Quantum Langevin approach to cavity QED with molecules

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Abstract

We develop a quantum Langevin equations approach to describe the interaction between light and molecular systems modeled 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

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 modes is described by Holstein Hamiltonian:

\[
H = \omega_0 \sigma_0 + \sum_{\ell} \omega_{\ell} \sigma_\ell + \lambda \sigma_0 [\rho + 1] \sigma_{\rho} \Rightarrow \text{Franck-Condon physics}
\]

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

\[
F(\omega, T) = \frac{4\omega_0^2}{\pi^2} \sum_{\ell} \frac{\gamma_\ell}{\omega_\ell^2 + \omega_0^2} \rightarrow \text{Poissonian distribution}
\]

Holstein-Hamiltonian diagonalizable via polaron-transformation:

\[
\tilde{H} = \tilde{D}^2 \tau^2 - \omega_0 \tau \Rightarrow \text{analytically solvable set of equations}
\]

Cavity-molecule spectroscopy

Coupled cavity-molecule system leads to occurrence 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:

\[
\frac{d\rho_{\ell\ell}^{\text{pol}}}{dt} = -\gamma_{\ell\ell} \rho_{\ell\ell}^{\text{pol}} + \sqrt{2\gamma} \rho_{\ell\ell}^{\text{pol}} + \sqrt{2\gamma} \rho_{\ell\ell}^{\text{pol}} \Rightarrow \text{Brownian motion behaviour}
\]

derived electron-phonon coupling leading to phonon wings in spectroscopy

Problems

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, going beyond the Markovian model assumed here

derive electron-phonon coupling leading to phonon wings in spectroscopy

Cavity-molecule spectroscopy

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

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

\[
\text{FRET process:} \quad \text{absorption} \quad \text{emission}
\]

Prospects

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derive electron-phonon coupling leading to phonon wings in spectroscopy


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References: