Stochastic Scattering Theory for Excitation-Induced Dephasing

Hao Li, Ajay Ram Srimath Kandada, Carlos Silva, and Eric R. Bittner

TSRC Workshop on Exciton/Photon Interactions for Quantum Systems
Telluride, CO June 8$^{\mathrm{th}}$, 2021

Department of Chemistry, University of Houston

Excitation-Induced Dephasing and Shift - 1

VOLUME 71, NUMBER 8 PHYSICAL REVIEW LETTERS 23 AUGUST 1993

Transient Nonlinear Optical Response from Excitation Induced Dephasing in GaAs

Hailin Wang, Kyle Ferrio, and Duncan G. Steel
H. M. Randall Laboratory, The University of Michigan, Ann Arbor, Michigan 48109

Y. Z. Hu, R. Binder, and S. W. Koch
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

PHYSICAL REVIEW B **66**, 045309 (2002)

Role of excitation-induced shift in the coherent optical response of semiconductors

Justin M. Shacklette and Steven T. Cundiff*
JILA, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309

$$\dot{\rho}_{12} = \frac{i}{\hbar}\omega_{21}\rho_{12} + \frac{i}{\hbar}V_{12}\left(\rho_{11} - \rho_{22}\right)$$

$$\begin{aligned}\dot{\rho}_{12} = \quad & -(\gamma_0 + \underbrace{\gamma' N\rho_{22}}_{\text{EID}})\rho_{12} + i(\omega_0 + \underbrace{\omega' N\rho_{22}}_{\text{EIS}})\rho_{12} + \frac{i}{\hbar}V_{12}\left(\rho_{11} - \rho_{22}\right) \\ = \quad & i\left[(\omega_0 + i\gamma_0) + \left(\omega' + i\gamma'\right)N\rho_{22}\right]\rho_{12} + \frac{i}{\hbar}V_{12}\left(\rho_{11} - \rho_{22}\right)\end{aligned}$$

Excitation-Induced Dephasing and Shift - 2

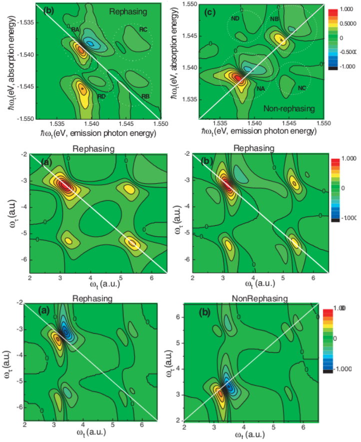

Figure 1: Real 2D spectra of light- and heavy- excitons in GaAs quantum wells. Top: experiment; middle: V-system and EID; bottom: EID+EIS.

- Model of V-system w/o or with EID shows *absorptive* line shape.
- Including EIS reproduces the *dispersive* line feature.
- In the Green's function approach, EID and EIS correspond to the exciton self-energy renormalization.
- Different techniques to decompose a 2D spectrum into its real and imaginary parts.
- Many-body interactions in the Hamiltonian.

[1] X. Li, T. Zhang, C. N. Borca and S. T. Cundiff, *Phy. Rev. Lett.* **96**, 057406 (2006)

2D Hybrid Metal-Halide Perovskites

PHYSICAL REVIEW MATERIALS **2**, 064605 (2018)

Exciton-polaron spectral structures in two-dimensional hybrid lead-halide perovskites

Stefanie Neutzner,[1] Félix Thouin,[2] Daniele Cortecchia,[1] Annamaria Petrozza,[1]
Carlos Silva,[2,3,*] and Ajay Ram Srimath Kandada[1,2,3,†]

nature materials ARTICLES
https://doi.org/10.1038/s41563-018-0262-7
Corrected: Author Correction

Phonon coherences reveal the polaronic character of excitons in two-dimensional lead halide perovskites

Félix Thouin[1], David A. Valverde-Chávez[2], Claudio Quarti[3], Daniele Cortecchia[4], Ilaria Bargigia[2],
David Beljonne[3], Annamaria Petrozza[4], Carlos Silva[1,2*] and Ajay Ram Srimath Kandada[1,2,4*]

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

ACS EDITORS' CHOICE
pubs.acs.org/JPCL Perspective

Exciton Polarons in Two-Dimensional Hybrid Metal-Halide Perovskites

Ajay Ram Srimath Kandada* and Carlos Silva*

Many-Body Exciton Model

- k-space Hamiltonian within the mean-field limit

$$\hat{H} = \sum_k \hbar\omega_k \hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}\sum_{kk'q} V_q \hat{a}_{k+q}^\dagger \hat{a}_{k'-q}^\dagger \hat{a}_{k'} \hat{a}_k,$$

$$V_q = \frac{1}{(2\pi)^3}\int V(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}.$$

- Separate $k = 0$ and $k \neq 0$ terms and only keep two-body interactions involving no more than two $k \neq 0$ states,

$$\begin{aligned}\hat{H} \approx & \hbar\omega_0 \hat{a}_0^\dagger \hat{a}_0 + \frac{V_0}{2}\hat{a}_0^\dagger \hat{a}_0^\dagger \hat{a}_0 \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_0 \sum_{q\neq 0}\left[(V_0 + V_q)\hat{a}_q^\dagger \hat{a}_q\right] \\ & + \hat{a}_0^\dagger \hat{a}_0^\dagger \sum_{q\neq 0}\frac{V_q}{2}\hat{a}_q \hat{a}_{-q} + \hat{a}_0 \hat{a}_0 \sum_{q\neq 0}\frac{V_q}{2}\hat{a}_q^\dagger \hat{a}_{-q}^\dagger + \sum_{q\neq 0}\hbar\omega_q \hat{a}_q^\dagger \hat{a}_q\end{aligned}$$

Distinguishing System and Bath

- $s-$wave scattering approximation $V_q \approx V_0$.
- $k = 0$ excitons as system of interest

$$\hat{H}_0 = \hbar\omega_0 \hat{a}_0^\dagger \hat{a}_0 + \frac{V_0}{2} \hat{a}_0^\dagger \hat{a}_0^\dagger \hat{a}_0 \hat{a}_0 + 2V_0 \hat{a}_0^\dagger \hat{a}_0 \hat{A}^\dagger \hat{A} \\ + \gamma_2 \hat{a}_0^\dagger \hat{a}_0^\dagger \hat{B}\hat{B} + \gamma_2^* \hat{a}_0 \hat{a}_0 \hat{B}^\dagger \hat{B}^\dagger.$$

- $\hat{A}$ and $\hat{B}$ are collective operators of background $k \neq 0$ excitons

$$\hat{A}^\dagger \hat{A} = \sum_{q\neq 0} \hat{a}_q^\dagger \hat{a}_q, \quad \gamma_2 \hat{B}\hat{B} = \frac{V_0}{2} \sum_{q\neq 0} \hat{a}_q \hat{a}_{-q}.$$

- $2V_0 \hat{a}_0^\dagger \hat{a}_0 \hat{A}^\dagger \hat{A}$ – direct dipole interactions between $k = 0$ and $k \neq 0$ excitons – interaction with a Markovian bath $\hat{A}^\dagger \hat{A}$.
- $\hat{B}/\hat{B}^\dagger$ terms – the annihilation/creation of excitons in pair (momentum conserved) – will be dropped.

Heisenberg-Langevin Eqns for Damped Harmonic Oscillator

- Reservoir Hamiltonian interacting with a dissipative bath $\hat{b}_i/\hat{b}_i^\dagger$

$$\hat{H}_{\mathrm{res}} = \hbar\Omega\left(\hat{A}^\dagger\hat{A} + 1/2\right) + \sum_i g_i\left(\hat{b}_i^\dagger\hat{A} + \hat{A}^\dagger\hat{b}_i\right) + \sum_i \hbar\omega_i\left(\hat{b}_i^\dagger\hat{b}_i + 1/2\right)$$

$$\partial_t\hat{A} = -\left(\frac{\Gamma}{2} + i\Delta\right)\hat{A} + \hat{F}(t)$$

- Γ is the spontaneous emission rate, Δ is the energy shift.
- $\hat{F}(t)$ remains a quantum operator that depends on the reservoir variable and can be considered as a Langenvin force due to it correlation functions.

$$\hat{F}(t) = -\frac{i}{\hbar}\sum_i g_i\hat{\hat{b}}_i(t_0)e^{i(\Omega-\omega_i)t}$$

Effective System Hamiltonian

- Population of $k \neq 0$ exciton is treated as a collective variable $N(t)$ as sources of quantum noise and dissipation

$$\hat{H}_0 = \hbar\omega_0 \hat{a}_0^\dagger \hat{a}_0 + \frac{V_0}{2} \hat{a}_0^\dagger \hat{a}_0^\dagger \hat{a}_0 \hat{a}_0 + 2V_0 \hat{a}_0^\dagger \hat{a}_0 N(t)$$

- Interaction picture

$$\begin{aligned}\hat{a}_0(t) &= \exp\left[\frac{i}{\hbar}\int_0^t \hat{H}_0(\tau)d\tau\right] \hat{a}_0 \exp\left[-\frac{i}{\hbar}\int_0^t \hat{H}_0(\tau)d\tau\right] \\ &= \exp\left[-i\omega_0 t - iV_0 t\hat{n}_0 - i2V_0\int_0^t N(\tau)d\tau\right] \hat{a}_0 \equiv \hat{U}(t)\hat{a}_0\end{aligned}$$

- Transition dipole

$$\hat{\mu}(t) = \mu\left[\hat{a}_0^\dagger(t) + \hat{a}_0(t)\right]$$

Ornstein-Uhlenbeck Stochastic Process

- Ornstein-Uhlenbeck process to describe the background exciton population $N(t)$

$$dN(t) = -\gamma N(t)dt + \sigma dW(t).$$

- $dW(t)$ represents a Wiener process.
- $N(t) = N(0)e^{-\gamma t} + \sigma \int_0^t e^{-\gamma(t-s)} dW_s$.
- Mean: $\langle N(t) \rangle = e^{-\gamma t} N_0$, where $N_0 = \langle N(0) \rangle$.
- Autocorrelation function

$$\begin{aligned} \mathrm{Cov}[N(s), N(t)] &\equiv \langle [N(s) - \langle N(s) \rangle] [N(t) - \langle N(t) \rangle] \rangle \\ &= \langle N(s)N(t) \rangle - \langle N(s) \rangle \langle N(t) \rangle. \end{aligned}$$

- *Quadratic Variation*: $(dW_t)^2 = dt$.
- *Itô isometry* states that for an arbitrary adapted process $f(t)$

$$\left\langle \left(\int_0^t f(s) dW_s \right)^2 \right\rangle = \left\langle \int_0^t f(s)^2 ds \right\rangle .$$

- Autocorrelation function

$$\mathrm{Cov}[N(s), N(t)] = \sigma_{N_o}^2 e^{-\gamma(s+t)} + \frac{\sigma^2}{2\gamma} \left[e^{-\gamma|t-s|} - e^{-\gamma(t+s)} \right]$$

- $\sigma_{N_o}^2$ is the variance of the background population at $t = 0$.

$$\begin{aligned}S^{(1)}(t) =&\frac{i}{\hbar}\langle[\hat{\mu}(t),\hat{\mu}(0)]\rho(-\infty)\rangle = \frac{\mu^2}{\hbar}\left(\langle[\hat{a}^\dagger(t),\hat{a}(0)]\rho(-\infty)\rangle - c.c\right)\\ =& -\frac{2\mu^2}{\hbar}\,\mathrm{Im}\left\{\left\langle \exp\left[i\omega_0 t + iV_0 t\hat{n}_0 + i2V_o\int_0^t N(\tau)d\tau\right]\right.\right.\\ &\left.\left.\times\left[\left(e^{-iV_0 t}-1\right)\hat{n}_0 - 1\right]\rho(-\infty)\right\rangle\right\}\end{aligned}$$

Cumulant expansion

$$\left\langle \exp\left[i2V_o\int_0^t N(\tau)d\tau\right]\right\rangle = \exp[i2V_o g_1(t)]\exp\left[-2V_o^2 g_2(t)\right]\cdots$$

$$\begin{aligned}g_1(t) =& \int_0^t \langle N(\tau)\rangle d\tau = \frac{N_0}{\gamma}\left(1-e^{-\gamma t}\right),\\ g_2(t) =& \int_0^t\int_0^t \mathrm{Cov}\left[N(\tau),N(\tau')\right]d\tau' d\tau\\ =&\frac{\sigma^2}{2\gamma^3}\left(2\gamma t + 4e^{-\gamma t} - e^{-2\gamma t} - 3\right) + \frac{\sigma_{N_o}^2}{\gamma^2}\left(1-e^{-\gamma t}\right)^2\end{aligned}$$

Comparison to Kubo-Anderson Theory - 1

- Kubo-Anderson model describes a stochastic fluctuation about a *stationary* state

$$N(t) = N_{\mathrm{s}} + \delta N(t),\ \langle \delta N(t) \rangle = 0.$$

- Kubo covariance $\langle \delta N(t) \delta N(0) \rangle = \sigma_K^2 e^{-\gamma t}$,
- Ornstein-Uhlenbeck covariance

$$\langle N(s), N(t) \rangle = \sigma_{N_o}^2 e^{-\gamma(s+t)} + \tfrac{\sigma^2}{2\gamma} \left[e^{-\gamma|t-s|} - e^{-\gamma(t+s)} \right]$$

- σ_K^2 is unitless whereas σ^2 carries unit of $\left[t^{-1} \right]$.
- Cumulant expansion on the exponential term of $N(t)$

$$\left\langle \exp\left[2iV_o \int_0^t N(\tau) d\tau \right] \right\rangle = \exp[i2V_o N_{\mathrm{s}} t] \exp\left[-\frac{4V_o^2 \sigma_K^2}{\gamma^2} \left(e^{-\gamma t} + \gamma t - 1 \right) \right]$$

Comparison to Kubo-Anderson Theory - 2

$$g_1^{\mathrm{K}}(t) = N_{\mathrm{s}} t, \quad g_1(t) = \frac{N_0}{\gamma}\left(1 - e^{-\gamma t}\right).$$

$$g_2^{\mathrm{K}}(t) = \frac{2\sigma_K^2}{\gamma^2}\left(e^{-\gamma t} + \gamma t - 1\right),$$

$$g_2(t) = \frac{\sigma^2}{2\gamma^3}\left(2\gamma t + 4e^{-\gamma t} - e^{-2\gamma t} - 3\right) + \frac{\sigma_{N_o}^2}{\gamma^2}\left(1 - e^{-\gamma t}\right)^2$$

$$= \left(\frac{\sigma_{N_o}^2}{\gamma^2} - \frac{3\sigma^2}{2\gamma^3}\right) + \frac{2}{\gamma^3} e^{-\gamma t}\left(\sigma^2 - \gamma\sigma_{N_o}^2\right) - \frac{e^{-2\gamma t}}{2\gamma^3}\left(\sigma^2 - 2\gamma\sigma_{N_o}^2\right) + \frac{\sigma^2}{\gamma^2} t$$

- Define $\kappa = \sigma^2 - 2\gamma\sigma_{N_0}^2$. $\kappa > 0$ or $\kappa < 0$ corresponds to the facts that the initial excitation is narrow or broad compared to the later fluctuation.
- When $\kappa = 0$ and giving $\sigma_K^2 = \sigma^2/2\gamma = \sigma_{N_0}^2$,

$$g_2(t) = \frac{\sigma^2}{\gamma^3}\left(e^{-\gamma t} + \gamma t - 1\right) = g_2^{\mathrm{K}}(t)$$

Comparison to Kubo-Anderson Theory - 3

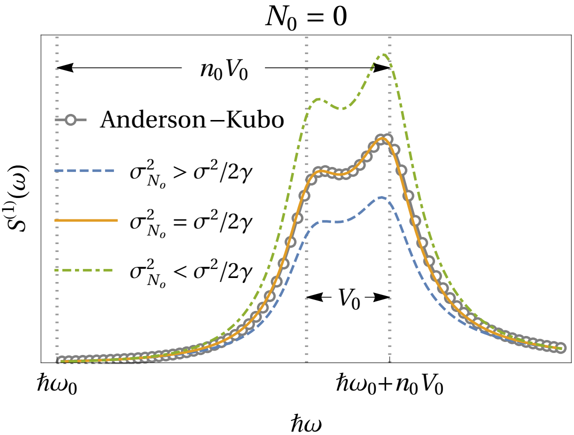

Figure 2: The linear response function comparison between the non-stationary and the Anderson-Kubo (AK) model in the case of zero initial background population N_0 at different distributions $\sigma^2_{N_0} = 0.25$, 0.125, and 0.04 fs^{-1}. Other parameters are $V_o = 10\ \mathrm{meV}$, $\gamma = 0.01\ \mathrm{fs}^{-1}$, $\sigma^2 = 0.0025\ \mathrm{fs}^{-1}$.

Non-Stationary Spectra

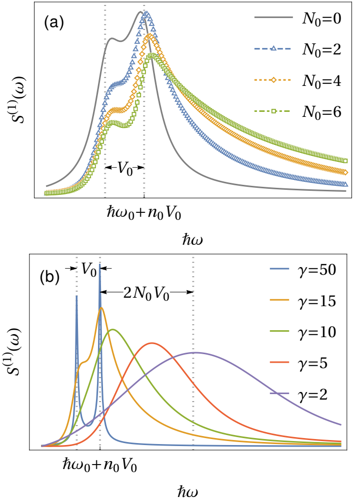

Figure 3: Linear response function with varied background population (a) and relaxation rates (b).

- ⋆ *Blocking*: background population supresses absorption intensity.
- ⋆ *Energy shift*: absorption peak blue shift with background population.
- ⋆ *Broadening*: tailing into high energy due to background evolution, also observed in 2D spectra.
- ⋆ *Biexciton*: peak split by V_0 due to biexciton interaction.
- ⋆ Homogeneous/inhomogeneous limit, Lorentzian/Gaussian line shape.

$$S^{(3)}(\tau_3,\tau_2,\tau_1) = i^3\langle\hat{\mu}(\tau_3)\,[\hat{\mu}(\tau_2),[\hat{\mu}(\tau_1),[\hat{\mu}(0),\rho(-\infty)]]]\rangle.$$

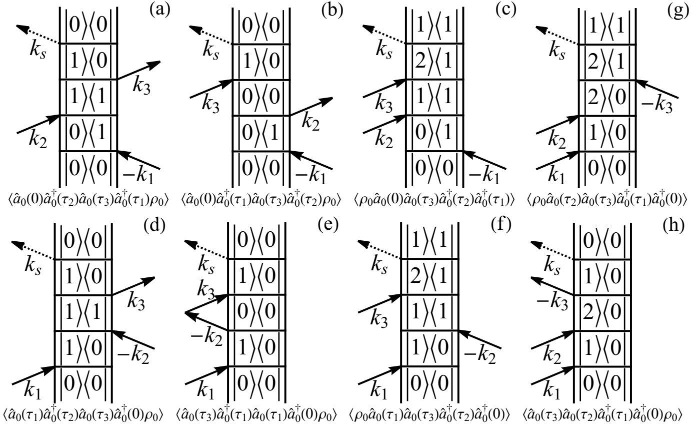

Figure 4: Double-sided Feynman Diagrams for correlation functions with rephasing phase matching: (a) R_{2a}, (b) R_{3a}, (c) R^*_{1b}, non-rephasing phase matching: (d) R_{1a}, (e) R_{4a}, (f) R^*_{2b}, and double quantum coherence: (g) R^*_{3b}, (h) R_{4b}.

Autocorrelation Function and Response Function

- Up to 2nd order cumulant expansion, we only need the *mean* and *covariance* of the involved stochastic process to evaluate the optical response function.

$$
\begin{aligned}
&\int_0^t \int_0^{t'} \mathrm{Cov}\left[N(\tau), N(\tau')\right] d\tau' d\tau = \\
&\quad \frac{\sigma^2}{2\gamma^3}\left[2\gamma\ \min(t,t') + 2e^{-\gamma t} + 2e^{-\gamma t'} - e^{-\gamma|t'-t|} - e^{-\gamma(t'+t)} - 2\right] \\
&\quad + \frac{\sigma_{N_o}^2}{\gamma^2}\left[e^{-\gamma(t+t')} - e^{-\gamma t} - e^{-\gamma t'} + 1\right].
\end{aligned}
$$

2D Spectra - 1

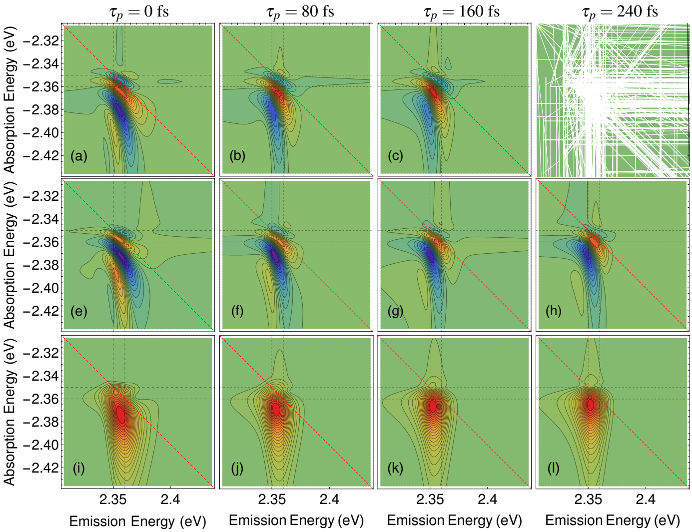

Figure 5: Rephasing spectra at different waiting time τ. From top to bottom: real, imaginary, and norm.

2D Spectra - 2

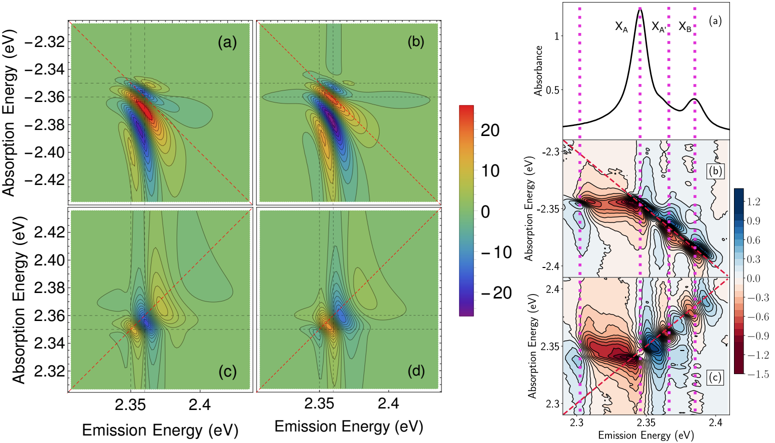

Figure 6: Left: theoretical real and imaginary spectra of rephasing [(a) and (b)] and nonrephasing [(c) and (d)] phase matching. Right: spectra of $(\mathrm{PEA})_2\mathrm{PbI}_4$ at 5K, from top to bottom: linear absorption, rephasing real, and nonrephasing real. Population time of $\tau_p = 0$ fs.

2D Lineshape Evolution

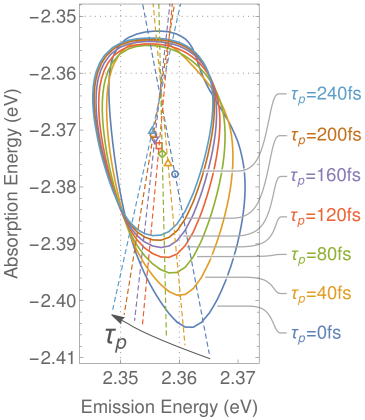

Figure 7: Exciton 2D coherent lineshape contour at half-maximum intensity as a function of waiting time, shown with the center of mass and one of the principle axes.

- ⋆ The peak narrows, rotates, and distorts as exciton co-evolves with background population.
- ⋆ The center peak red shifts as interactions with background population diminished - EIS.
- ⋆ Lineshape evolution is attributed to the nontrivial 1st order cumulant $g_1 \neq 0$ as a result of nonstationary background population.

Summary

- We propose a stochastic model for spectroscopic lineshapes in the presence of a co-evolving and non-stationary background population of excitations.
- Optical excitons are coupled to an incoherent background via scattering mediated by screened Coulomb coupling.
- The Heisenberg EOM for optical excitons are driven by a stochastic population variable which can be characterized as an Ornstein-Uhlenbeck process.
- The SDEs can be solved using Itô calculus, and the resulting autocorrelation functions allow us to evaluate optical response functions.
- The non-stationary feature of the model produces nonlinear spectral shifts and asymmetries.
- The model does not hinge upon a specific stochastic model or an specific environmental noise-source

Acknowledgements

- ⋆ Prof. Eric R. Bittner (UH)
- ⋆ Prof. Carlos Silva (GATech)
- ⋆ Prof. Ajay Ram Srimath Kandada (Wake Forest)
- ⋆ Dr. Félix Thouin




University of Houston
Georgia Institute of Technology

Full Hamiltonian

$$
\begin{aligned}
\hat{H} =& \hbar\omega_0 \hat{a}_0^\dagger \hat{a}_0 + \frac{V_0}{2} \hat{a}_0^\dagger \hat{a}_0^\dagger \hat{a}_0 \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_0 \sum_{q\neq 0} \left[(V_0 + V_q) \hat{a}_q^\dagger \hat{a}_q \right] \\
&+ \hat{a}_0^\dagger \hat{a}_0^\dagger \sum_{q\neq 0} \frac{V_q}{2} \hat{a}_q \hat{a}_{-q} + \hat{a}_0 \hat{a}_0 \sum_{q\neq 0} \frac{V_q}{2} \hat{a}_q^\dagger \hat{a}_{-q}^\dagger + \sum_{q\neq 0} \hbar\omega_q \hat{a}_q^\dagger \hat{a}_q \\
&+ \sum_{\substack{k,q\neq 0 \\ k\neq q}} V_q \left(\hat{a}_{k-q}^\dagger \hat{a}_q^\dagger \hat{a}_0 \hat{a}_k + \hat{a}_{k+q}^\dagger \hat{a}_0^\dagger \hat{a}_q \hat{a}_k \right) + \frac{V_0}{2} \sum_{k,k'\neq 0} \hat{a}_k^\dagger \hat{a}_{k'}^\dagger \hat{a}_k \hat{a}_{k'} \\
&+ \sum_{\substack{k,k',q\neq 0 \\ k\neq -q, k'\neq q}} \frac{V_q}{2} \hat{a}_{k+q}^\dagger \hat{a}_{k'-q}^\dagger \hat{a}_{k'} \hat{a}_k
\end{aligned}
$$

Correlation Functions of $\hat{F}(t)$

$$\langle \hat{F}(t')\hat{F}(t)\rangle = \langle \hat{F}^\dagger(t')\hat{F}^\dagger(t)\rangle = 0 \tag{1}$$

$$\langle \hat{F}^\dagger(t')\hat{F}(t)\rangle = \sum_i \frac{|g_i|^2}{\hbar^2}\langle n_i\rangle e^{i(\Omega-\omega_i)(t-t')} \tag{2}$$

$$\langle \hat{F}(t)\hat{F}^\dagger(t')\rangle = \sum_i \frac{|g_i|^2}{\hbar^2}(\langle n_i\rangle + 1)e^{i(\Omega-\omega_i)(t-t')}. \tag{3}$$