The exciton propagator in the presence of the phonons field ($\Lambda$) is red-shifted with respect to the bare exciton propagator ($L$), and a satellite peak appears above the exciton peak in $\Lambda$.

IV. CONCLUSION

In summary, we have derived a rigorous expression for the exciton-phonon coupling self-energy to lowest order in the electron-phonon interaction and in the limit of low exciton density. Through the exciton-phonon coupling matrix elements, the optically accessible excitons may scatter into optically dark finite-momentum exciton states, resulting in an energy renormalization and a finite lifetime for the optical excitations. Our expressions takes into account the electron-hole interaction, and improve upon approximate expressions found in the literature by naturally enforcing energy conservation.

We implemented this theory on a two-dimensional two-band model and computed the temperature-dependent energy shift and lifetimes of the optical excitons. This model allowed
us to compare our exciton-phonon self-energy with an approximate expression which we call the uncorrelated exciton (UE) approximation. We showed that the previously used approximation overestimates the inverse lifetime by an order of magnitude, making this approximation unreliable. We conclude that, in physical systems with strong electron-hole interaction such as low-dimensional materials, it is necessary to use the exact exciton-phonon coupling theory to compute accurately the lifetime of optical excitations. The UE approximation also overestimates the temperature-dependent shift of the energy of the excitons by 20–40% in our two-band model. We interpret this result as an upper bound for the error induced by this approximation in realistic systems.

The scheme developed in this paper readily applies to the study of exciton diffusion dynamics. A main challenge in applying this theory is the computation of finite-momentum excitons energies and wavefunctions. While such calculation has been demonstrated, a full sampling of the Brillouin zone remains computationally expensive and would benefit from interpolation techniques.

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1 G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano, V. R. Cooper, et al., Recent Advances in Two-Dimensional Materials beyond Graphene, ACS Nano 9, 11509 (2015).
2 T. Mueller and E. Malic, Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors, npj 2D Materials and Applications 2, 1 (2018).
3 J. R. Schabbley, H. Yu, G. Clark, P. Rivera, J. S. Ross, K. L. Seyler, W. Yao, and X. Xu, Valleytronics in 2D materials, Nature Reviews Materials 1, 1 (2016).
4 K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. H. C. Neto, 2D materials and van der Waals heterostructures, Science 353 (2016).
5 M. V. Kovalenko, L. Protesescu, and M. I. Bodnarchuk, Properties and potential optoelectronic applications of lead halide perovskite nanocrystals, Science 358, 745 (2017).
6 E. Shi, Y. Gao, B. P. Finkenauer, Akriti, A. H. Coffey, and L. Dou, Two-dimensional halide perovskite nanomaterials and heterostructures, Chemical Society Reviews 47, 6046 (2018).
7 S. Chen and G. Shi, Two-Dimensional Materials for Halide Perovskite-Based Optoelectronic Devices, Advanced Materials 29, 1605448 (2017).
8 H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, and L. Huang, Exciton Dynamics in Suspended Monolayer and Few-Layer MoS2 2D Crystals, ACS Nano 7, 1072 (2013).
9 L. Yuan, T. Wang, T. Zhu, M. Zhou, and L. Huang, Exciton Dynamics, Transport, and Annihilation in Atomically Thin Two-Dimensional Semiconductors, The Journal of Physical Chemistry Letters 8, 3371 (2017).
10 D. Kozawa, R. Kumar, A. Carvalho, K. Kumar Amara, W. Zhao, S. Wang, M. Toh, R. M. Ribeiro, A. H. Castro Neto, K. Matsuda, et al., Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides, Nature Communications 5, 4543 (2014).
11 C. Ruppert, A. Chernikov, H. M. Hill, A. F. Rigosi, and T. F. Heinz, The Role of Electronic and Phononic Excitation in the Optical Response of Monolayer WS2 after Ultrafast Excitation, Nano Letters 17, 644 (2017).
12 A. Raja, M. Selig, G. Berghäuser, J. Yu, H. M. Hill, A. F. Rigosi, L. E. Brus, A. Knorr, T. F. Heinz, E. Malic, et al., Enhancement of Exciton–Phonon Scattering from Monolayer to Bilayer WS2, Nano Letters 18, 6135 (2018).
13 L. Li, M.-F. Lin, X. Zhang, A. Britz, A. Krishnamoorthy, R. M., R. K. Kalia, A. Nakano, P. Vashishta, P. Ajayan, et al., Phonon-Suppressed Auger Scattering of Charge Carriers in Defective Two-Dimensional Transition Metal Dichalcogenides, Nano Letters 19, 6078 (2019).
14 Z. Chi, H. Chen, Z. Chen, Q. Zhao, H. Chen, and Y.-X. Weng, Ultrafast Energy Dissipation via Coupling with Internal and External Phonons in Two-Dimensional MoS2, ACS Nano 12, 8961 (2018).
15 M. Selig, G. Berghäuser, A. Raja, P. Nagler, C. Schiller, T. F. Heinz, T. Korn, A. Chernikov, E. Malic, and A. Knorr, Exciton linewidth and coherence lifetime in monolayer transition metal dichalcogenides, Nature Communications 7, 13279 (2016).
16 X. Gong, O. Voznyy, A. Jain, W. Liu, R. Sabatini, Z. Piotkowski, G. Walters, G. Bappi, S. Nokhrin, O. Bushuyev, et al., Electron–phonon interaction in efficient perovskite blue emitters, Nature Materials 17, 550 (2018).
17 Y. Lv, C. Yin, C. Zhang, X. Wang, Z.-G. Yu, and M. Xiao, Exciton-acoustic phonon coupling revealed by resonant excitation of single perovskite nanocrystals, Nature Communications 12, 2192 (2021).
18 G. Strinati, Effects of dynamical screening on resonances at inner-shell thresholds in semiconductors, Physical Review B 29, 5718 (1984).
19 G. Strinati, Application of the Green’s functions method to the study of the optical properties of semiconductors, La Rivista del Nuovo Cimento (1978-1999) 11, 1 (2008).
20 S. Albrecht, L. Reining, R. Del Sole, and G. Onida, Ab initio calculation of excitonic effects in the optical spectra of semiconductors, Physical review letters 80, 4510 (1998).
21 L. X. Benedict, E. L. Shirley, and R. B. Bohn, Theory of optical absorption in diamond, Si, Ge, and GaAs, Physical Review B 57, R9385 (1998).
22 M. Rohlfing and S. G. Louie, Excitonic Effects and the Optical Absorption Spectrum of Hydrogenated Si Clusters, Physical Review Letters 80, 3320 (1998).
23 M. Rohlfing and S. G. Louie, Electron-Hole Excitations in Semiconductors and Insulators, Physical Review Letters 81, 2312 (1998).
24 M. Rohlfing and S. G. Louie, Electron-hole excitations and optical spectra from first principles, Physical Review B 62, 4927 (2000).
25 G. Oida, L. Reining, and A. Rubio, Electronic excitations: density-functional versus many-body Green’s-function approaches, Rev. Mod. Phys. 74, 601 (2002).
26 X. Gonze, First-principles responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm, Physical Review B 55, 10337 (1997).
27 X. Gonze and C. Lee, Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory, Physical Review B 55, 10355 (1997).
28 S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Reviews of Modern Physics 73, 515 (2001).
29 F. Giustino, Electron-phonon interactions from first principles, Reviews of Modern Physics 89, 015003 (2017).
30 A. Miglio, V. Brousseau-Couture, E. Godbout, G. Antonius, Y.-H. Chan, S. G. Louie, M. Côté, M. Giannozzi, and X. Gonze, Predominance of non-adiabatic effects in zero-point renormalization of the electronic band gap, npj Computational Materials 6, 1 (2020).
31 S. Poncé, W. Li, S. Reichardt, and F. Giustino, First-principles calculations of charge carrier mobility and conductivity in bulk semiconductors and two-dimensional materials, Reports on Progress in Physics 83, 036501 (2020).
32 M. S. Hybertsen and S. G. Louie, Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies, Phys. Rev. B 34, 5390 (1986).
33 Z. Li, G. Antonius, M. Wu, F. H. da Jornada, and S. G. Louie, Electron-Phonon Coupling from Ab Initio Linear-Response Theory within the GW Method: Correlation-Enhanced Interactions and Superconductivity in Ba$_{1-x}$K$_x$BiO$_3$, Physical Review Letters 122, 186402 (2019).
34 M. Bernardi, D. Vigil-Fowler, J. Lischner, J. B. Neaton, and S. G. Louie, Ab Initio Study of Hot Carriers in the First Picosecond after Sunlight Absorption in Silicon, Physical Review Letters 112, 257402 (2014).
35 A. Molina-Sánchez, D. Sangalli, L. Wirtz, and A. Marini, Ab Initio Calculations of Ultrashort Carrier Dynamics in Two-Dimensional Materials: Valley Depolarization in Single-Layer WS$_2$, Nano Letters 17, 4549 (2017).
36 F. Caruso, Nonequilibrium Lattice Dynamics in Monolayer MoS$_2$, The Journal of Physical Chemistry Letters , 1734 (2021).
37 A. Marini, Ab Initio Finite-Temperature Excitons, Physical Review Letters 101, 106405 (2008).
38 D. Y. Qi, F. H. da Jornada, and S. G. Louie, Optical Spectrum of MoS$_2$: Many-Body Effects and Diversity of Exciton States, Physical Review Letters 111, 216805 (2013).
39 A. Molina-Sánchez, M. Palummo, A. Marini, and L. Wirtz, Temperature-dependent excitonic effects in the optical properties of single-layer MoS$_2$, Physical Review B 93, 155435 (2016).
40 M. Zacharias, C. E. Patrick, and F. Giustino, Stochastic Approach to Phonon-Assisted Optical Absorption, Physical Review Letters 115, 177401 (2015).
41 M. Zacharias, One-shot calculation of temperature-dependent optical spectra and phonon-induced band-gap renormalization, Physical Review B 94 (2016).
42 M. Zacharias and F. Giustino, Theory of the special displacement method for electronic structure calculations at finite temperature, Physical Review Research 2, 013357 (2020).
43 S. Brem, M. Selig, G. Berghaeuser, and E. Malic, Exciton Relaxation Cascade in two-dimensional Transition Metal Dichalcogenides, Scientific Reports 8, 8238 (2018).
44 S. Brem, J. Zipfel, M. Selig, A. Raja, L. Waldecker, J. D. Ziegler, T. Taniguchi, K. Watanabe, A. Chernikov, and E. Malic, Intrinsc lifetime of higher excitonic states in tungsten diselenide monolayers, Nanoscale 11, 12381 (2019).
45 D. Christiansen, M. Selig, E. Malic, R. Ernstorfer, and A. Knorr, Theory of exciton dynamics in time-resolved ARPES: Intra- and inter-valley scattering in two-dimensional semiconductors, Physical Review B 100, 205401 (2019).
46 H.-Y. Chen, D. Sangalli, and M. Bernardi, Exciton-Phonon Interaction and Relaxation Times from First Principles, Physical Review Letters 125, 107401 (2020).
47 P. Cudazzo, First-principles description of the exciton-phonon interaction: A cumulant approach, Physical Review B 102 (2020).
48 M. R. Filip, J. B. Haber, and J. B. Neaton, Phonon Screening of Excitons in Semiconductors: Halide Perovskites and Beyond, Physical Review Letters 127, 067401 (2021).
49 L. Adamska and P. Umar, Bethe-Salpeter equation approach with electron-phonon coupling for exciton binding energies, Physical Review B 103, 075201 (2021).
50 The Supplemental Material presents a more detailed derivation of the IEHPP self-energy and the self-energy completion term within the two-band model, as well as its band convergence properties.
51 M. van Schilfgaarde, T. Kotani, and S. Faleev, Quasiparticle Self-Consistent GW Theory, Physical Review Letters 96 (2006).
52 G. Antonius, S. Poncé, P. Boulanger, M. Côté, and X. Gonze, Many-Body Effects on the Zero-Point Renormalization of the Band Structure, Physical Review Letters 112, 215501 (2014).
53 X. Gonze and J.-P. Vigneron, Density-functional approach to nonlinear-response coefficients of solids, Physical Review B 39, 13120 (1989).
54 A. Marini, S. Poncé, and X. Gonze, Many-body perturbation theory approach to the electron-phonon interaction with density-functional theory as a starting point, Physical Review B 91, 224310 (2015).
55 P. B. Allen and V. Heine, Theory of the temperature dependence of electronic band structures, Journal of Physics C: Solid State Physics 9, 2305 (1976).
56 S. Poncé, G. Antonius, Y. Gillet, P. Boulanger, J. Laflamme Janssen, A. Marini, M. Côté, and X. Gonze, Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation, Physical Review B 90, 214304 (2014).
57 G. D. Mahan, Many-Particle Physics, third edition ed. (Kluwer Academic / Plenum Publishers, New York, 2000).
58 F. Brown-Altvater, G. Antonius, T. Rangel, M. Giannozzi, C. Draxl, X. Gonze, S. G. Louie, and J. B. Neaton, Band gap renormalization, carrier mobilities, and the electron-phonon self-energy in crystalline naphthalene, Physical Review B 101, 165102 (2020).
59 B. Laikhtman, Are excitons really bosons?, Journal of Physics: Condensed Matter 19, 295214 (2007).
60 C. D. Spataru, S. Ismail-Beigi, R. B. Capaz, and S. G. Louie, Theory and Ab Initio Calculation of Radiative Lifetime of Excitons in Semiconducting Carbon Nanotubes, Physical Review Letters 95, 247402 (2005).
61 D. Gunlycke and F. Tseng, Triangular lattice exciton model, Physical Chemistry Chemical Physics 18, 8579 (2016).
D. Y. Qiu, T. Cao, and S. G. Louie, Nonanalyticity, Valley Quantum Phases, and Lightlike Exciton Dispersion in Monolayer Transition Metal Dichalcogenides: Theory and First-Principles Calculations, Physical Review Letters 115, 176801 (2015).

G. Berghäuser and E. Malic, Analytical approach to excitonic properties of MoS$_2$, Physical Review B 89, 125309 (2014).

M. Selig, G. Berghäuser, M. Richter, R. Bratschitsch, A. Knorr, and E. Malic, Dark and bright exciton formation, thermalization, and photoluminescence in monolayer transition metal dichalcogenides, 2D Materials 5, 035017 (2018).
Theory of the Exciton-Phonon Coupling: Supplemental information

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I. QUASIPARTICLE PROPAGATORS AND FREQUENCY SUMMATIONS

This section presents the Matsubara formalism used and a few important Matsubara summations that lead to the analytic expressions of the different self-energies presented in the manuscript. The transform between imaginary time and imaginary frequency for a quantity $A$ (either a propagator or a self-energy) is

$$A(\tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} e^{-i\omega_n \tau} A(i\omega_n) ; \quad A(i\omega_n) = \int_{0}^{\beta} d\tau e^{i\omega_n \tau} A(\tau) \quad (S.1)$$

where $\beta = 1/k_B T$, and the Matsubara frequencies are defined as

$$\omega_n = \frac{2n\pi}{\beta} \quad \text{(bosons)} ; \quad \omega_m = \frac{(2m+1)\pi}{\beta} \quad \text{(fermions)} \quad (S.2)$$

Throughout the paper, we use $i\omega_n$ and $i\omega_l$ for bosonic frequencies, and $i\omega_m$ for fermionic frequencies. We will recover all the retarded quantities on the real frequency axis using a real positive infinitesimal number $\eta$ and the analytic continuation

$$A^R(\omega) = \lim_{i\omega_n \to \omega + i\eta} A(i\omega). \quad (S.3)$$

In this formalism, the one-particle propagator is

$$G_{ii'}(i\omega_m) = \frac{1}{i\omega_m - \epsilon_i - \epsilon_{i'}} \delta_{ii'} \quad (S.4)$$

while the phonon propagator is

$$D_\lambda(i\omega_l) = \frac{1}{i\omega_l - \omega_\lambda} - \frac{1}{i\omega_l + \omega_\lambda} \quad (S.5)$$

Note that $D_\lambda(i\omega_l) = D_\lambda(-i\omega_l)$. The bare electron-hole propagator is

$$L_{vv'}(i\omega_n) = \frac{f(\epsilon_v) - f(\epsilon_{v'})}{i\omega_n - (\epsilon_v - \epsilon_{v'})} \delta_{vv'} \quad (S.6)$$

And the bare exciton propagator is

$$L_{SS'}(i\omega_n) = \frac{1}{i\omega_n - \Omega_S} \delta_{SS'} \quad (S.7)$$

For the phonon propagator, the summation over bosonic Matsubara frequencies yields

$$-\frac{1}{\beta} \sum_{\lambda} D_\lambda(i\omega_l) = 2N_B(\omega_\lambda) + 1 \quad (S.8)$$
where \( N_B(\omega) \) is the Bose-Einstein distribution defined as

\[
N_B(\omega) = \frac{1}{e^{\beta \omega} - 1} \quad (S.9)
\]

For the one-particle propagator, the summation over fermionic Matsubara frequencies yields

\[
\frac{1}{\beta} \sum_m G^0_{ii}(i\omega_m) = f(\varepsilon_i) \quad (S.10)
\]

where \( f(\omega) \) is the Fermi-Dirac distribution defined as

\[
f(\omega) = \frac{1}{e^{\beta \omega} + 1} \quad (S.11)
\]

assuming that \( \omega \) is measured from the chemical potential \( \mu \). The bare electron-hole propagator is expressed as the convolution of two one-particle propagators

\[
L^0_{vc,vc}(i\omega_n) = \frac{1}{\beta} \sum_m G^0_{vv}(i\omega_m)G^0_{cc}(i\omega_m + i\omega_n) \quad (S.12)
\]

Upon computing the one-particle electron-phonon self-energy, we encounter a summation of the type

\[
-\frac{1}{\beta} \sum_\lambda D_\lambda(i\omega_h)G^0_{ii}(i\omega_l + i\omega_m) = \frac{N_B(\omega_\lambda) + 1 - f(\varepsilon_i)}{i\omega_m - \varepsilon_i - \omega_\lambda} + \frac{N_B(\omega_\lambda) + f(\varepsilon_i)}{i\omega_m - \varepsilon_i + \omega_\lambda} \quad (S.13)
\]

while, for the IEHPP self-energy \( \Xi^0 \), we encounter summations of the type

\[
-\frac{1}{\beta} \sum_\lambda D_\lambda(i\omega_h) L^0_{vc,vc}(i\omega_l + i\omega_n)
= \left( f(\varepsilon_v) - f(\varepsilon_c) \right) \left[ \frac{N_B(\omega_\lambda) + 1 + n(\varepsilon_c - \varepsilon_v)}{i\omega_n - (\varepsilon_c - \varepsilon_v) - \omega_\lambda} + \frac{N_B(\omega_\lambda) - n(\varepsilon_c - \varepsilon_v)}{i\omega_n - (\varepsilon_c - \varepsilon_v) + \omega_\lambda} \right]
\approx \frac{N_B(\omega_\lambda) + 1}{i\omega_n - (\varepsilon_c - \varepsilon_v) - \omega_\lambda} + \frac{N_B(\omega_\lambda)}{i\omega_n - (\varepsilon_c - \varepsilon_v) + \omega_\lambda} \quad (S.14)
\]

The last approximation results from the large-band-gap approximation, which is explained in appendix II.
II. LARGE BAND GAP APPROXIMATION

In order to arrive at an expression for all the contributions to $\Xi^0$, we will take advantage of the large-band-gap approximation for the one-particle occupation numbers, namely

\begin{align}
  f(\epsilon_v) & \approx 1 \quad \forall \ v \\
  f(\epsilon_c) & \approx 0 \quad \forall \ c 
\end{align}

(S.15) \hspace{1cm} (S.16)

For materials with band gaps larger than 1 eV, this approximation holds for temperatures up to 10,000 K. As a result, the bare electron-hole propagator writes

\begin{equation}
  L_{\nu'\nu'}^0(i\omega_n) \approx \frac{1}{i\omega_n - (\epsilon_c - \epsilon_v)} \delta_{\nu'\nu} \delta_{\nu'\nu'}
\end{equation}

(S.17)

And we have the identity

\begin{equation}
  G_{\nu\nu}^0(i\omega_m)G_{\nu'\nu'}^0(i\omega_m + i\omega_n) = L_{\nu,\nu'}^0(i\omega_n)[G_{\nu\nu}^0(i\omega_m) - G_{\nu'\nu'}^0(i\omega_m + i\omega_n)]
\end{equation}

(S.18)

Using this result, we can show that

\begin{equation}
  G_{\nu\nu}^0(i\omega_m)G_{\nu'\nu'}^0(i\omega_m + i\omega_n) = L_{\nu,\nu'}^0(i\omega_n)L_{\nu'\nu'}^0(i\omega_n)\delta_{\nu'\nu}

  \times \left\{ \left[ G_{\nu\nu}^0(i\omega_m + i\omega_n) - \frac{1}{2}[G_{\nu\nu}^0(i\omega_m) + G_{\nu'\nu'}^0(i\omega_m)] \right]

  + \frac{1}{2} \left[ L_{\nu,\nu'}^0(i\omega_n) + L_{\nu',\nu'}^0(i\omega_n) \right] G_{\nu\nu}^0(i\omega_m)G_{\nu'\nu'}^0(i\omega_m) \right\}
\end{equation}

(S.19)

which has been symmetrized in $(\nu, \nu')$. The third line of Eq. (S.19) gives a contribution that is exactly zero if it is summed along a frequency-independent term, such as the DW self-energy. Its contribution is also zero when evaluated at $i\omega_n = \epsilon_c - \epsilon_v$, and is vanishing in the neighborhood of this value. It will thus be neglected. To simplify the notation, we introduce the symmetrization symbol $\mathcal{S}$, which, for a quantity $A_{\nu\nu'\nu'}$, means

\begin{equation}
  \mathcal{S}[A_{\nu\nu'\nu'}] = \frac{1}{2}(A_{\nu\nu'\nu'} + A_{\nu'\nu'\nu}).
\end{equation}

(S.20)

Quantities with two or three indices are obtained by a contraction of indices and symmetrize as

\begin{align}
  \mathcal{S}[A_{\nu\nu'\nu}] & = \frac{1}{2}(A_{\nu\nu'\nu} + A_{\nu'\nu\nu}) \\
  \mathcal{S}[A_{\nu\nu'\nu'}] & = \frac{1}{2}(A_{\nu\nu'\nu'} + A_{\nu'\nu'\nu}) \\
  \mathcal{S}[A_{\nu'\nu}] & = \frac{1}{2}(A_{\nu'\nu} + A_{\nu'\nu})
\end{align}

(S.21)
Hence, we arrived at the approximation

\[ G_{vv}(i\omega_m)G_{v'v'}^{0}(i\omega_m)G_{cc}^{0}(i\omega_m + i\omega_n) \approx L_{vc,vc}^{0}(i\omega_n)L_{v'c',v'c'}^{0}(i\omega_n) \]

\[ \times \mathcal{S} \left[ G_{cc}^{0}(i\omega_m + i\omega_n) - G_{vv}^{0}(i\omega_m) \right] \delta_{cc'} \]  

(S.22)

A similar reasoning gives

\[ G_{cc}^{0}(i\omega_m + i\omega_n)G_{c'c'}^{0}(i\omega_m + i\omega_n)G_{vv}^{0}(i\omega_m) \approx L_{vc,vc}^{0}(i\omega_n)L_{v'c',v'c'}^{0}(i\omega_n) \]

\[ \times \mathcal{S} \left[ G_{vv}^{0}(i\omega_m) - G_{cc}^{0}(i\omega_m + i\omega_n) \right] \delta_{vv'} \]  

(S.23)

Another result from the large-band-gap approximation is

\[ G_{cc}^{0}(i\omega_n + i\omega_n)G_{vc}^{0}(i\omega_m + i\omega_m - i\omega_l)G_{c'c'}^{0}(i\omega_n) \]

\[ = L_{vc,vc}^{0}(i\omega_n)L_{v'c',v'c'}^{0}(i\omega_n) \left[ G_{vv}^{0}(i\omega_m) - G_{cc}^{0}(i\omega_n + i\omega_m) \right] \]

\[ \times \left[ G_{v'c'}^{0}(i\omega_n - i\omega_l) - G_{c'c'}^{0}(i\omega_n + i\omega_m - i\omega_l) \right] \]  

(S.24)

and

\[ \sum_{m} \left[ G_{vv}^{0}(i\omega_m) - G_{cc}^{0}(i\omega_n + i\omega_m) \right] \left[ G_{v'v'}^{0}(i\omega_m - i\omega_l) - G_{c'c'}^{0}(i\omega_n + i\omega_m - i\omega_l) \right] \]

\[ \approx - \left[ L_{v'c',v'c'}^{0}(i\omega_n + i\omega_l) + L_{vc,vc}^{0}(i\omega_n - i\omega_l) \right] \]  

(S.25)

Finally, we assume that all phonon frequencies are much smaller than the band gap and the exciton energies. This approximation allows us to write

\[ f(\varepsilon_i \pm \omega_{\lambda}) \approx f(\varepsilon_i) \]  

(S.26)

and

\[ N_B(\omega_{\lambda}) \gg N_B(\varepsilon_c - \varepsilon_v) \]

\[ N_B(\omega_{\lambda}) \gg N_B(\Omega_S) \]  

(S.27)

for any pair of valence and conduction states with energies \( \varepsilon_v \) and \( \varepsilon_c \), any exciton energy \( \Omega_S \), and any phonon energy \( \omega_{\lambda} \).
III. MORE DETAILED DERIVATION OF $\Xi^0$

We proceed to a detailed derivation of the IEHPP self-energy $\Xi^0$ by expanding $\Lambda^0$ from Eq. (18). To the lowest order in the perturbation, the self-energy will be given by

$$\Xi_{vc,v'c'}^0(i\omega_n) = L_{vc,vc}^{-1}(i\omega_n) \left[ \Lambda_{vc,v'c'}^0(i\omega_n) - L_{vc,v'c'}^{-1}(i\omega_n) \right] L_{v'c',v'c'}^{-1}(i\omega_n)$$

Hence, each term in $\Lambda^0$ beyond $L^0$ contributes to $\Xi^0$.

The first set of terms are called the Debye-Waller terms, since they involve the second-order electron-phonon coupling potential. They write

$$\Lambda_{vc,v'c'}^{0\text{DW}}(i\omega_n) = \Sigma_{vc'c}^{\text{DW}} \left[ \frac{1}{\beta} \sum_m G_{cc}^0(i\omega_m) G_{c'c'}^0(i\omega_m) G_{v'v}^0(i\omega_m - i\omega_n) \right]$$

$$+ \sum_{v,v'}^{\text{DW}} \left[ \frac{1}{\beta} \sum_m G_{vv}^0(i\omega_m) G_{v'v'}^0(i\omega_m) G_{cc'}^0(i\omega_m + i\omega_n) \right]$$

(S.29)

where

$$\Sigma_{ii'}^{\text{DW}} = -\sum_\lambda \frac{g_\lambda^{(2)}}{\beta} \sum_l D_\lambda(i\omega_l)$$

(S.30)

We recover Eq. (18) for $\Sigma^{\text{DW}}$ by making use of Eq. (S.8). The next set of terms are called the Fan-Migdal (FM) terms. They write

$$\Lambda_{vc,v'c'}^{0\text{FM}}(i\omega_n) = -\frac{1}{\beta} \sum_m \left\{ \Sigma_{vc'c}^{\text{FM}}(i\omega_m) \left[ G_{cc}^0(i\omega_m) G_{c'c'}^0(i\omega_m) G_{v'v}^0(i\omega_m - i\omega_n) \right] \right.$$  

$$+ \sum_{v,v'}^{\text{FM}}(i\omega_m) \left[ G_{vv}^0(i\omega_m) G_{v'v'}^0(i\omega_m) G_{cc'}^0(i\omega_m + i\omega_n) \right]\}$$

(S.31)

where

$$\Sigma_{ii'}^{\text{FM}}(i\omega_n) = -\sum_{\lambda,\lambda'}^\beta g_{i\lambda,\lambda'} g_{i'\lambda'}^{*} \frac{1}{\beta} \sum_l D_\lambda(i\omega_l) G_{\lambda\lambda'}^0(i\omega_n + i\omega_l)$$

(S.32)

We recover Eq. (19) for $\Sigma^{\text{FM}}$ by making use of Eq. (S.13). The last set of terms are called the phonon exchange terms. They write

$$\Lambda_{vc,v'c'}^{0\text{X}}(i\omega_n) = -\sum_\lambda g_{c'c\lambda} g_{v'v\lambda}^{*} \frac{1}{\beta^2} \sum_{lm} G_{cc}^0(i\omega_m + i\omega_l) G_{c'c'}^0(i\omega_m + i\omega_l - i\omega_l)$$

$$\times G_{v'v'}^0(i\omega_m - i\omega_l) G_{vv}^0(i\omega_m) D_\lambda(i\omega_l)$$

(S.33)

Using Eq. (S.19) and Eq. (S.22), the Debye-Waller contribution to $\Xi^0$ is

$$\Xi_{vc,v'c'}^{0\text{DW}} = \frac{1}{\beta} \sum_m \Sigma_{vv'}^{\text{DW}} \left[ G_{cc}^0(i\omega_m + i\omega_l) - G_{vv}^0(i\omega_m) \right] \delta_{cc'}$$

$$+ \sum_{cc'}^{\text{DW}} \left[ G_{vv'}^0(i\omega_m - i\omega_l) - G_{cc}^0(i\omega_m) \right] \delta_{vv'}$$

(S.34)
Within the large-bandgap-approximation, the Debye-Waller term is simply

\[
\Sigma^{0D_W}_{vc,v'c'}(i\omega_n) = \Sigma^{D_W}_{cc'} \delta_{vc'} - \Sigma^{D_W}_{cc'} \delta_{cc'}
\]  \hspace{1cm} (S.35)

To obtain the FM term contribution, we insert Equations (S.31) into (S.28), and use (S.22) and (S.23), giving

\[
\Sigma^{0FM}_{vc,v'c'}(i\omega_n) = \frac{1}{\beta} \sum_{m} \Sigma^{FM}_{v'v}(i\omega_m) \mathcal{G}^0_{cc'}(i\omega_m + i\omega_n) - G^0_{vv}(i\omega_m) \\
+ \Sigma^{FM}_{cc'}(i\omega_m) \mathcal{G}^0_{v'v}(i\omega_m - i\omega_n) = -G^0_{cc}(i\omega_m) \delta_{cc'} + \Sigma^{FM}_{cccc'}(i\omega_m) \mathcal{G}^0_{cc'}(i\omega_m) \delta_{vc'} \hspace{1cm} (S.36)
\]

We split the FM term into two contributions: the dynamical FM term (FMd) and the static FM term (FMs). We define the dynamical Fan term as

\[
\Sigma^{0FMd}_{vc,v'c'}(i\omega_n) = \frac{1}{\beta} \sum_{m} \Sigma^{FM}_{v'v}(i\omega_m) \mathcal{G}^0_{cc'}(i\omega_m + i\omega_n) + \Sigma^{FM}_{cc'}(i\omega_m) \mathcal{G}^0_{v'v}(i\omega_m - i\omega_n) \hspace{1cm} (S.37)
\]

and the static FM term as

\[
\Sigma^{0FMs}_{vc,v'c'} = -\frac{1}{\beta} \sum_{m} \Sigma^{FM}_{vv'}(i\omega_m) \mathcal{G}^0_{vv} - \Sigma^{FM}_{cccc'}(i\omega_m) \mathcal{G}^0_{cc'} + \Sigma^{FM}_{cccc'}(i\omega_m) \mathcal{G}^0_{cc'} \delta_{vc'} \hspace{1cm} (S.38)
\]

We use Eq. (S.37) to express the one-particle self-energy as a convolution of the Green’s functions of an electron and a phonon, and use Eq. (S.12) to write

\[
\Sigma^{0FMd}_{vc,v'c'}(i\omega_n) = -\frac{1}{\beta} \sum_{m} \sum_{\lambda} \sum_{v''v'''} \theta(\mathcal{G}^0_{cc'}(i\omega_m + i\omega_n)) \times [g_{v''v''} g_{v''v'''}^* \delta_{cc''v'''} \delta_{v''v'} + g_{cc''v'''} \delta_{vc'} + g_{cc''v'''} \delta_{vc'}]
\]

and

\[
\Sigma^{0FMs}_{vc,v'c'} = \frac{1}{\beta} \sum_{m} \sum_{\lambda} \sum_{v''v'''} \theta(\mathcal{G}^0_{cc'}(i\omega_m)) \times [g_{cc''v'''} \delta_{vc'} + g_{cc''v'''} \delta_{vc'} \mathcal{G}^0_{cc'} \delta_{cc'} \hspace{1cm} (S.39)
\]

To obtain the phonon exchange term contribution, we insert Equations (S.33) into (S.28), and use (S.24) and (S.25), giving

\[
\Sigma^{0X}_{vc,v'c'}(i\omega_n) = g_{c''v'} g_{v''v'''} \delta_{vc'} \frac{1}{\beta} \sum_{\lambda} \left[ \mathcal{G}^0_{vc,v'c'}(i\omega_m + i\omega_n) + \mathcal{G}^0_{vc,v'c'}(i\omega_m + i\omega_n) \right] D_{\lambda}(i\omega_n) \hspace{1cm} (S.41)
\]

Performing the imaginary frequency summation, we obtain Eq. (??).
IV. COMPLETION TERM WITHIN THE TWO-BAND MODEL

In the present calculation, the wavevector basis allows for a maximum of $N_k$ exciton states, but the first $N$ exciton states are actually computed. The exciton-phonon self-energy therefore includes a completion term to account for the missing transitions. Let $|k, q\rangle$ denote the state with one hole at wavevector $k$ and one electron in the conduction band at wavevector $k + q$, such that $\langle k, q| S, q \rangle = A^S(k, q)$. The electron-phonon coupling operator is

$$V_{ep}(q) = \sum_k g_c |k, q\rangle \langle k, \Gamma| - g_v |k - q, q\rangle \langle k, \Gamma|$$ (S.42)

We complete the self-energy using the equivalent completion phase space of the non-interacting self-energy, that is

$$\Xi_0^0(k, \omega) = \sum_{k', q} \frac{\langle k, \Gamma| V_{ep}(q) |k', q\rangle \langle k', q| V_{ep}(q)^* |k, \Gamma\rangle}{\omega - (E_{k'q_c} - E_{k'v}) \pm \omega_0 + i\eta} P_\pm(T) = \sum_q \Xi_0^0(k, \omega, q)$$

In the exciton basis, the non-interacting self-energy is non-diagonal, but we consider a diagonal element $(S, S)$

$$\Xi_0^{SS}(\Gamma, \omega) = \sum_{k', q} \frac{g_{SS'}(\Gamma, q) g_{SS'}^*(\Gamma, q) A^{S'*}(k', q) A^{S'}(k', q)}{\omega - (E_{k'q_c} - E_{k'v}) \pm \omega_0 + i\eta} P_\pm(T)$$

Given that

$$\sum_k A^{S'*}(k', q) A^{S'}(k', q) = \delta_{S', S'}$$ (S.43)

in the limit of weak exciton binding, $\Xi_0^{SS}$ must correspond to $\Xi_{SS}$, namely

$$\Xi_{SS}(Q, \omega, T) = \sum_q \sum_{S'} \frac{|g_{SS'}(Q, q)|^2}{\omega - \Omega_{S'} \pm \omega_0 + i\eta} P_\pm(T)$$

The completion term is the missing terms, when only the first $N$ excitons are included in the basis, that is

$$\Xi_{SS}^C(Q, \omega, T) = \sum_q \left\{ \sum_{S'} \frac{|g_{SS'}(Q, q)|^2 P_\pm(T)}{\omega - \Omega_{S'} \pm \omega_0 + i\eta} \frac{N}{\omega - \Omega_{S'} \pm \omega_0 + i\eta} \right\}$$

We first approximate the contribution of the $S'$ states as those of electron-hole pairs

$$\Xi_{SS}^C(Q, \omega, T) = \sum_q \left\{ \Xi_{SS}^0(\Gamma, \omega, q) - \sum_{S' = 1}^N \frac{|g_{SS'}(Q, q)|^2 P_\pm(T)}{\omega - \Omega_{S'} \pm \omega_0 + i\eta} \right\}$$
Next, define a $\mathbf{q}$-dependent effective energy parameter $E_{\text{eff}}(S, \mathbf{q})$ that allows to write the completion term as

$$
\Xi_{SS}^C(Q, \omega, T) = \sum_{\mathbf{q}} \left\{ \Xi_{SS}^0(\Gamma, \omega, \mathbf{q}) - \sum_{S'}^{N} \frac{|g_{SS'}(Q, \mathbf{q})|^2}{\omega - E_{\text{eff}}(S, \mathbf{q}) + i\eta} \right\} \quad (S.44)
$$

In the limit of complete basis ($N = N_k$), each pair of terms in Eq. (S.44) must cancel perfectly. In this limit, we have the sum rule

$$
\zeta_{\Gamma S}(\mathbf{q}) = \sum_{S'} |g_{SS'}(\Gamma, \mathbf{q})|^2 = |g_c|^2 + |g_v|^2 - 2g_v^* g_c A^S_S(\mathbf{k} + \mathbf{q}, \Gamma) A(S, \Gamma) \quad (S.45)
$$

Making use of this sum rule

$$
\frac{1}{\omega - E_{\text{eff}}(S, \mathbf{q}) + i\eta} = \frac{1}{\zeta_{\Gamma S}(\mathbf{q})} \Xi_{SS}^0(\Gamma, \omega, \mathbf{q}) \quad (S.46)
$$

We define the partial summation (when $N < N_k$)

$$
\tilde{\zeta}_{\Gamma S}(\mathbf{q}) = \sum_{S'}^{N} |g_{SS'}(\Gamma, \mathbf{q})|^2 \quad (S.47)
$$

which allows us to write

$$
\Xi_{SS}^C(Q, \omega, T) = \sum_{\mathbf{q}} \left( 1 - \frac{\tilde{\zeta}_{\Gamma S}(\mathbf{q})}{\zeta_{\Gamma S}(\mathbf{q})} \right) \Xi_{SS}^0(\Gamma, \omega, \mathbf{q}) \quad (S.48)
$$

This is the final expression for the completion term of the exciton-phonon coupling self-energy. As shown in Fig. S.1, the completion term significantly speeds up the convergence of the self-energy with respect to the number of exciton bands.
FIG. S.1. Convergence of the exciton-phonon self-energy for $S = 0$ with respect to the number of exciton bands, with (blue) and without (orange) the completion term. The dashed line represents the limit of complete basis ($N = N_k$) where both lines are expected to meet.