Phonon-driven femtosecond dynamics of excitons in crystalline pentacene from first principles

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abstract

Non-radiative exciton relaxation processes are critical for energy transduction efficiencies in optoelectronic materials. These processes are strongly coupled to the underlying crystal structure and its associated electron, exciton, and phonon band structures. At early stages after photoexcitation, thermalization– and in particular, the occupation of long-lived, optically dark states, determines the efficiency of photon energy transfer and functionality in energy conversion materials. Here, we present a first-principles approach to explore exciton relaxation pathways in pentacene, a paradigmatic molecular crystal and optoelectronic semiconductor. We compute the momentum- and band-resolved exciton-phonon interactions and use them to analyze key scattering channels. We find that exciton intraband transitions and dark-state occupation have similar timescales. We further show how the nature of real-time propagation of the exciton wavepacket is connected with the longitudinal- transverse exciton splitting, stemming from crystal anisotropy, and concomitant coupling of the anisotropic exciton and phonon dispersions. Our results provide a framework for understanding time-resolved exciton propagation and energy transfer in molecular crystals and beyond.

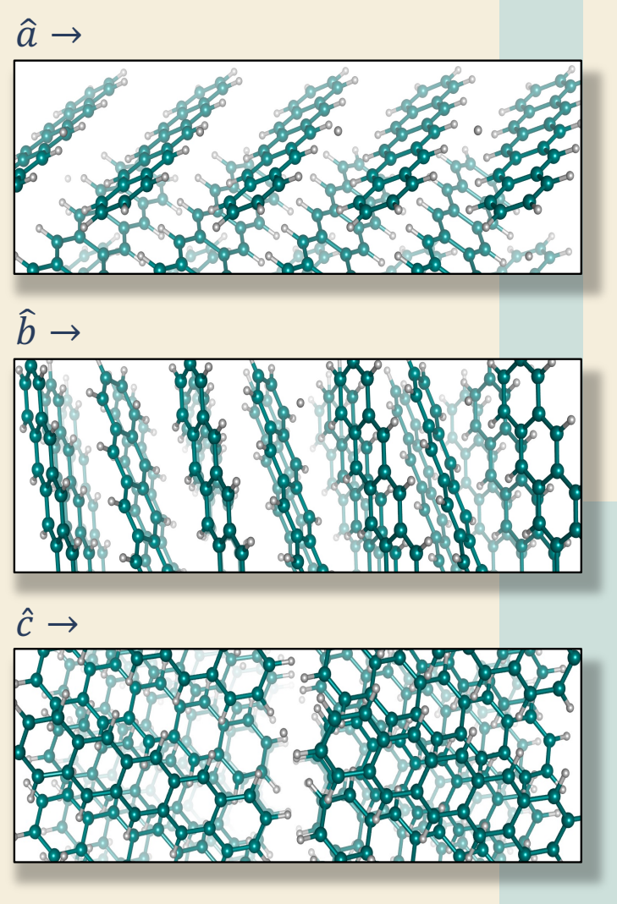
Motivation

Understand the relation between
crystal structure → exciton dispersion → exciton dynamics
& (lifetime, decay rates and diffusion)
Exciton-phonon interaction
via predictive *ab-initio* methods

Crystal Structure

Pentacene crystal
paradigmatic model system

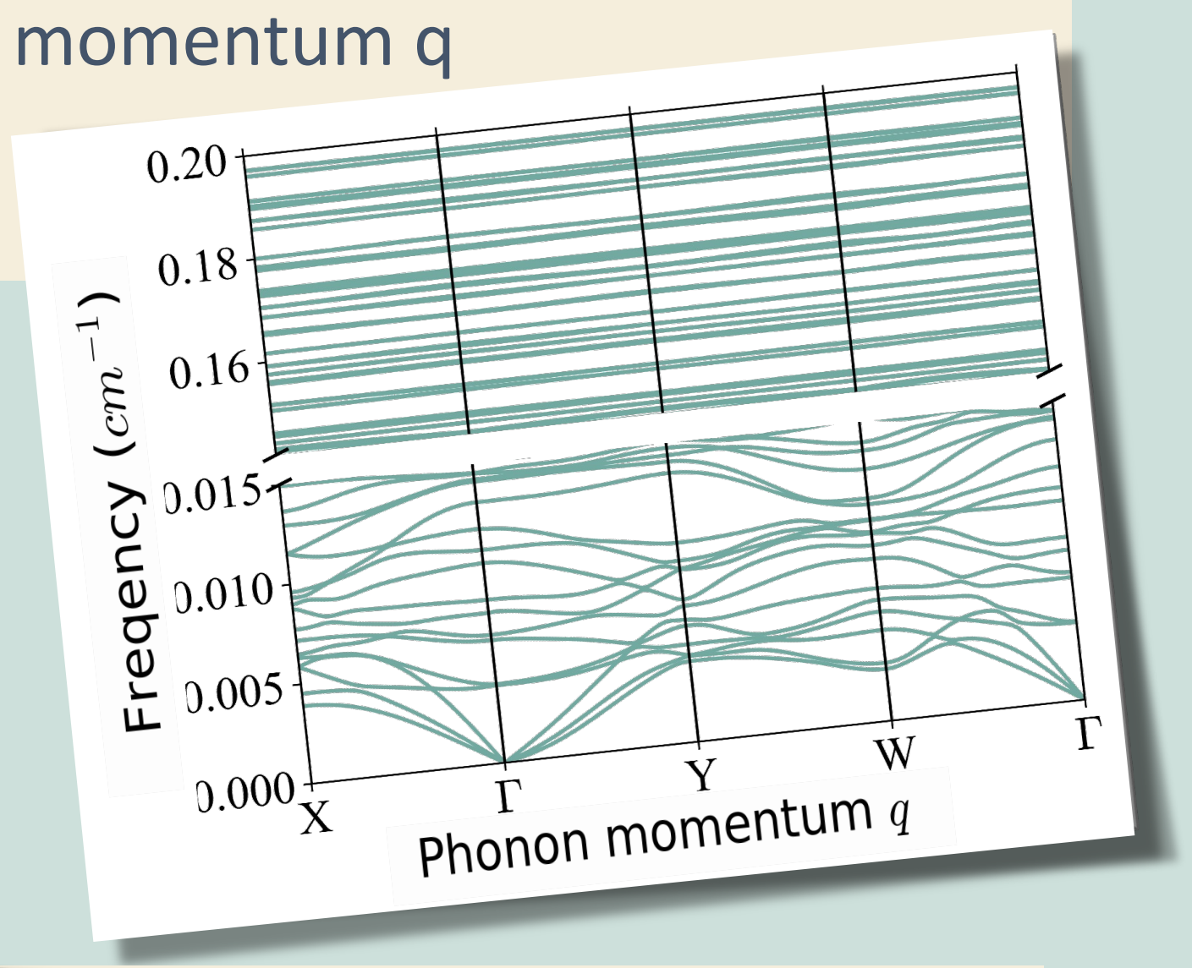
- Molecular crystal
  - VdW stacked molecular layers
- Widely experimentally explored
- Complex exciton decay processes
- Long exciton lifetimes



Key structural feature- **Anisotropy**

Phonon dispersion

Phonon dispersion calculated via DFPT:
phonon modes ν
Phonon momentum q

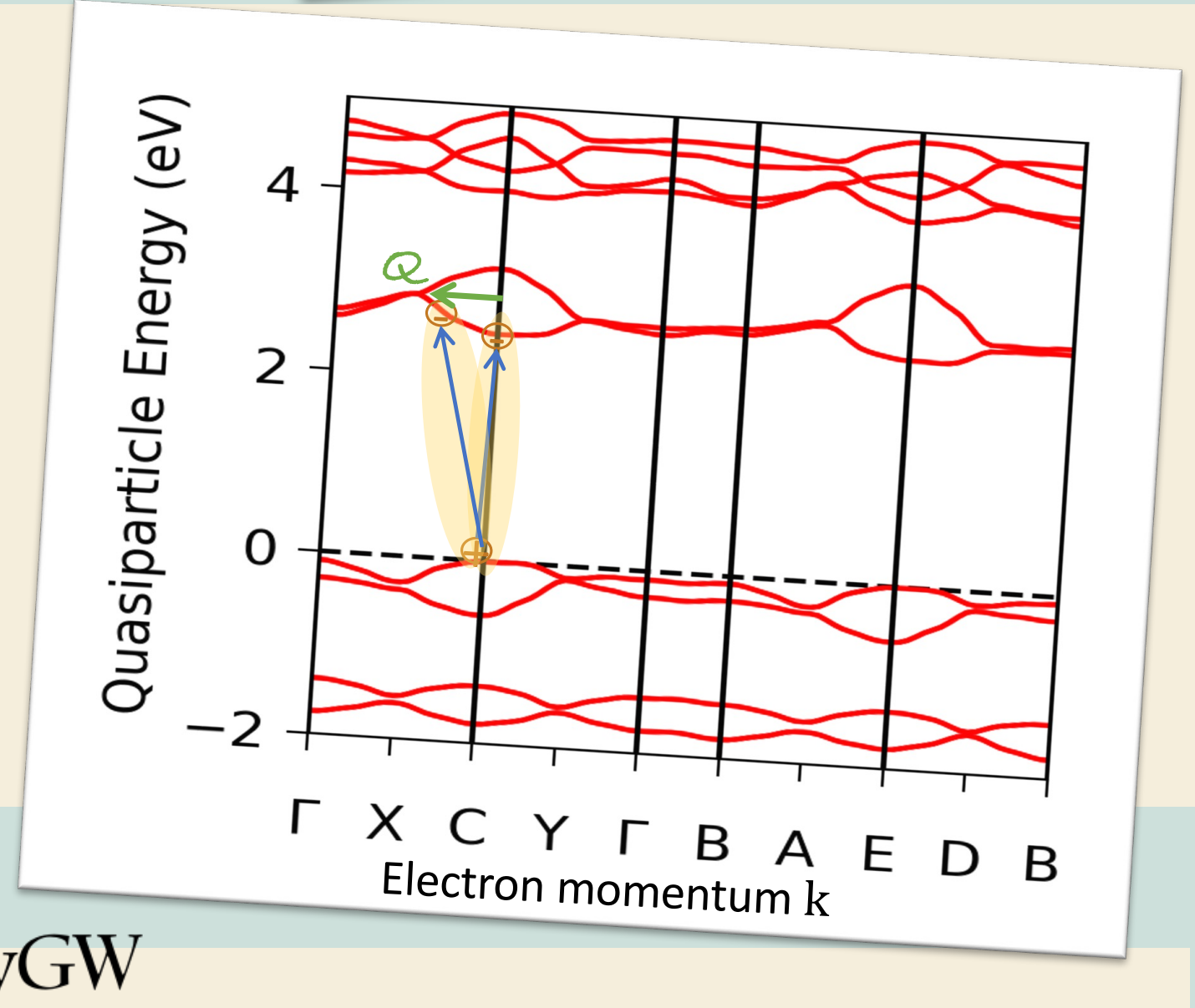


Electronic Structure

A quasi-particle picture is calculated via the GW approximation within many-body perturbation theory

$$\left(-\frac{\nabla^2}{2}+v_H+\Sigma(E)+v_{ext}\right)G_1(E)=EG_1(E)$$

$$\Sigma(E)=iG_1W$$



Exciton Dispersion

BerkeleyGW

The excitonic picture is calculated from the Bethe-Salpeter equation, with finite Q:

$$(E_{ck+Q}-E_{vk})A^{SQ}_{vck}+\sum_{v'c'k'}\langle vk;ck+Q|K^{eh}|v'k';c'k'+Q\rangle A^{SQ}_{v'c'k'}=\Omega_S(Q)A^{SQ}_{vck}$$

$$|SQ\rangle=\sum_{cvk}A^{SQ}_{cvk}|ck+Q\rangle\otimes|vk\rangle$$

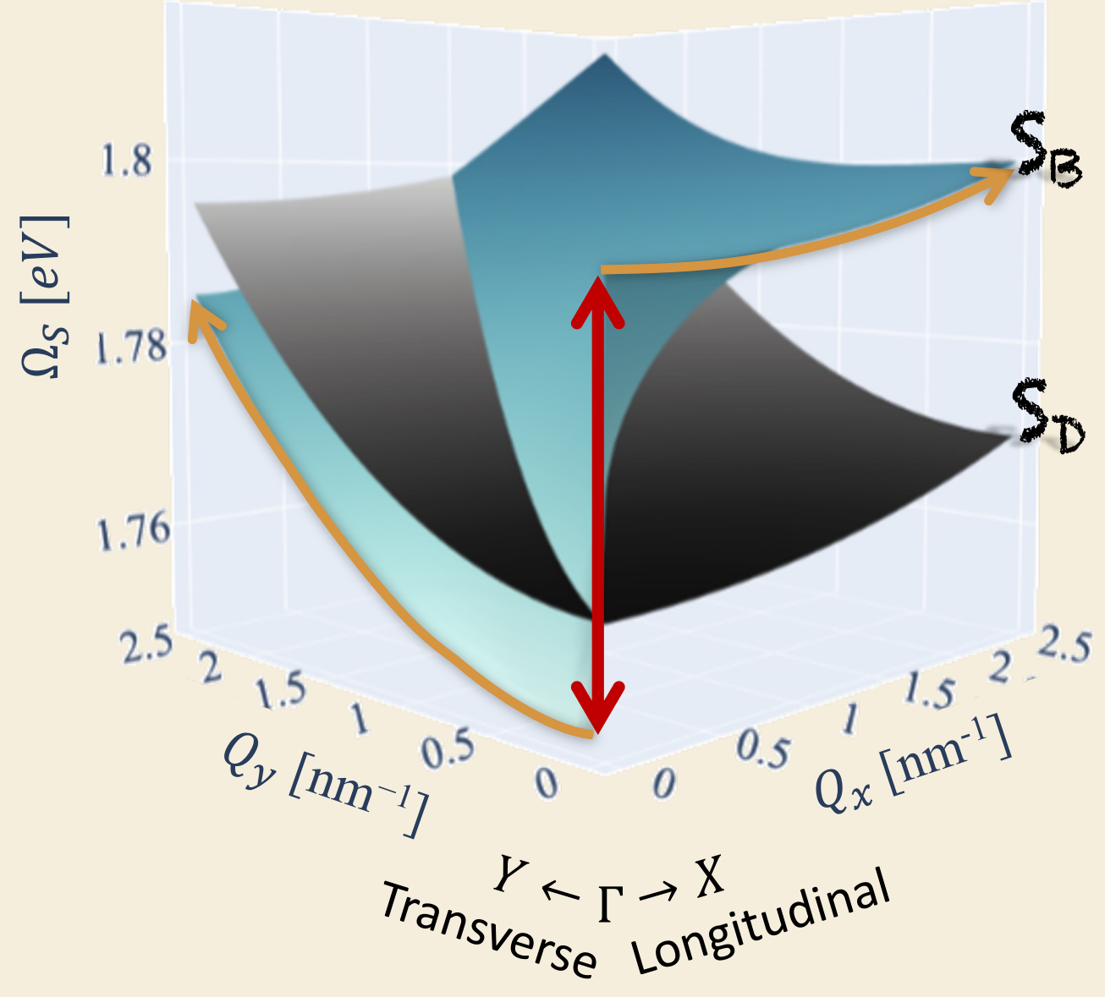
Exciton finite momentum Q :
momentum difference in the electron-hole pair

Exciton dispersion:

Pentacene crystal low-lying singlet states
[**D** (dark at Q=0), **B** (bright at Q=0)]

$$\Omega_S(Q)=\Omega_S(0)+C\cdot\cos^2(\theta)+\frac{\hbar^2}{2}\left(\frac{Q_x^2}{M_x^*}+\frac{Q_y^2}{M_y^*}\right)$$

Structural anisotropy manifested in the
- angular dispersion
- L-T split



$$K^x\propto|Q\cdot p|^2v(Q)$$

Exciton-phonon interaction

The probability for S(Q)→S’(Q+q) scattering via interaction with phonon (qν)

Coupling:

$$g_{SS'\nu}(Q,q)=\sum_{cc'vk}\left[A^{SQ+q}_{cvk}\right]^*g_{cc'\nu}(k+Q,q)\,A^{S'Q}_{c'vk}$$ electron-phonon

$$-\sum_{cvv'k}\left[A^{SQ+q}_{cvk}\right]^*g_{v'v\nu}(k,q)A^{S'Q}_{cv'k+q}$$ hole-phonon

electron(hole)-phonon coupling From DFPT

$$g_{mn\nu}(k,q)=\frac{1}{\sqrt{2\omega_{q\nu}}}\langle mk+q|\Delta_{q\nu}V^{DFT}|nk\rangle$$

Scattering times

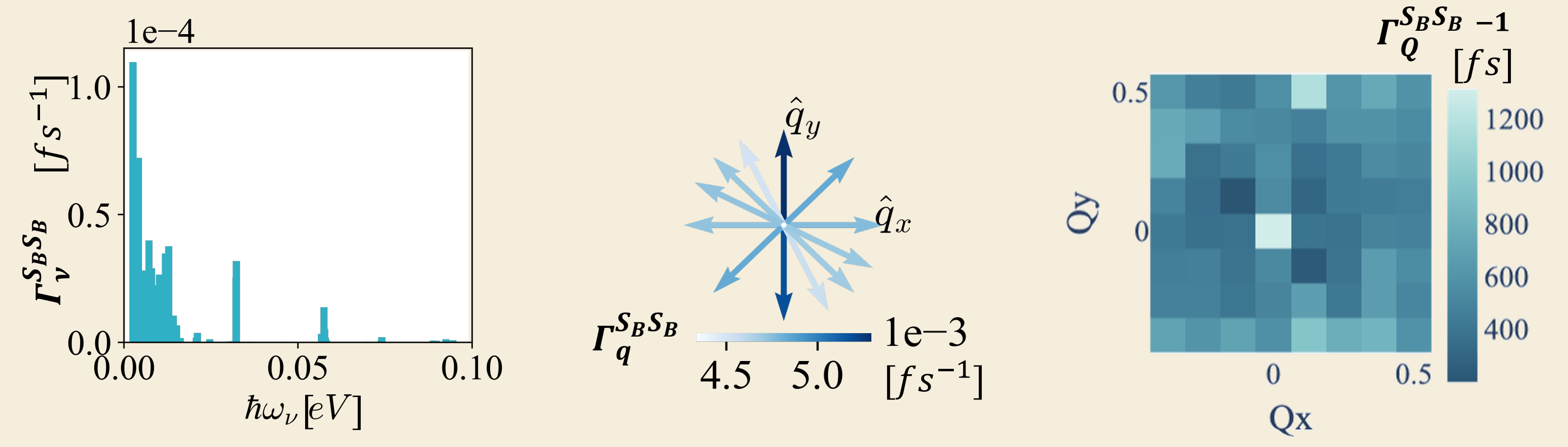
Scattering time:
Fermi’s golden rule

$$\Gamma_{SS'}=\frac{1}{N_QN_q}\cdot\frac{2\pi}{\hbar}\sum_{Q,q,\nu}|g_{SS'\nu}(Q,q)|^2\cdot\rho(\Delta\Omega_s\pm\hbar\omega_{q\nu})$$

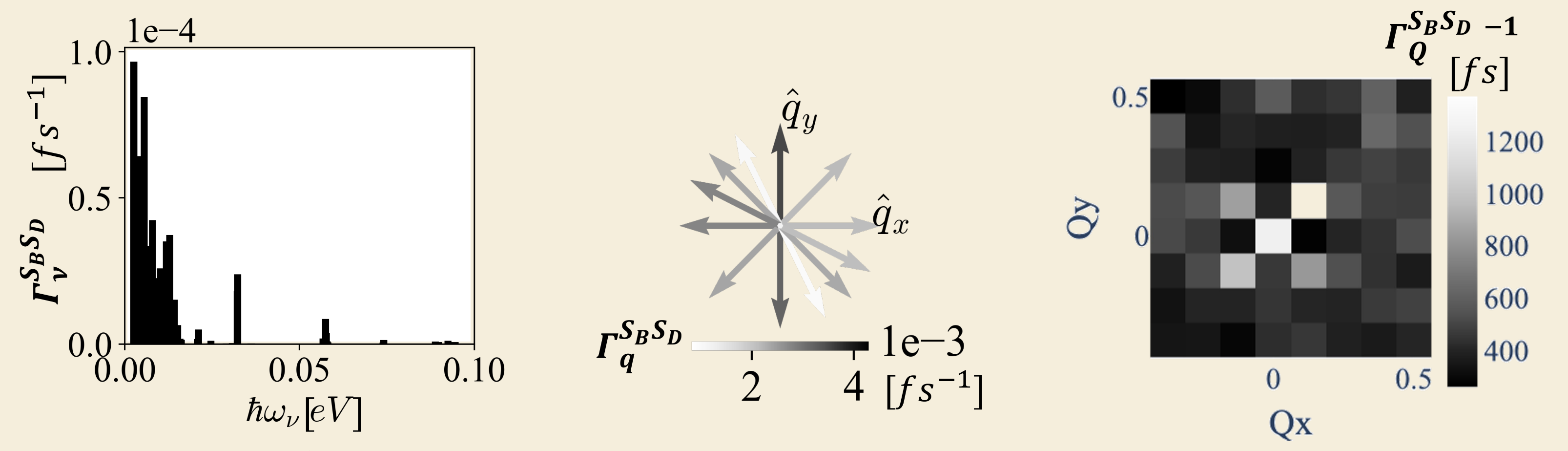
phonon occupation & energy conservation

Mode and momentum analysis:

Intra-band: $S_B\rightarrow S_B$

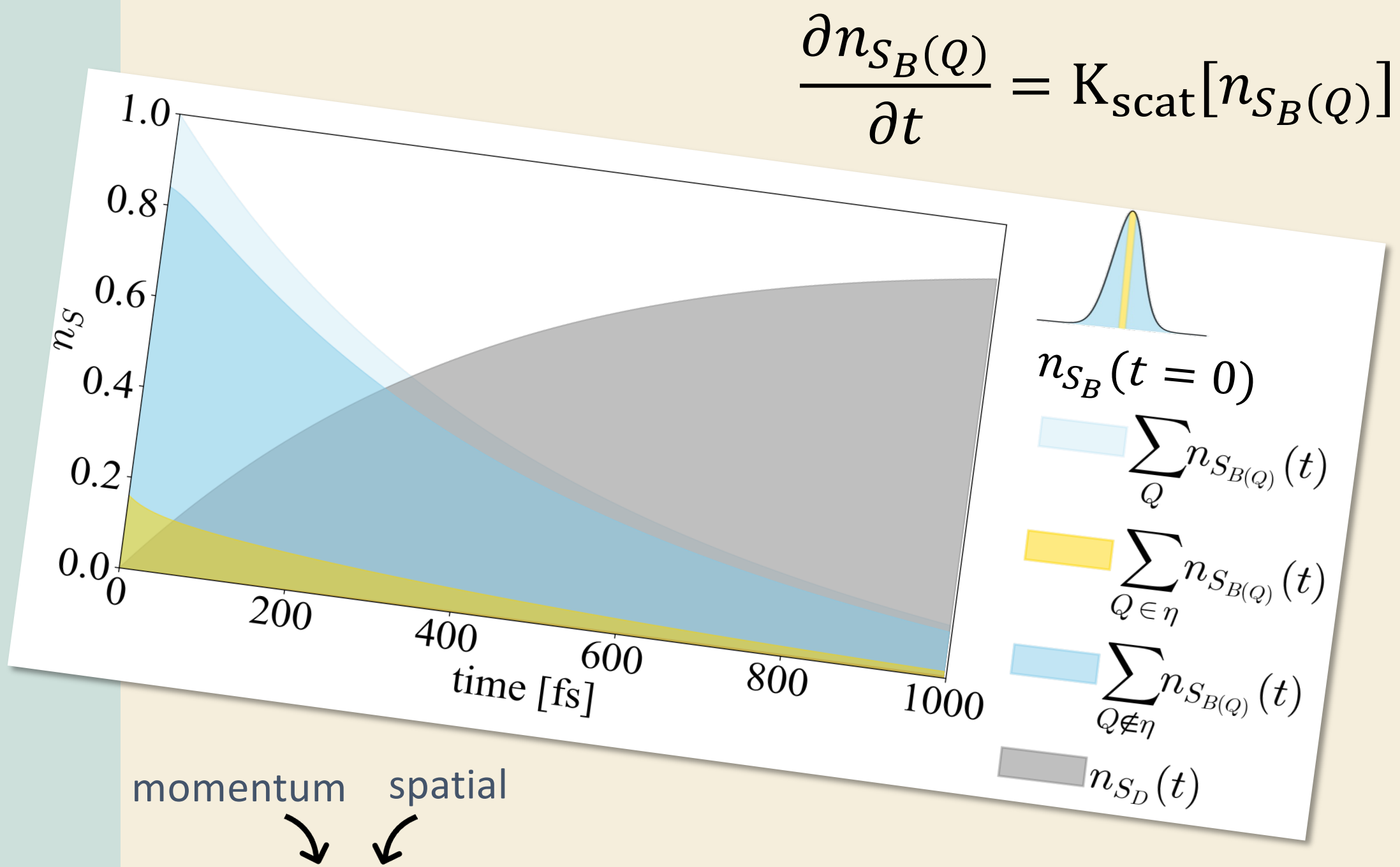


Inter-band: $S_B\rightarrow S_D$



Dominance of low-frequency phonons
Dominance of phonons with momentum along Γ-Y
Similar time scales for inter- and intra-band transitions

Kinetic framework



$S_B(Q)\rightleftarrows S_B(Q')$ Intra-band scattering

$$\frac{\partial n_{S_B(Q)}}{\partial t}=\mathrm{K_{scat}}[n_{S_B(Q)}]=\sum_q\Gamma^{S_B(Q+q)S_B(Q)}_{Qq}\cdot n_{S_B(Q+q)}-\sum_q\Gamma^{S_B(Q)S_B(Q+q)}_{Qq}\cdot n_{S_B(Q)}$$

$S_B(Q)\rightarrow S_D(Q')$ Inter-band scattering

$$-\Gamma^{S_B(Q)S_D}_{Q}\cdot n_{S_B(Q)}$$ $\dashrightarrow TT$

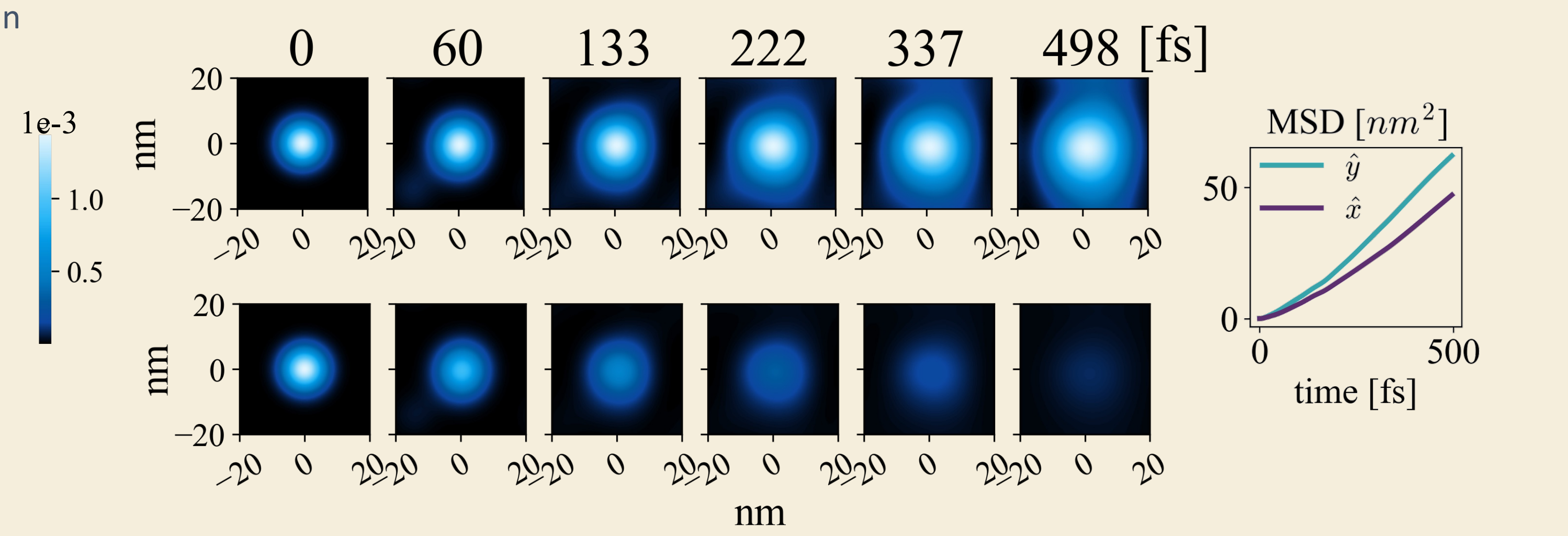
Radiative decay

$$-\Gamma^{rad}_{S_B(Q)}\cdot n_{S_B(Q)}\,\delta_{Q,\Gamma}$$

momentum spatial

$$\frac{\partial n_{S_B(Q,R)}}{\partial t}=-\frac{\partial n_{S_B(Q,R)}}{\partial R}\cdot\frac{\partial\Omega_{S_B}}{\partial Q}-K_{scat}[n_{S_B(Q)}]$$

exciton distribution
Ballistic propagation
scattering



- Anisotropic propagation due to interplay between exciton and phonon properties
- Intraband transitions dominate at early times
- Complement mechanism to singlet fission

static & dynamic structural effects in exciton evolution from first principles

Key references:

- Qiu, D.Y., Cohen, G., Novichkova, D. and Refaely-Abramson, S., “Signatures of Dimensionality and Symmetry in Exciton Band Structure: Consequences for Exciton Dynamics and Transport”, *Nano Lett.*, *21*(18), pp.7644-7650, 2021
- Antonius, G., and Louie, S. G., “Theory of exciton-phonon coupling”, Phys. Rev. B, 105, 085111, 2022