

Unified First-Principles Formula for Time-Resolved ARPES Spectra of Coherent and Incoherent Excitons beyond the Dilute Limit

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Despite major experimental progresses in time-resolved and angle-resolved photoemission spectroscopy, a quantitative, microscopic framework for interpreting exciton-induced modifications of electronic band structures—applicable even beyond the low-density limit—is still lacking. Here, we close this gap by introducing a unified approach that links the dynamics of coherent and incoherent excitons to distinct and experimentally observable excitonic sidebands. Our central result is a general, first-principles formula for time-resolved photoemission spectra, applicable across a broad range of temperatures, excitation densities, and pump-probe delays. This advance provides a predictive tool for quantitatively tracking excitonic dynamics in complex materials.

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Introduction—The concept of excitons as quasiparticles in semiconductors and insulators has long been central to the interpretation of optical spectra, where it underpins the understanding of subgap resonances and above-gap structures in absorbance and reflectance measurements [1]. Optical probes, however, are fundamentally restricted to bright, zero-center-of-mass-momentum excitons and primarily access their energies. By contrast, angle-resolved photoemission spectroscopy (ARPES) reveals a far richer and more detailed picture [2–4]. In particular, time-resolved ARPES (TR-ARPES) has recently emerged as a powerful platform for exciton physics, enabling direct access to bright, momentum-dark, and spin-dark excitons [5–12]. Beyond exciton energies, TR-ARPES uniquely resolves excitonic wave functions in both band and momentum space [13–17].

Although TR-ARPES [18] has led to informative experimental spectra, a rigorous connection with the underlying exciton dynamics is still lacking. After pumping below the band gap, the nonequilibrium exciton fluid [19–23] drives the motion of the nuclear lattice. The scattering between electrons and phonons destroys exciton coherence [24–29] and diffuses excitons [30–33]. Bright coherent excitons are converted—typically in less than a few hundreds of femtoseconds [34–36]—into bright and dark incoherent excitons. TR-ARPES spectra of *coherent* excitons have been successfully described [37–41]. However, a first-principles

many-body framework for the *incoherent* regime—applicable even beyond the domain of low excitation densities—remains underdeveloped [42–45]. In this Letter, we identify distinct signatures of coherent and incoherent excitons in the TR-ARPES signal and provide a unified theory of excitonic sidebands emerging from different exciton states. The main finding is a ready-to-use first-principles formula for interpreting TR-ARPES spectra across a wide range of temperatures, excitation densities, and pump-probe delays.

Photocurrent—The rate of photoelectrons with energy ϵ and parallel momentum $\mathbf{k}$, ejected by a high-energy probe pulse $a(t) = ae^{-i\omega_0 t} + \text{H.c.}$ impinging on the crystal after a delay τ from the pump, is proportional to [42,46]

$$I_{\mathbf{k}}(\tau, \epsilon) \propto -i|a|^2 \sum_{\mu\mu'} D_{\mu\mathbf{k}}(\epsilon) D_{\mu'\mathbf{k}}^*(\epsilon) G_{\mu\mu'\mathbf{k}}^<(\tau, \omega_0 - \epsilon), \quad (1)$$

where $D_{\mu\mathbf{k}}(\epsilon)$ is the photoemission matrix element for an electron with band-momentum index $(\mu\mathbf{k})$. Henceforth, we use $\mu = c$ for conduction bands and $\mu = v$ for valence bands. The D are *independent* of the nonequilibrium many-body state probed by ARPES and are not discussed further here; they can be calculated by different means [47–50].

The nonequilibrium electronic properties of the crystal are encoded in the Fourier transform, $G^<(\tau, \omega)$, of the lesser Green's function $G^<(t, t')$ with respect to the time difference $t - t'$ for a given center-of-mass time (delay) $\tau = (t + t')/2$. In the quasiparticle approximation $G_{\mu\mu'\mathbf{k}}^<(\tau, \omega) = \delta_{\mu\mu'} 2\pi i f_{\mu\mathbf{k}}(\tau) \delta[\omega - \epsilon_{\mu\mathbf{k}}(\tau)]$, and the spectrum is peaked at the quasiparticle energies $\epsilon_{\mu\mathbf{k}}(\tau)$ —with an intensity proportional to the nonequilibrium populations $f_{\mu\mathbf{k}}(\tau)$. Since our primary interest is in the excitonic

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sidebands appearing above the valence band maximum, we focus exclusively on the contribution of conduction electrons to the photoemission signal. Consequently, we restrict the sum over μ, μ' in Eq. (1) to the conduction bands.

TR-ARPES formula—The interacting nonequilibrium $G^<$ for conduction electrons can be calculated from [51]

$$G_{\mathbf{k}}^<(\tau, \omega) = G_{\mathbf{k}}^R(\tau, \omega) \Sigma_{\mathbf{k}}^<(\tau, \omega) G_{\mathbf{k}}^A(\tau, \omega), \quad (2)$$

where all quantities are matrices with conduction-band indices. We remark that this way of calculating $G^<$ differs from earlier attempts [42,43], which rely on the fluctuation-dissipation ansatz $G_{\mathbf{k}}^<(\tau, \omega) = if(\omega - \mu_c)A_{\mathbf{k}}(\tau, \omega)$, where f is the Fermi function with a conduction-band chemical potential μ_c fixed by the excitation density, and $A_{\mathbf{k}}(\tau, \omega)$ is the nonequilibrium spectral function. This ansatz is problematic for frequencies ω below the gap since, at finite temperature and/or out of equilibrium, the addition and removal energies overlap. The retarded and advanced Green's functions,

$$G_{\mathbf{k}}^R(\tau, \omega) = [G_{\mathbf{k}}^A(\tau, \omega)]^\dagger = [\omega - \mathcal{E}_{\mathbf{k}}(\tau) - \Sigma_{\mathbf{k}}^R(\tau, \omega)]^{-1}, \quad (3)$$

with $[\mathcal{E}_{\mathbf{k}}(\tau)]_{\mu\mu'} \equiv \delta_{\mu\mu'}\epsilon_{\mu\mathbf{k}}(\tau)$, and the lesser Green's function in Eq. (2) can be calculated once an approximation for the electronic self-energy Σ is available.

Let us consider pump fields with frequencies below the band gap, ensuring that only discrete states are explored during the time evolution. We demonstrate below that the Hartree plus statically screened exchange (HSEX) effectively captures the coherent regime, while the T-matrix plus exchange accurately describes the incoherent regime. Remarkably, the full self-energy can be compactly expressed as

$$\Sigma_{cc'\mathbf{k}}^R(\tau, \omega) = \sum_{\lambda\mathbf{Q}v} \sigma_{cc'\mathbf{k}}^{\lambda\mathbf{Q}v}(\tau, \omega), \quad (4a)$$

$$\begin{aligned} \Sigma_{cc'\mathbf{k}}^<(\tau, \omega) = & \sum_{\lambda\mathbf{Q}v} f[\omega - E_{\lambda\mathbf{Q}}(\tau) - \epsilon_{v\mathbf{k}-\mathbf{Q}}(\tau)] \\ & \times [\sigma_{cc'\mathbf{k}}^{\lambda\mathbf{Q}v}(\tau, \omega) - \sigma_{cc'\mathbf{k}}^{\lambda\mathbf{Q}v*}(\tau, \omega)], \end{aligned} \quad (4b)$$

where the sum runs over all valence bands and over all exciton states λ of momentum $\mathbf{Q}$. In the Fermi function of Eq. (4b), the quasiparticle energies $\epsilon_{\mu\mathbf{k}}(\tau)$ and exciton energies $E_{\lambda\mathbf{Q}}(\tau)$ are those of the *nonequilibrium* system. The key quantity in Eq. (4) is the function

$$\sigma_{cc'\mathbf{k}}^{\lambda\mathbf{Q}v}(\tau, \omega) = K_{cv\mathbf{k}}^{\lambda\mathbf{Q}} \frac{N_{\lambda\mathbf{Q}}(\tau)}{\omega - E_{\lambda\mathbf{Q}}(\tau) - \epsilon_{v\mathbf{k}-\mathbf{Q}}(\tau) + i\eta} K_{c'\mathbf{k}}^{\lambda\mathbf{Q}*} - i\eta, \quad (5)$$

where η is a positive infinitesimal, and the amplitude

$$K_{cv\mathbf{k}}^{\lambda\mathbf{Q}} = (\epsilon_{c\mathbf{k}}^{\text{eq}} - \epsilon_{v\mathbf{k}-\mathbf{Q}}^{\text{eq}} - E_{\lambda\mathbf{Q}}^{\text{eq}}) A_{cv\mathbf{k}-\mathbf{Q}}^{\lambda\mathbf{Q}} \quad (6)$$

is expressed in terms of the equilibrium band structure $\epsilon_{\mu\mathbf{k}}^{\text{eq}}$, exciton energies $E_{\lambda\mathbf{Q}}^{\text{eq}}$, and wave functions $A_{cv\mathbf{k}}^{\lambda\mathbf{Q}}$. Notably, the full self-energy depends only on the *total* number of excitons at the probing time τ [33],

$$N_{\lambda\mathbf{Q}}(\tau) = \delta_{\mathbf{Q},\mathbf{0}} |\rho_{\lambda}(\tau)|^2 + N_{\lambda\mathbf{Q}}^{\text{inc}}(\tau), \quad (7)$$

with $|\rho_{\lambda}|^2$ the number of coherent excitons, and $N_{\lambda\mathbf{Q}}^{\text{inc}}$ the number of incoherent excitons. In Supplemental Material [52] we present a practical method to extract the non-equilibrium energies $\epsilon_{\mu\mathbf{k}}(\tau)$ and $E_{\lambda\mathbf{Q}}(\tau)$ directly from $N_{\lambda\mathbf{Q}}(\tau)$. Equations (2)–(5) are the main result of this Letter. They provide a first-principles formula to calculate TR-ARPES spectra for any pump-probe delay, and for a wide range of temperatures and excitation densities. The only input quantities are the exciton populations $N_{\lambda\mathbf{Q}}(\tau)$, which can be determined by, e.g., solving the excitonic Bloch equations [33,35,54,55].

Coherent regime—Here, we briefly revisit the theory of the coherent regime, and offer an alternative perspective. Without any loss of generality we set the time origin, $t = 0$, after the action of the pump pulse. For weak pumping the excitation density is low, and the state of the system at positive times is given by the quantum superposition $|\Psi(t)\rangle = |\Psi_g\rangle + \sum_{\lambda} \rho_{\lambda}(t) |\lambda\mathbf{0}\rangle$, where $|\Psi_g\rangle$ is the ground state and $|\lambda\mathbf{Q}\rangle = \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^{\lambda\mathbf{Q}} \hat{d}_{c\mathbf{k}+\mathbf{Q}}^\dagger \hat{d}_{v\mathbf{k}} |\Psi_g\rangle$ are the exciton states of momentum $\mathbf{Q}$ —here, $\hat{d}_{\mu\mathbf{k}}$ is the annihilation operator for electrons in band μ with momentum $\mathbf{k}$. As the pump pulse can only excite bright excitons, $|\Psi(t)\rangle$ contains exclusively excitons of vanishing momentum, $\mathbf{Q} = \mathbf{0}$. The coefficients $\rho_{\lambda}(t) = \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^{\lambda\mathbf{0}*} \langle \Psi(t) | \hat{d}_{v\mathbf{k}}^\dagger \hat{d}_{c\mathbf{k}} | \Psi(t) \rangle$ are the exciton polarizations, and their square modulus yields the number of coherent excitons; see Eq. (7). The system is described by the state $|\Psi(t)\rangle$ up to times smaller than the exciton lifetimes. Such time window defines the coherent regime. From the knowledge of $|\Psi(t)\rangle$ we can directly calculate $G^<$ [52], and hence the TR-ARPES spectrum. We refer to this strategy as the “Lehmann approach,” since it is based on expanding the many-body state in eigenstates of the Hamiltonian. The same $G^<$ can be obtained from Eq. (2) using the HSEX self-energy; see Eq. (12). The explicit form of the HSEX self-energy can be readily derived by projecting the equations of motion for the Green's function [37,38] onto the conduction-band subspace. The final result is Eq. (4) with σ evaluated in $N_{\lambda\mathbf{Q}} = \delta_{\mathbf{Q},\mathbf{0}} |\rho_{\lambda}|^2$; see Supplemental Material for details [52]. The advantage of the many-body formulation over the Lehmann approach is that it successfully extends beyond the domain of low excitation densities [41].

Incoherent regime—In the incoherent regime the polarization ρ_{λ} vanishes, and consequently the HSEX self-energy in Eqs. (4) vanishes too. In this regime, the electronic

subsystem is described by an ensemble of bright and dark incoherent excitons. The transition from a pure state to an ensemble is a general phenomenon in systems interacting with a bath, such as electrons interacting with phonons in our case. It has been demonstrated in an exactly solvable two-band model [28,56], and it is also a consequence of the excitonic Bloch equations [33,35,54,55].

A heuristic theory for the photocurrent in the incoherent regime can be effectively developed for low excitation densities. According to the excitonic Bloch equations the incoherent ensemble is described by the many-body density matrix $\hat{\rho} = |\Psi_g\rangle\langle\Psi_g| + \sum_{\lambda\mathbf{Q}} N_{\lambda\mathbf{Q}}^{\text{inc}} |\lambda\mathbf{Q}\rangle\langle\lambda\mathbf{Q}|$. From the knowledge of $\hat{\rho}$ we can calculate $G^<$ [52], which in turn allows us to determine the TR-ARPES spectrum. This is the Lehmann approach of the incoherent regime [27,28,42,44,57]. Establishing the many-body diagrammatic approximation underlying this approach would lift the low-density constraint, and pave the way toward a fully first-principles treatment of TR-ARPES spectra in the incoherent regime.

At present, the state-of-the-art many-body approximation is largely based on the T-matrix diagrams [42,43,58,59]. Previous studies reported excitonic sidebands appearing as replicas of the conduction bands [42,43], in apparent contradiction to the Lehmann approach, which instead predicts replicas of the valence bands. Another issue pertains to the intensity of the photoemission signal, proportional to $|A_{cv\mathbf{k}}^{\lambda\mathbf{Q}}|^2$. The exciton wave functions satisfy the Bethe Salpeter equation, whose kernel is the sum of the bare Coulomb interaction v (direct term) and the screened interaction W (exchange term) [1,51,60], i.e.,

$$(\epsilon_{c\mathbf{k}+\mathbf{Q}}^{\text{eq}} - \epsilon_{v\mathbf{k}}^{\text{eq}}) A_{cv\mathbf{k}}^{\lambda\mathbf{Q}} - \sum_{c'\mathbf{v}'\mathbf{k}'} K_{cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'}^{\mathbf{Q}} A_{c'\mathbf{v}'\mathbf{k}'}^{\lambda\mathbf{Q}} = E_{\lambda\mathbf{Q}}^{\text{eq}} A_{cv\mathbf{k}}^{\lambda\mathbf{Q}}, \quad (8)$$

with

$$K_{cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'}^{\mathbf{Q}} = W_{c\mathbf{k}+\mathbf{Q},v'\mathbf{k}'v\mathbf{k},c'\mathbf{k}'+\mathbf{Q}} - v_{c\mathbf{k}+\mathbf{Q},v'\mathbf{k}'c'\mathbf{k}'+\mathbf{Q}} v_{v\mathbf{k}}. \quad (9)$$

Thus, a pure T-matrix self-energy (containing only W) cannot yield the Lehmann intensity of the signal.

To reconcile many-body theory with the Lehmann approach we consider the four self-energy diagrams of Fig. 1—the gray circle is the exchange-correlation (xc) function L , the wiggly line is the bare interaction v , and the double wiggly line is the statically screened interaction W . The first diagram in Fig. 1 is the T-matrix self-energy, and we refer to the sum of all four diagrams as the T-matrix plus exchange (TX) self-energy. Notice that the zeroth order xc function is simply GG . Consequently, the lowest-order T-matrix diagram has the same topology as the (second-Born) bubble diagram, except that *both* interaction lines are screened. This raises the issue of a possible double counting of screening diagrams, which we address below.

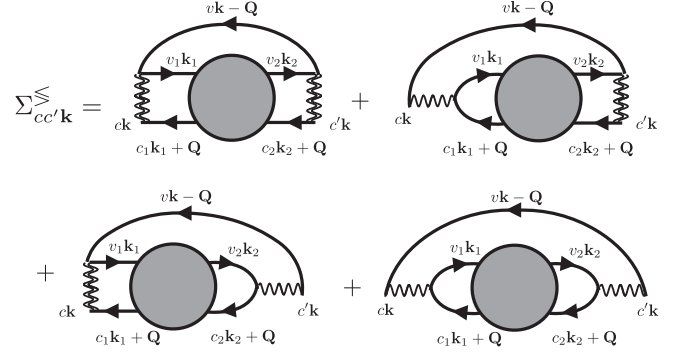


FIG. 1. TX self-energy for the Green's function in the incoherent regime. We represent Green's functions G with solid lines, bare interactions v with wiggly lines, screened interactions W with double wiggly lines, and the xc function L with a gray circle.

The diagrammatic equation of Fig. 1 is an approximation for the *lesser* and *greater* self-energy, not for the time (or contour) ordered Σ . Accordingly, the bubble diagram with two W lines does not emerge from T matrix, rather from GW . Indeed, $\Sigma_{GW}^< = iG^<W^< = iG^<W^R P^<W^A$, where $P^< = iG^<G^>$ [51]. Evaluating the screened interaction in the static approximation, $W^R = W^A = W$, we recover the lowest order (first) diagram in Fig. 1. Thus, there is no double counting issue. We also observe that the first diagram does not include the *full* GW self-energy, since the bottom Green's function is summed over conduction bands only. The missing contributions are recovered by adding the fourth diagram in Fig. 1. In fact, this diagram has the structure $Gv\chi v = G(W - v)$, χ being the density response function, and G is summed over the valence bands. In summary, the lesser and greater self-energies of Fig. 1 incorporate the full GW self-energy, but handle W differently depending on the Green's function band indices. If G has conduction indices then W is statically screened, whereas for valence indices W is dynamically screened.

Taking into account the definition of the HSEX kernel in Eq. (9), the TX self-energy of Fig. 1 can be written as

$$\Sigma_{cc'\mathbf{k}}^<(t, t') = -i^2 \sum_{\substack{c_1 c_2 v_1 v_2 v \\ \mathbf{k}_1 \mathbf{k}_2 \mathbf{Q}}} K_{cv\mathbf{k}-\mathbf{Q}, c_1 v_1 \mathbf{k}_1}^{\mathbf{Q}} L_{c_1 v_1 \mathbf{k}_1, c_2 v_2 \mathbf{k}_2}^{\mathbf{Q}}(t, t') \times K_{c'\mathbf{k}-\mathbf{Q}, c_2 v_2 \mathbf{k}_2}^{\mathbf{Q}*} G_{v\mathbf{k}-\mathbf{Q}}^<(t, t'), \quad (10)$$

from which we can extract the retarded self-energy according to

$$\Sigma_{cc'\mathbf{k}}^R(\tau, \omega) = i \int \frac{d\omega'}{2\pi} \frac{\Sigma_{cc'\mathbf{k}}^>(\tau, \omega) - \Sigma_{cc'\mathbf{k}}^<(\tau, \omega)}{\omega - \omega' + i\eta} - i\eta. \quad (11)$$

Expanding the xc function L in the excitonic basis [33,42], and approximating the Green's function at the quasiparticle level, we obtain Eq. (4a) with σ evaluated in $N_{\lambda\mathbf{Q}} = N_{\lambda\mathbf{Q}}^{\text{inc}}$ —we refer the reader to Supplemental Material for the

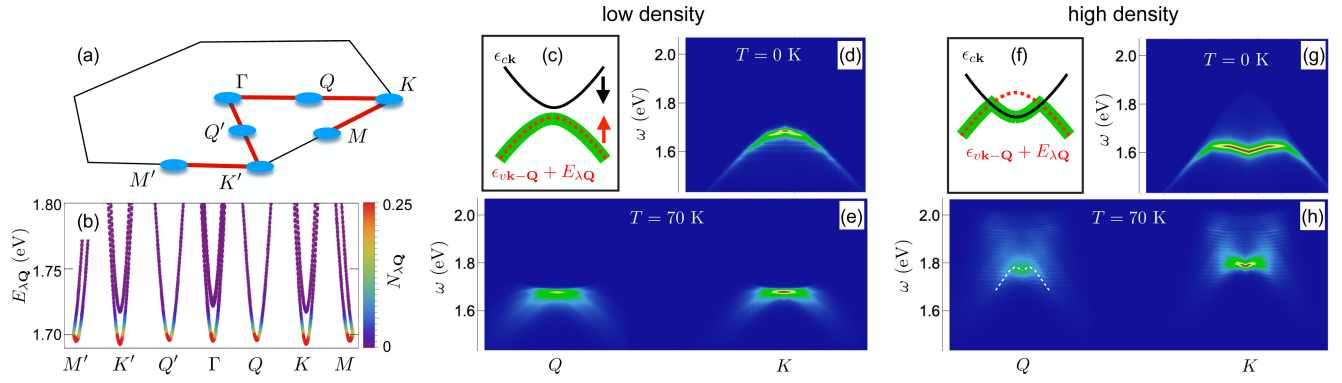


FIG. 2. (a) First Brillouin zone and location of a few high symmetry points. (b) Exciton band structure of the equilibrium WSe₂ ML along the red path illustrated in panel (a)—curves are colored according to the thermal occupation of excitons at temperature $T = 70$ K and excitation density $n_c = 10^{13}$ cm⁻². (c),(f) Illustration of conduction band and replica of valence band at low [panel (c)] and moderate [panel (f)] excitation densities. (d),(e),(g),(h) TR-ARPES spectrum (in arbitrary units) for low [panels (d), (e)] and high [panels (g), (h)] excitation densities at different temperatures: $n_c = 10^{11}$ cm⁻² and $T = 0$ K [panel (d)]; $n_c = 10^{11}$ cm⁻² and $T = 70$ K [panel (e)]; $n_c = 4 \times 10^{12}$ cm⁻² and $T = 0$ K [panel (g)]; $n_c = 10^{13}$ cm⁻² and $T = 70$ K [panel (h)].

derivation [52]. This result agrees with that of a pure T-matrix calculation [43] only if the exciton energies and wave functions remain unchanged upon setting the bare v to zero in Eq. (9), which is generally not the case.

Equation (10) is only used to extract Σ^R . The lesser self-energy in Eq. (2) is derived from σ according to Eq. (4b), ensuring consistency with the self-energy in the coherent regime [52]. As we see below [Eq. (16)], such consistency is essential not only for recovering the results of the Lehmann approach but also for extending the theory beyond the low-density limit.

Low density—In the low-density limit $N_{\lambda\mathbf{Q}}$ is infinitesimal, and $E_{\lambda\mathbf{Q}}(\tau)$ and $\epsilon_{\mu\mathbf{k}}(\tau)$ are well approximated by their equilibrium values. To lowest order in the excitation density, Eq. (2) yields

$$G_{cc'\mathbf{k}}^<(\tau, \omega) = \lim_{\eta \rightarrow 0} \frac{1}{\omega - \epsilon_{c\mathbf{k}}^{\text{eq}} + i\eta} \Sigma_{cc'\mathbf{k}}^<(\tau, \omega) \frac{1}{\omega - \epsilon_{c'\mathbf{k}}^{\text{eq}} - i\eta} \\ = 2\pi i \sum_{\lambda\mathbf{Q}} N_{\lambda\mathbf{Q}}(\tau) A_{cv\mathbf{k}-\mathbf{Q}}^{\lambda\mathbf{Q}} A_{c'\mathbf{k}-\mathbf{Q}}^{\lambda\mathbf{Q}*} \\ \times \delta(\omega - E_{\lambda\mathbf{Q}}^{\text{eq}} - \epsilon_{v\mathbf{k}-\mathbf{Q}}^{\text{eq}}), \quad (12)$$

where we use Eq. (6). This result agrees with the Lehmann approach both in the coherent ($N_{\lambda\mathbf{Q}} = \delta_{\mathbf{Q}\mathbf{0}} |\rho_{\lambda}|^2$) and incoherent ($N_{\lambda\mathbf{Q}} = N_{\lambda\mathbf{Q}}^{\text{inc}}$) regimes [52]. It also agrees with the removal part of the spectral function in the incoherent regime presented in Ref. [43].

Inserting Eq. (12) in the photocurrent formula Eq. (1) we find

$$I_{\mathbf{k}}(\tau, \epsilon) \propto |a|^2 \sum_{\lambda\mathbf{Q}} N_{\lambda\mathbf{Q}}(\tau) \sum_v \left| \sum_c D_{c\mathbf{k}}(\epsilon) A_{cv\mathbf{k}-\mathbf{Q}}^{\lambda\mathbf{Q}} \right|^2 \\ \times 2\pi \delta(\epsilon_{v\mathbf{k}-\mathbf{Q}}^{\text{eq}} + E_{\lambda\mathbf{Q}}^{\text{eq}} - \epsilon + \omega_0). \quad (13)$$

This formula extends the theory of Refs. [42,44] to multiple bands, and corrects the ansatz in Ref. [57] by placing the sum over conduction bands inside the square modulus. According to Eq. (13), a $\lambda\mathbf{Q}$ exciton generates a replica of the valence bands shifted in energy by $E_{\lambda\mathbf{Q}}^{\text{eq}}$ and in momentum by $\mathbf{Q}$; see Fig. 2(c). If the lowest-energy exciton, say λ_0 , is bright, and the system is resonantly pumped at this transition, then $\rho_{\lambda}(\tau) \propto \delta_{\lambda\lambda_0}$. At low temperatures, phonon scattering into higher-energy states is suppressed, so that the coherent λ_0 exciton can only decay into an incoherent λ_0 exciton of vanishing momentum. Conservation of the total number of excitons [33] implies $N_{\lambda\mathbf{Q}}(\tau) \propto \delta_{\lambda\lambda_0} \delta_{\mathbf{Q}\mathbf{0}}$, independent of τ . In this scenario, the TR-ARPES signal is therefore identical in the coherent and incoherent regimes [61]. Revealing the coherence of the system with TR-ARPES requires a probe field with a duration comparable to the exciton period [38].

An important feature of Eq. (12) is that the total number of carriers in the conduction band is given by

$$N_c(\tau) = -i \int \frac{d\omega}{2\pi} \sum_{c\mathbf{k}} G_{cc\mathbf{k}}^<(\tau, \omega) = \sum_{\lambda\mathbf{Q}} N_{\lambda\mathbf{Q}}(\tau), \quad (14)$$

where the normalization of the exciton wave functions $\sum_{c\mathbf{k}} |A_{c\mathbf{k}}^{\lambda\mathbf{Q}}|^2 = 1$ has been used. In other words, in the low-density limit N_c is the same as the total number of excitons, as it should be. We remark that this property would not be satisfied if we had included only the T-matrix diagram in the self-energy.

Beyond low density—The formula Eq. (2) for $G^<$ simplifies if the wave function of the occupied exciton states have a predominant contribution on a single conduction band and valence band, say c_0 and v_0 . In this case, $K_{c\mathbf{k}}^{\lambda\mathbf{Q}} = \delta_{cc_0} \delta_{vv_0} K_{c_0v_0\mathbf{k}}^{\lambda\mathbf{Q}}$, and the quantity σ in Eq. (5) has one

single nonvanishing entry for $c = c' = c_0$. This implies also that the self-energy is nonvanishing only for $c = c' = c_0$. Defining $\Delta_{\mathbf{k}}^{\lambda\mathbf{Q}}(\tau) \equiv \sqrt{N_{\lambda\mathbf{Q}}(\tau)} K_{c_0 v_0 \mathbf{k}}^{\lambda\mathbf{Q}}$, and omitting the dependence of the various quantities on τ , we have

$$G_{c_0 c_0 \mathbf{k}}^R(\omega) = \frac{1}{\omega - \epsilon_{c_0 \mathbf{k}} - \sum_{\lambda\mathbf{Q}} \frac{|\Delta_{\mathbf{k}}^{\lambda\mathbf{Q}}|^2}{\omega - E_{\lambda\mathbf{Q}} - \epsilon_{v_0 \mathbf{k}-\mathbf{Q}} + i\eta} + i\eta}. \quad (15)$$

To gain insight into this problem, we assume that only a discrete number of excitons $\lambda_j \mathbf{Q}_j$ are populated, and that $\Delta_{\mathbf{k}}^j \equiv \Delta_{\mathbf{k}}^{\lambda_j \mathbf{Q}_j}$ are nonvanishing in small and nonoverlapping regions $\mathcal{R}^j$ of the first Brillouin zone. Then, for $\mathbf{k} \in \mathcal{R}^j$ only $\lambda_j \mathbf{Q}_j$ contributes to the sum in the denominator of Eq. (15). This allows us to calculate $G_{c_0 c_0 \mathbf{k}}^<$ analytically [52], and find

$$G_{c_0 c_0 \mathbf{k}}^<(\omega) \simeq 2\pi i \sum_j \frac{E_{\lambda_j \mathbf{Q}_j} + \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j} - E_{\mathbf{k},j}^-}{E_{\mathbf{k},j}^+ - E_{\mathbf{k},j}^-} \delta(\omega - E_{\mathbf{k},j}^-), \quad (16)$$

where

$$E_{\mathbf{k},j}^{\pm} = \frac{1}{2} \left[\epsilon_{c_0 \mathbf{k}} + E_{\lambda_j \mathbf{Q}_j} + \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j} \pm \sqrt{(\epsilon_{c_0 \mathbf{k}} - E_{\lambda_j \mathbf{Q}_j} - \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j})^2 + 4|\Delta_{\mathbf{k}}^j|^2} \right]. \quad (17)$$

To lowest order in $|\Delta_{\mathbf{k}}^j|$ (low-density limit) we can approximate the argument of the Dirac delta as $E_{\mathbf{k},j}^- \simeq E_{\lambda_j \mathbf{Q}_j}^{\text{eq}} + \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j}^{\text{eq}}$, and the prefactor of the Dirac delta as $|\Delta_{\mathbf{k}}^j|^2 / (\epsilon_{c_0 \mathbf{k}} - E_{\lambda_j \mathbf{Q}_j}^{\text{eq}} - \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j}^{\text{eq}})^2 = N_{\lambda_j \mathbf{Q}_j} |A_{c_0 v_0 \mathbf{k}}^{\lambda_j \mathbf{Q}_j}|^2$; the resulting $G^<$ correctly agrees with Eq. (12). Increasing the excitation density, the nonequilibrium energy $E_{\lambda_j \mathbf{Q}_j}(\tau) + \epsilon_{v_0 \mathbf{k}-\mathbf{Q}_j}(\tau)$ might overcome $\epsilon_{c_0 \mathbf{k}}(\tau)$, leading to a hybridization (proportional to $|\Delta_{\mathbf{k}}^j|$) between the conduction band and the replica of the valence band; see Fig. 2(f). This scenario has been thoroughly investigated in the coherent regime [37,38,40]—hence for $\mathbf{Q} = \mathbf{0}$ —and is associated with a BEC-BCS crossover of the coherent exciton fluid [21,22]. Our result in Eq. (16) indicates that the same phenomenon can also occur in the incoherent regime. In particular, the excitonic sidebands induced by a sizable population of incoherent excitons of momentum $\mathbf{Q}$ might resemble the conduction bands hybridized with a $\mathbf{Q}$ -shifted replica of the valence bands.

TR-ARPES in WSe₂ monolayer—We consider a WSe₂ monolayer (ML) at low ($n_c \sim 10^{11} \text{ cm}^{-2}$) and moderate ($n_c \sim 10^{13} \text{ cm}^{-2}$) excitation densities $n_c = N_c/A$, where A is the area of the sample. The WSe₂ ML is a direct gap semiconductor, with a calculated band gap at the K and K'

points [Fig. 2(a)] estimated to be $\sim 2 \text{ eV}$ [62]. For sufficiently long times after pumping, the exciton populations follow a Bose distribution $N_{\lambda\mathbf{Q}} = [e^{(E_{\lambda\mathbf{Q}} - \mu_X)/T} - 1]^{-1}$, where T is the temperature and μ_X is self-consistently calculated from Eq. (14). In Fig. 2(b) we show the equilibrium exciton band structure, and how excitons are distributed at temperature $T = 70 \text{ K}$; numerical details are reported in Supplemental Material [52]. The low-energy landscape is characterized by several (almost) degenerate excitons, in agreement with Refs. [5,63], the lowest excitons being at K and K' .

At zero temperature, only the degenerate excitons with momenta $\mathbf{Q}$ at K and K' are populated. Along the path $\Gamma - K - \Gamma$, and for low values of n_c , the spectrum features a single sideband for momenta $\mathbf{k}$ near K [Fig. 2(d)]. This is the replica of $\epsilon_{v\mathbf{k}-\mathbf{Q}}$ with $\mathbf{Q}$ at the inequivalent K point, which is the same as $\epsilon_{v\mathbf{k}}$ with $\mathbf{k}$ around K' . The replica is shifted in energy by $\sim E_{\lambda\mathbf{Q}}^{\text{eq}}$, and the intensity of the signal is proportional to $|A_{c v \mathbf{k}-\mathbf{Q}}^{\lambda\mathbf{Q}}|^2$, in agreement with Eq. (12). Increasing n_c , the exciton energies undergo a blueshift while the band gap shrinks [Figs. 2(c) and 2(f)]. The replica of the valence band hybridize with the conduction band, and the excitonic sideband acquires the shape of a Mexican hat [well described by Eq. (17)], as shown in Fig. 2(g).

At temperatures $T = 70 \text{ K}$, exciton states with momenta near other high symmetry points (M , Q , and Γ) also become populated; see Fig. 2(b). Along the path $\Gamma - K - \Gamma$, and for low values of n_c , a second replica of the valence band appears for momenta $\mathbf{k}$ near Q [Fig. 2(e)]. This emerges from excitons with $-\mathbf{Q}$ around Q , leading to a replica of $\epsilon_{v\mathbf{k}}$ with $\mathbf{k}$ around K . As the exciton energies are almost degenerate, the two replicas in Fig. 2(e) are located in the same spectral range. Compared to Fig. 2(d), the signal appears blurred—this is due to the presence of exciton states with momenta close to, but not exactly at, the high symmetry points. The additional excitonic sideband around the Q point persists at higher excitation densities, but its shape turns into a Mexican hat [see Fig. 2(h)], again in agreement with Eq. (17).

Conclusions—We presented a first-principles approach to excitons in TR-ARPES, bridging the coherent and incoherent regimes through a unified formula that depends solely on the total number of excitons at the pump-probe delay τ . Applicable across a wide range of temperatures and excitation densities, our formula provides a powerful tool for understanding and engineering nonequilibrium band structures of excitonic materials. Band hybridization with dark excitons enables controlled shifts of the valence bands in both energy and momentum, and to reshape them into a Mexican-hat dispersion. In particular, the mechanism of Refs. [39,64] naturally extends to the incoherent regime, enabling control over the topological character of excited materials through exciton wave function symmetries. This points to a promising avenue for realizing nonequilibrium

topological phases with lifetimes reaching the picosecond timescale.

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