Quantum Langevin approach to cavity QED with molecules Michael Reitz, Christian Sommer and Claudiu Genes¹ ¹ Max Planck Institute for the Science of Light, Erlangen, Germany

Abstract

We develop a quantum Langevin equations approach to describe the interaction between light and molecular systems modelled as quantum emitters coupled to a multitude of vibrational modes via a Holstein-type interaction. The formalism allows for analytical derivations of absorption and fluorescence profiles both in the transient and steady state regimes of molecules outside and inside optical cavities. We also derive expressions for the cavity-modified radiative emission branching ratio of a single molecule, cavity transmission in the strong coupling regime and Förster resonance energy transfer between donor-acceptor molecules.

Model

Phonon bath

Cavity-molecule spectroscopy

- Coupled cavity-molecule system leads to occurence of polaron-polariton physics, where the hybrid light-matter states between the light field and the bare electronic transition (polaritons) are additionally dressed by vibrational states (polarons)
- analytically solvable set of equations:

 $\frac{d(\sigma \mathcal{D}^{\dagger})}{dt} = -(\gamma + i\omega_e)\sigma \mathcal{D}^{\dagger} + ga\mathcal{D}^{\dagger} + \sqrt{2\gamma}\mathcal{D}^{\dagger}\sigma_{\rm in}$

 $\frac{d(a\mathcal{D}^{\dagger})}{dt} = -\left[\kappa + i\left(\omega_c - \lambda^2 \nu\right)\right] - g\sigma \mathcal{D}^{\dagger} + \eta_c e^{-i\omega_\ell t} \mathcal{D}^{\dagger} + \sqrt{2\kappa} \mathcal{D}^{\dagger} a_{\rm in}$



- Organic molecules coupled to confined light fields are promising candidates for room temperature quantum technologies due to large dipole moment and stable Frenkel excitons
- Two-level system approximation not well suited due to strong electron-vibrations coupling
- Coupling between electrons and vibrational mode is described by Holstein Hamiltonian:

 $H = (\omega_e + \lambda^2 \nu) \sigma^{\dagger} \sigma + \nu b^{\dagger} b - \lambda \nu (b^{\dagger} + b) \sigma^{\dagger} \sigma \quad => \text{Franck-Condon physics}$ two-level system vibration coupling

 $F(\omega)$

Spectral density function $F(\omega, T)$ contains all informations about the vibrational modes:



For $\lambda > 0$ dissipatively-induced polariton crosstalk leads to asymmetric polariton emission. The polaritons couple with rate

$$\kappa_{\rm UL} = \frac{1}{2} \frac{\lambda^2 \nu^2 \Gamma^2}{\Gamma^2 + (\omega_+ - \omega_- - \nu)^2}$$



In Purcell regime: branching ratio can be modified as recently shown in [2]: $\alpha_{\text{cav}} = \frac{(1+C_{00})e^{-\sum_k \lambda_k^2}}{1+C_{00}e^{-\sum_k \lambda_k^2}} \quad \text{with OPL-cooperativity} \quad C_{00} = \frac{g_{00}^2}{\kappa\gamma} \quad \text{where} \quad g_{00} = ge^{-\sum_k \lambda_k^2}$

FRET process

Förster resonance energy transfer (FRET) important process in nature (photosynthesis) and science (e.g. for probing molecular structure)



Single-molecule spectroscopy

Holstein-Hamiltonian diagonalizable via polaron-transformation:

 $\tilde{H} = \mathcal{D}^{\sigma^{\dagger}\sigma} H \left(\mathcal{D}^{\dagger} \right)^{\sigma^{\dagger}\sigma} = \omega_e \sigma^{\dagger}\sigma + \nu b^{\dagger}b$ where $\mathcal{D} = e^{\lambda(b^{\dagger}-b)}$

Inder weak driving conditions an integrable set of equations in polaron-shifted frame can be derived:
$$\frac{db_k}{dt} = -(\Gamma_k + i\nu_k) b_k + \sqrt{2\Gamma} b_{in}^k$$

$$\frac{d(\sigma D^{\dagger})}{dt} = -[\gamma - i(\omega_\ell - \omega_e)] \sigma D^{\dagger} + \sqrt{2\gamma} D^{\dagger} \Sigma_{in}$$

$$\frac{\partial D(t) D(t')}{\partial t} = \sum_m s_m^{\lambda} e^{-m(\Gamma + i\nu)(t - t')}$$

$$\frac{\partial D(t) D(t')}{\partial t} = \sum_m s_m^{\lambda} e^{-m(\Gamma + i\nu)(t - t')}$$
Poissonian distribution $e^{-\lambda^2} \frac{\lambda^{2m}}{m!}$
which allows for the calculation of any system property (such as emission or absorption spectra)

absorption

OPL branching ratio: $\alpha = e^{-\sum_k \lambda_k^2}$

Fast vibrational decay can render transfer unidirectional with high efficiency and rate

$$\kappa_{\rm ET} = \sum_{n_{\rm A}, n_{\rm D}} \frac{2s_{n_{\rm D}}^{\lambda_{\rm D}} s_{n_{\rm A}}^{\lambda_{\rm A}} \left(n_{\rm A} \Gamma_{\rm A} + n_{\rm D} \Gamma_{D}\right) \Omega(r)^2}{(n_{\rm A} \Gamma_{\rm A} + n_{\rm D} \Gamma_{D})^2 + (\Delta - n_{\rm A} \nu_{\rm A} - n_{\rm D} \nu_{\rm D})^2}$$



revealing overlap condition between D and A



Prospects

use input-output formalism developed in [3] to explore collective dynamics of many interaction molecules and identify role of collective dark states, superradiance/subradiance



- develop a proper model for the phonon bath, goind beyond the Markovian model assumed here => Brownian motion behaviour
- derive electron-phonon coupling leading to phonon wings in spectroscopy



[1] M. Reitz, C. Sommer, C. Genes. Quantum Langevin approach to cavity quantum electrodynamics with molecules. arXiv:1812.08592 (2018) [2] D. Wang, H. Kelkar, D. Martin-Cano, et al., *Turning a molecule into a coherent two-level quantum system, Nature Physics (2019)* [3] D. Plankensteiner, C. Sommer, M. Reitz, H. Ritsch, C. Genes, Enhanced collective Purcell effect of coupled quantum emitter systems, arXiv:1811.03442 (2018)

 $S_{\rm abs}(\omega_{\ell} - \omega_{e}) = \eta_{\ell}^{2} \sum_{m} \frac{s_{m}^{\gamma} \left[\gamma - \frac{1}{\left[\gamma + m\Gamma\right]^{2} + \frac{1$



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