A theoretical approach to strong coupling of organic molecules with arbitrary photonic structures

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Motivation & goal

Over the last few years, pioneering experimental and theoretical demonstrations have shown that molecular properties and reactions can be modified under strong coupling in (nano)photonic systems [1-4].
However, most models used to treat such effects use strongly simplified models that do not take into account the realistic modal structure of the photonic system.

Our purpose is to theoretically study collective strong coupling of many organic molecules to modes in arbitrary cavity geometries, using a realistic description of the molecules and the modal structure of the photonic modes. Commonly used mean-field or Maxwell-Bloch approaches have some fundamental weaknesses (e.g., they are not able to describe spontaneous emission). We thus apply the cumulant-expansion method to take into account higher-order correlations (up to second or third) in the system. We provide some benchmark results for this approach in different situations.

Model

$$\hat{\mathcal{H}} = \sum_n \omega_n \hat{a}_n^\dagger \hat{a}_n + \frac{\Omega_0}{2}\sigma^z + \sum_n g_n \cdot (\hat{a}_n^\dagger \sigma^- + \hat{a}_n \sigma^+) - \mu \cdot E(t)(\hat{\sigma}^+ + \hat{\sigma}^-)$$

$$\sum_n g_n^2 = \int J(\omega) d\omega \qquad g_n = \sqrt{J(\omega_n)\Delta\omega}$$

Cumulant expansion $\langle \hat{a}\cdot\hat{b}\rangle = \langle\hat{a}\rangle\cdot\langle\hat{b}\rangle + \langle\hat{a}\cdot\hat{b}\rangle_c$

$$\langle\hat{a}\cdot\hat{b}\cdot\hat{c}\rangle = \langle\hat{a}\rangle\cdot\langle\hat{b}\rangle\cdot\langle\hat{c}\rangle + \langle\hat{a}\rangle\cdot\langle\hat{b}\cdot\hat{c}\rangle_c + \langle\hat{b}\rangle\cdot\langle\hat{a}\cdot\hat{c}\rangle_c + \langle\hat{c}\rangle\cdot\langle\hat{a}\cdot\hat{b}\rangle_c + \langle\hat{a}\cdot\hat{b}\cdot\hat{c}\rangle_c$$

Equations

1st order: $\partial_t\langle\hat{a}_n\rangle = -i\omega_n\langle\hat{a}_n\rangle - ig_n\langle\sigma^-\rangle$ $\quad \partial_t\langle\hat{\sigma}^-\rangle = -i\Omega_0\langle\hat{\sigma}^-\rangle + ig_n\langle\hat{a}\rangle\cdot\langle\hat{\sigma}^z\rangle - i\mu E(t)\cdot\langle\hat{\sigma}^z\rangle$ $\quad \partial_t\langle\hat{\sigma}^z\rangle = -2i\,g_n\left(\langle\hat{a}\rangle\cdot\langle\sigma^+\rangle - \langle\hat{a}^\dagger\rangle\cdot\langle\hat{\sigma}^-\rangle\right) + 2i\mu E(t)(\langle\sigma^+\rangle - \langle\sigma^-\rangle)$ **Mean-field**

2nd order: $\partial_t\langle\hat{a}_n\rangle = -i\omega_n\langle\hat{a}_n\rangle - ig_n\langle\sigma^-\rangle$ $\quad \partial_t\langle\hat{\sigma}^-\rangle = -i\Omega_0\langle\hat{\sigma}^-\rangle + ig_n\langle\hat{a}\cdot\hat{\sigma}^z\rangle - i\mu E(t)\cdot\langle\hat{\sigma}^z\rangle$ $\quad \partial_t\langle\hat{\sigma}^z\rangle = -2i\sum_n g_n\left(\langle\hat{a}_n\cdot\sigma^+\rangle - \langle\hat{a}_n{}^\dagger\cdot\hat{\sigma}^-\rangle\right) + 2i\mu E(t)(\langle\sigma^+\rangle - \langle\sigma^-\rangle)$

New set of equations is needed $\partial_t\langle\hat{a}_n^\dagger\cdot\hat{a}_m\rangle_c = i(\omega_n - \omega_m)\langle\hat{a}_n{}^\dagger\cdot\hat{a}_m\rangle_c + ig_n\langle\hat{a}\cdot\sigma^+\rangle - ig_m\langle\hat{a}_n^\dagger\sigma^-\rangle$ $\quad \partial_t\langle\hat{a}_n^\dagger\cdot\hat{a}_m^\dagger\rangle_c = i(\omega_n + \omega_m)\langle\hat{a}_n{}^\dagger\cdot\hat{a}_m^\dagger\rangle_c + ig_n\langle\hat{a}_m^\dagger\sigma^-\rangle - ig_m\langle\hat{a}_n^\dagger\sigma^-\rangle$

$$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^z\rangle_c = i\omega_n\langle\hat{a}_n{}^\dagger\cdot\hat{\sigma}^z\rangle_c - ig_n(1+\langle\hat{\sigma}^z\rangle)\langle\hat{\sigma}^+\rangle - 2i\sum_m g_m\left(\langle\hat{a}_m^\dagger\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^-\rangle_c - \langle\hat{a}_m\rangle\cdot\langle\hat{a}_n^\dagger\cdot\sigma^+\rangle_c + \langle\hat{\sigma}^-\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{a}_m^\dagger\rangle_c - \langle\sigma^+\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{a}_m\rangle_c\right) + 2i\mu E(t)\cdot\left(\langle\hat{a}_n^\dagger\hat{\sigma}^+\rangle_c - \langle\hat{a}_n^\dagger\hat{\sigma}^-\rangle_c\right)$$

$$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^+\rangle_c = i(\omega_n+\Omega_0)\langle\hat{a}_n{}^\dagger\cdot\hat{\sigma}^+\rangle_c - ig_n\langle\hat{\sigma}^+\rangle\cdot\langle\sigma^+\rangle - i\sum_m g_m\left(\langle\hat{a}_m^\dagger\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^z\rangle_c + \langle\hat{\sigma}^z\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{a}_m^\dagger\rangle_c\right) + i\mu E(t)\cdot\langle\hat{a}_n^\dagger\hat{\sigma}^z\rangle_c$$

$$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^-\rangle_c = i(\omega_n-\Omega_0)\langle\hat{a}_n{}^\dagger\cdot\hat{\sigma}^-\rangle_c + ig_n\left(\frac{1+\langle\hat{\sigma}^z\rangle}{2} - \langle\hat{\sigma}^+\rangle\cdot\langle\sigma^-\rangle\right) + i\sum_m g_m\left(\langle\hat{a}_m\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^z\rangle_c + \langle\hat{\sigma}^z\rangle\cdot\langle\hat{a}_n^\dagger\cdot\hat{a}_m\rangle_c\right) - i\mu E(t)\cdot\langle\hat{a}_n^\dagger\hat{\sigma}^z\rangle_c$$

3rd order in the populations: $\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}^-\rangle_c = i(\omega_n-\Omega_0)\langle\hat{a}_n{}^\dagger\cdot\hat{\sigma}^-\rangle_c + ig_n\left(\frac{1+\langle\hat{\sigma}^z\rangle}{2} - \langle\hat{\sigma}^+\rangle\cdot\langle\sigma^-\rangle\right) + i\sum_m g_m\left(\langle\hat{a}_n^\dagger\cdot\hat{a}_m\cdot\hat{\sigma}^z\rangle_c - \langle\hat{a}_n^\dagger\rangle\cdot\langle\hat{a}_m\rangle\cdot\langle\hat{\sigma}^z\rangle - \langle\hat{a}_n^\dagger\rangle\cdot\langle\hat{a}_m\cdot\hat{\sigma}^z\rangle_c\right) - i\mu E(t)\cdot\langle\hat{a}_n^\dagger\hat{\sigma}^z\rangle_c$

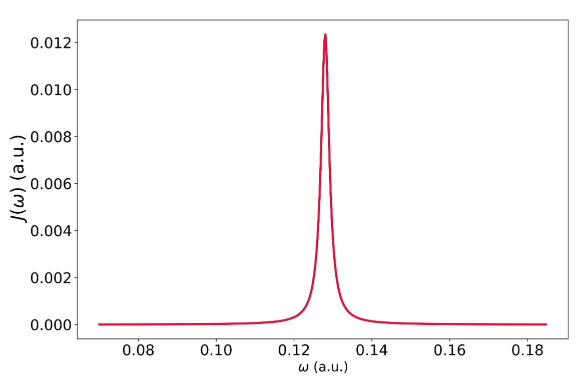
One equation is added $\partial_t\langle\hat{a}_n^\dagger\cdot\hat{a}_m\cdot\hat{\sigma}^z\rangle = i(\omega_n-\omega_m)\langle\hat{a}_n{}^\dagger\cdot\hat{a}_m\cdot\hat{\sigma}^z\rangle - ig_n\langle\hat{a}_m\cdot\sigma^+\rangle + ig_m\langle a_m^\dagger\cdot\hat{\sigma}^-\rangle - 2i\sum_l g_l\left(\langle\hat{a}_n^\dagger\hat{a}_m\hat{a}_l\hat{\sigma}^+\rangle - \langle\hat{a}_n^\dagger\hat{a}_l^\dagger\hat{a}_m\hat{\sigma}^-\rangle\right) + 2i\mu E(t)\cdot\left(\langle\hat{a}_n\cdot\hat{a}_m\cdot\hat{\sigma}^+\rangle - \langle\hat{a}_n^\dagger\cdot\hat{a}_m\cdot\hat{\sigma}^+\rangle\right)$

Describing spontaneous emission

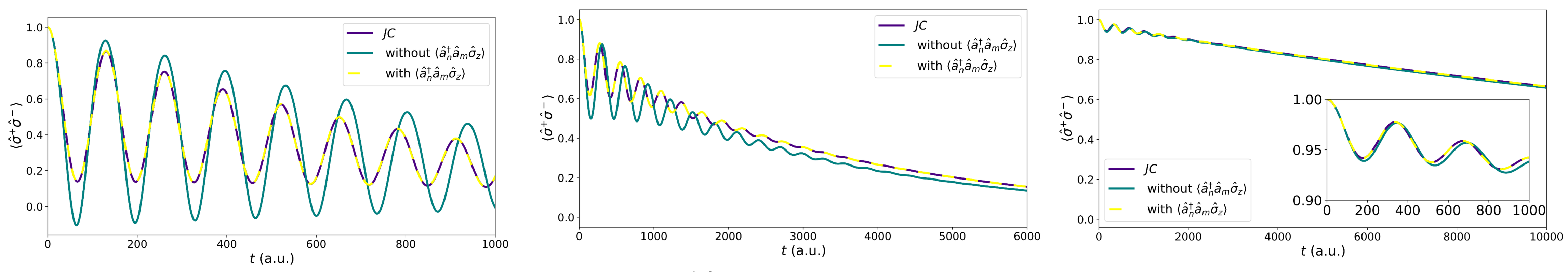
Lorentzian spectral density

$$J(\omega) = \frac{a_0\gamma_c/2}{(\omega-\omega_c)^2 + i(\gamma_c/2)^2}$$

Approximately describes common situations such as a quantum emitter (QE) coupled to a single isolated mode, or to short-range modes near a metallic surface [5].



$E(t) = 0$



Bare QE lifetime

We compare the cumulant expansion of second and third order with the Jaynes-Cummings model, as the dynamical evolution of the QE in the Jaynes-Cummings model is identical the same as the one with a Lorentzian spectral density [5].

Third order in the cumulant that connects the population of the 2-level system and the photon number is mandatory to describe correctly the decay of the atom. This is because fluctuations of the photon number can cause significant changes in the inversion in the regimen where the interaction is more significant than the losses [6]. Therefore as the lifetime of the atom increases (dipole moment decreases), the second-order description improves.

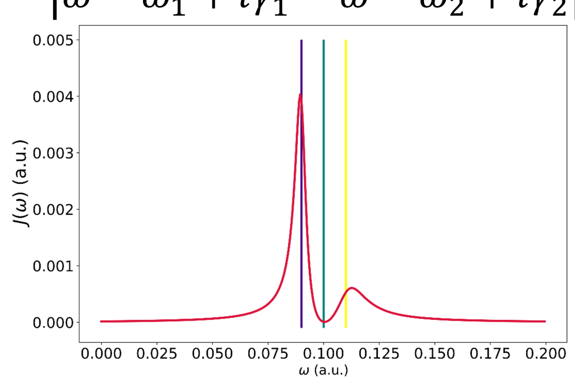
Hybrid spectral density $\quad J(\omega) = a_0\left|\frac{1}{\omega-\omega_1+i\gamma_1} + \frac{\phi}{\omega-\omega_2+i\gamma_2}\right|^2$

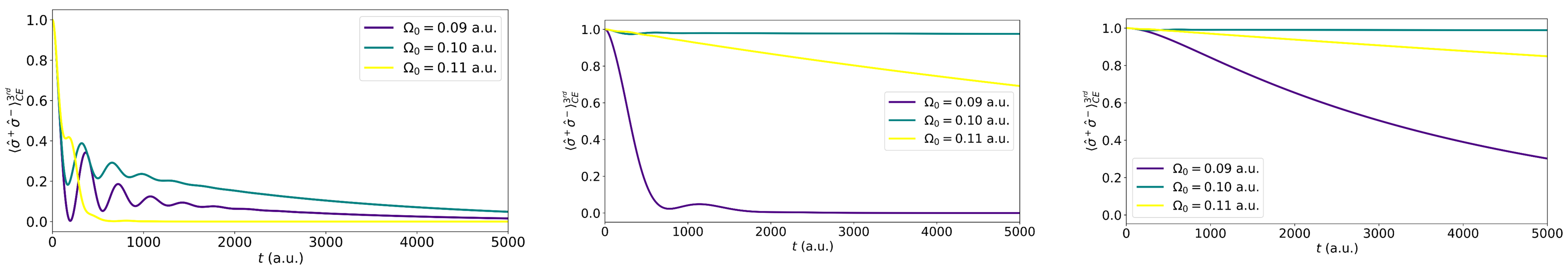
ϕ is a complex number chosen so that $J(\omega) = 0$ at $\omega = 0.1$ a.u.

Approximately describes a hybrid device, as the one studied in [7].

At $\omega = 0.1$ a.u. $J(\omega) = 0$.

The QE dynamics is shown at this frequency and at both resonances.





Bare QE lifetime

As before, the direction of the arrow indicates a longer lifetime of the QE . The cumulant expansion method is able to describe the dynamics of more complex spectral densities.

In the weak coupling regime, the QE and the photonic modes are decoupled, so the QE just "see" the spectral density at the frequency of the QE. Then, at $\omega = 0.1$ a.u. the QE does not decay (as $J(0.1) = 0$) and this behavior holds even when the decay at other resonances is enhanced. When the strong coupling regime is entered, off-resonant photonic modes become important and Rabi oscillations can be seen at this frequency. The behavior of the QE when tuned to the peaks of the spectral density is the one expected.

Including more than one emitter

Although the decay of a single emitter can be described accurately using the third order cumulant expansion, the dynamics under (strong) external driving by a coherent pulse, good approximations to the correct results are only obtained when for multiple emitters. However, in contrast to the mean-field approach (in which the number of emitters must be $N \to \infty$), the cumulant expansion produces correct results already for finite numbers of emitters [8]. A minimal complete model for this system can be obtained from macroscopic QED (see poster by J. Feist et al.), which contains N photonic continua for N emitters. Alternatively, it is possible to choose only a few physically motivated cavity modes, which implies that the interaction between different emitters must be added to the previous differential equations:

$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^z\rangle_c$ includes $ig_n(N-1)\langle\hat{\sigma}_1^z\cdot\hat{\sigma}_2^+\rangle_c$

$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^-\rangle_c$ includes $ig_n(N-1)\langle\hat{\sigma}_1^+\cdot\hat{\sigma}_2^-\rangle_c$

$\partial_t\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^+\rangle_c$ includes $ig_n(N-1)\langle\hat{\sigma}_1^+\cdot\hat{\sigma}_2^+\rangle_c$

$$\partial_t\langle\hat{\sigma}_1^+\cdot\hat{\sigma}_2^-\rangle_c = -i\sum_n g_n\left(\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^-\rangle_c - \langle\hat{a}_n\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^+\rangle_c\right)$$

$$\partial_t\langle\hat{\sigma}_1^+\cdot\hat{\sigma}_2^+\rangle_c = 2i\Omega_0\langle\hat{\sigma}_1^+\cdot\hat{\sigma}_2^+\rangle - 2i\sum_n g_n\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^+\rangle_c$$

$$\partial_t\langle\hat{\sigma}_1^z\cdot\hat{\sigma}_2^z\rangle_c = -4i\sum_n g_n\left(\langle\hat{a}_n\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^z\rangle_c - \langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^z\rangle_c\right)$$

$$\partial_t\langle\hat{\sigma}_1^z\cdot\hat{\sigma}_2^+\rangle_c = i\Omega_0\langle\hat{\sigma}_1^z\cdot\hat{\sigma}_2^+\rangle - 2i\sum_n g_n\left(\langle\hat{a}_n\cdot\hat{\sigma}_1^+\cdot\hat{\sigma}_2^+\rangle - \langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^-\cdot\hat{\sigma}_2^+\rangle\right) - i\sum_n g_n\langle\hat{a}_n^\dagger\cdot\hat{\sigma}_1^z\cdot\hat{\sigma}_2^z\rangle$$

Conclusions

- Cumulant expansion to second order is derived. To describe the correct decay of an emitter we need to take into account the third order in the cumulant of the number of photons and the inversion of the emitter.
- This method allows us to describe this decay for different spectral densities, whatever its dependence on ω.
- Under (strong) external driving, convergence is only obtained when multiple emitters are treated.

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