Many-body exciton elastic scattering in Ruddlesden-Popper metal halides

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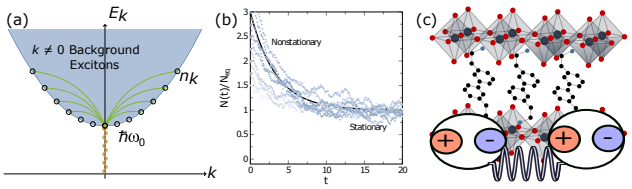

Figure 1: (a) Schematic representation of optical absorption of excitons and exciton-exciton scattering with a background population, where the dispersion relation is in the exciton representation and $\vec{k} = \vec{k_e} + \vec{k_h}$ is the exciton wavevector. (b) Time evolution of population $N(t)/N_{\mathrm{eq}}$ from an initial nonstationary state produced by exciton injection. Individual trajectories are represented by blue dots. Asymptotically, the function reaches a stationary state that yields the Anderson-Kubo limit. (c) Crystal structure of $(PEA)_2PbI_4$ with schematic representation of Coulomb-correlated exciton-exciton elastic scattering.

It is well recognized that many-body phenomena have a profound effect on the linear and non-linear optical lineshapes of semiconductors with reduced dimensionality, in which Coulomb correlations can be particularly strong due to decreased screening and quantum confinement effects. An important process that is highly relevant in exciton quantum dynamics is excitation induced dephasing (EID) [1, 2]. This can be described as the incoherent Coulomb elastic scattering between multiple excitons or between excitons and an electron-hole plasma generated with the excitation optical field. The scattering process gives rise to faster dephasing dynamics compared to the low-density pure-dephasing limit, and may be the dominant dephasing pathway at sufficiently high densities. In many systems, especially those with strong exciton-phonon coupling, the background excitations are transient and co-evolve with optical modes of the system and consequently a strictly incoherent kinetic description such as this mesoscopic approach or a kinetic Markovian Boltzmann-like scattering theory cannot describe coherence dynamics. In this work, excitons generated coherently by a sequence of time-ordered and phase-matched femtosecond pulses scatter from incoherent background excitons and thereby undergo EID, which is perceived via changes of the homogeneous linewidth. In a polycrystalline thin film of a prototypical two-dimensional single-layer metal-halide perovskite derivative, phenylethylammonium lead iodide $[(PEA)_2PbI_4]$, we find that EID affects the complex lineshape by mixing absorptive and dispersive features in the real and imaginary spectral components; the real component of the two-dimensional coherent spectrum initially displays a dispersive lineshape that evolves into an absorptive over the timescale in which EID couplings persist, and the imaginary component evolves in the converse fashion. Furthermore, we find that the homogeneous contribution to the spectral linewidth narrows with population time, indicating a dynamic slowing down of the dephasing rate as the EID correlations active at early time dissipate. We find that the dynamic line narrowing phenomenon is reproduced by a stochastic scattering theory that we developed to investigate the evolution of the two-dimensional coherent excitation lineshape [3]. Our theoretical model presents a means to represent the environment as nonstationary, leading to a rich evolution of the nonlinear coherent exciton lineshape. This presents opportunities to include microscopic understanding of many-body interactions that are dominant in condensed-matter systems on their quantum dynamics.

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[3] Srimath Kandada, A. R., Li, H., Thouin, F., Bittner, E. R., and Silva, C., "Stochastic scattering theory for excitation-induced dephasing: Time-dependent nonlinear coherent exciton lineshapes", J. Chem. Phys. 153(16), 2020.