Vibration Assisted Polariton Wavefunction Evolution in Organic Nanofibers.

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Formation of the composite photonic-excitonic particles, known as polaritons, is an emerging phenomenon in materials possessing strong coupling to light. The organic-based materials besides the strong light-matter interaction also demonstrate strong interaction of electronic and vibrational degrees of freedom. We utilize the Dirac-Frenkel variation principle to derive semiclassical equations for the vibration-assisted polariton wavefunction evolution when both types of interactions are treated as equally strong. By means of the approach, we study details of the polariton relaxation process and the mechanism of the polariton light emission. In particular, we propose the photon emission mechanism, which is realized when the polariton wave package exceeds the geometrical size of the nanosystem. To verify our conclusions we reproduce the fluorescence peak observed in experiment (Takazawa et al. Phys.Rev.Lett. 105:07401, 2010) and estimate the light-matter interaction parameter.

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When dye molecules are embedded in microstructures such as microcavities and nanofibers, the strong light-matter interaction can lead to formation of composite photon-exciton particles, known as exciton polaritons (EP), see Refs.\cite{14} and references therein. The systems with strong coupling draw a lot of attention due to their potential to cause changes in chemical reaction rates\cite{6,7} to show long-range particle propagation\cite{3,6,7}. The con-

\[ H = \hbar \sum_q \Lambda_{+q} Q_q^\dagger Q_q + \Lambda_{-q} P_q^\dagger P_q, \] (1)

in terms of the upper and lower polariton operators,

\[ Q_q = \cos \phi_q A_q + \sin \phi_q B_q; \] (2)
\[ P_q = -\sin \phi_q A_q + \cos \phi_q B_q. \] (3)

The upper and lower branches of the dispersion curve are \[ \Lambda_{\pm q} = \frac{1}{2} \left( \omega_q + \omega_{\pm q} \pm \sqrt{(\omega_q - \omega_{\pm q})^2 + 4g^2} \right), \] where \( g \) is the light-matter interaction strength parameter and \( \omega_{\pm q} \) is the exciton energy. The bosonic operators \( A_q \) (eqs. 2, 3) are the photon annihilation operators. The exciton operators \( B_q = \frac{1}{\sqrt{N}} \sum_m e^{-iqm} b_m \) \( (N \sim \) the number of molecules, \( b_m \) is the annihilation operator of an excitation on the \( m \)th molecule) under the standard assumption of small number of excitations also satisfy the standard bosonic commutator relations, so do the polarit-

In the spectra of organic-based polariton devices the interaction with vibrations is revealed through the vibronic replicas of the polariton dispersion curve.\cite{13,14} Therefore, both the interaction between light and molecular electron density, and the interaction of electron density with the molecular backbone vibrations must be considered as equally strong.\cite{14,15}

In Refs.\cite{13,15} the vibronic progression in EP fluorescent spectra has been explained with the help of the semiclassical rate equations, which describe the polariton states population evolution. However, for solution of transport and other dynamical problems, knowledge of the wavefunction evolution and spatial propagation might be more important. A few attempts to describe the polariton wavefunction has been done in Refs.\cite{1,2} without accounting of vibrations. In present article we derive from ab initio Hamiltonian a set of equations for the vibration assisted polariton wavefunction evolution.

In our set up the unpolarized laser light excites polaritons in a perfect molecular crystal. The free photons dispersion is \( \omega_q = cq/\sqrt{c^2 - 1} \), where \( c/\sqrt{c^2 - 1} \) is the speed of light in the media, and \( q \) is the wavevector absolute value. The polaritonic part, \( H_{pol} \), of the total Hamiltonian, \( \hat{H} = H_{pol} + H_{vib} + H_{ex} \) is modelled by the standard quadratic form Hamiltonian\cite{20,21}

The polariton Hamiltonian \( \hat{H}_{pol} \) is diagonalizable in the orthonormal basis \( |q, (u, M)\rangle \). Each \( |q, (u, M)\rangle \) con-
The exciton Hamiltonian $\hat{H}_{ex}$ accounts for the intermolecular interactions and imparts the momentum dependence to the exciton dispersion $\omega_{ex}$. In case of weakly coupled H-aggregated molecules (below we consider only this case) the short-range Frenkel exciton effective mass is large and we can neglect the $q$-dependence in $\omega_{ex}$. Note that the accounting of the vibrations shifts the energy of the molecular optical transition by half of the Stokes’ shift: $\omega_{ex} \rightarrow \omega_{ex} + \sum_{m} \Omega_{X} X_{m}^{2}$.

In organic molecules the frequency of the highest-frequency optically active (HFOA) mode is of one order of magnitude smaller ($\Omega_{\mu} \sim 1000 - 1500$ cm$^{-1}$) than the excitation energy $\omega_{0-0}$ (fig. 2 b) and $X_{0} \sim 0.7$. The HFOA modes are responsible for the vibronic repetitions in spectra. The low-frequency optically active (LFOA) modes’ frequencies ($\Omega_{\mu}$ with $\mu = 1, \ldots$) are comparable with the thermal energy $kT \sim 30$ meV, and the molecule equilibrates over the LFOA modes almost immediately (several picoseconds) after the excitation. One can effectively separate the polaritons corresponding to the $|0\rangle$-$|1\rangle$ and to the $|0\rangle$-$|0\rangle$ transitions. For the $|0\rangle$-$|1\rangle$ case the interaction parameter $g$ is suppressed by the Franc-Condorn factor $X_{\mu} e^{-X_{0}^{2}/2}$. The dispersion curve with the effective coupling $gX_{\mu} e^{-X_{0}^{2}/2}$ goes closer to the AP (see the curve $\lambda_{-q}$ in fig. 1 a). This makes the polariton formation channel less efficient than the channel of rapid non-radiative decay to the state $|0\rangle$.

The basis of coherent states, $|\sigma\rangle = \prod_{m,\mu} |\sigma_{m,\mu}\rangle$, provides a convenient description for LFOA vibrations. Each coherent state is parametrized by multidimensional complex-valued vector $\sigma_{m,\mu}$, which encodes the coherent state center (classical momentum $\sigma$) and coordinate $\mu$. To describe evolution of the expansion coefficients $F(\sigma, q, t)$ and $G(\sigma, q, t)$ we generalize the polariton basis set by introducing the time-dependent basis set $|\sigma(t), q, u\rangle$. Then we make use the approach, which is based on the Dirac-Frenkel variation principle and useful for description of quantum dynamics in systems with large number of vibration modes $^{23,27}$.

In the extended basis the EP wavefunction has the expansion $|\Psi(t)\rangle = \sum_{q} F(\sigma, q, t)e^{i\lambda_{q}+\xi t}|\sigma, q, 1\rangle + G(\sigma, q, t)e^{i\lambda_{q}-\xi t}|\sigma, q, 0\rangle$. Variation of the Schrödinger equation $\langle \Psi | \hbar \frac{d}{dt} - \hat{H} | \Psi \rangle = 0$ with respect to the bra-vector and equating to zero each term coming from the independent variations $\delta F$, $\delta G$, and $\delta c_{m,\mu}$ yields the system of equations of motion. For $u = 0$ it is

$$\delta \sigma_{m,\mu} : G^{*}(\sigma, q, t) (\sigma, q, 0) c_{m,\mu} \left( \hbar \frac{d}{dt} - \hat{H} \right) |\Psi\rangle = 0; \quad (5)$$

$$\delta \sigma_{m,\mu} : G^{*}(\sigma, q, t) (\sigma, q, 0) \frac{d}{dt} c_{m,\mu} \left( \frac{d}{dt} - \hat{H} \right) |\Psi\rangle = 0. \quad (6)$$

The eqs. (5), (6) completely describe evolution of the polariton wavefunction, subject to the initial conditions. Below we consider their explicit form in the mean field semiclassical approximation and neglect the upper
The emerging imaginary part in the term $\sigma_m,\mu$ its value has to be taken at the previous instant of time. The first equation (eq. 7) describes redistribution of the probability due to redistribution over non-polaritonic degrees of freedom. Note, that the Hamiltonian also includes the phonon-phonon interaction terms. In what follows we use the reasonable for molecular crystals assumption of uncorrelated optical vibration modes, i.e. no dispersion in the optical branch and all $\sigma_{m,\mu}$ are independent, while the acoustic phonons form the thermal bath.

The overdamped Brownian oscillator model provides a general and convenient way for incorporating the nuclear motion into the numerical study of the problem. Under assumption of continuous distribution of the oscillators parameters $\Omega_\mu$ and $X_\mu$, the effective dimensionless oscillator coordinate $u_m = \gamma^{-1} \left( \chi_m(t) \sum_\mu \Omega_\mu X_\mu^2 - u_m \right)$. In case of large damping we use the approximation $\sum_\mu \Omega_\mu X_\mu (\sigma_{m,\mu}^* + \sigma_{m,\mu}') \simeq 2\sqrt{2}u_m - i\chi_m(t)\sqrt{2}\gamma^{-1}\Delta t \sum_\mu \Omega_\mu X_\mu^2$. For convenience we assume that initially all vibrations are in the ground state, $u_m(0) = 0$, while $G(\sigma, q, t = 0)$ is distributed over various momenta far from AP (see Fig. 1b).

The typical numerical solution for the coefficient

$$
\frac{dG(\sigma, q, t)}{dt} = -i \sum_{\Delta q} G(\sigma, q - \Delta q, t) \sum_{m,\mu} \Omega_\mu X_\mu (\sigma_{m,\mu} + \sigma_{m,\mu}') \frac{e^{-i\Delta q m}}{N} e^{-i(\Lambda_{-q} - \Lambda_q) t} \cos \phi_q \cos \phi_q - \Delta q - \delta\Delta q,\mu \chi_m(t) \right) \right) \right) \right) \right)
$$

Eq. (8) is a classical Newton’s equations of an oscillator interacting with a bath, which equilibrium coordinate is shifted from zero by $X_\mu \chi_m(t)$. The factor $\chi_m$ (eq. 9) is the quantum expectation value of the polariton state projection on the exciton subspace. At the derivation of eq. (8) to avoid instabilities (see discussion in Ref. 27) we make summation over all $q$ and thus immerse the problem into the mean-field context.

The first equation (eq. 7) describes redistribution of the polariton wavefunction in the momentum space, which happens due to the energy flux from the polariton subsystem to the optically active vibrations and eventually to the bath. The prime at $\sigma_{m,\mu}'$ in eq. (7) means that its value has to be taken at the previous instant of time. The emerging imaginary part in the term $\sigma_{m,\mu}^* + \sigma_{m,\mu}'$ is responsible for the overall decrease of the quantum probability $|G(\sigma, q, t)|^2$ due to redistribution over non-polaritonic degrees of freedom. Note, that the Hamiltonian also includes the phonon-phonon interaction terms.

![Image](344x618 to 459x740)

FIG. 2: (a) The PL spectrum (solid black) of the thiacyanine-dye nanofiber compared with the PL monomer (red dashed) and H-aggregate (red dotted) spectra, reconstructed from the literature. The Lorentzian peak A is positioned at 2.593 eV and the peak B maximum is at 2.457 eV; (b) Jablonski diagram of HFOA transitions in the molecular aggregate; (c) The ladder-like diagram depicting the maximal contribution to the EP PL spectrum: two polaritons (vertical lines), initially created as the conjugated photons with the momentum $q_1$ and $q_2$, evolve due to interaction with the vibrational bath ($\sigma$) to AP and decay from there into two coherent photons ($A_q, A_q'$), which are detected by detector.
FIG. 3: The PL spectrum (solid line) calculated from the numerical equilibrium wavefunction (at $t_1 \sim 100 fs$). The parameters $\omega_m = 3.1 eV$, $g = 0.69 eV$, $\Gamma = 0.1 eV$, the momentum cut-off $5.00 \times 10^5 m^{-1}$, $q_0 = 1.08 \times 10^5 m^{-1}$, and the AP momentum $q_{AP} = 2.13 \times 10^5 m^{-1}$. The dashed Lorentzian line A is the same as in Fig. 2a.

$G(\sigma, q, t)$ is given in fig. 1b. The polariton wavefunction, during its evolution, scatters on the AP and forms very fast ($\sim 10 fs$) an interference pattern with the highest peaks at AP. It is worth mentioning, that the structure of the wavefunction is not an arbitrary but follows from the solution of eq. (7) in the steady state regime (see caption). We justify our approximate formula by the fact that the contributing peaks are sharp ($\Delta_q \sim 7 \times 10^6 m^{-1}$) and start to form very early ($\sim 10 fs$). The polaritons, initially created within a wide range of wavevectors, evolve quite long time ($t_1 \sim 100 fs$) and decay by irradiation of two free photons with almost equal momenta $q_{AP}$. Note that the choice of the decay time $t_1$ is dictated by two circumstances: (i) it is the time of efficient equilibration and (ii) at this time the factor $\chi_m$ maximum position reaches 200 nm, and thus goes out of the fiber width into the area where no more excitons can be created. The numerical spectrum is plotted in fig. 3 for the parameters given in the caption. Note that the $\omega_m$ is chosen to be close to the absorption maxima of the H-aggregate, while $g$ is tuned to reproduce the experimental peak A. The obtained value of $g$ is $\sim 0.7 eV$.

Concluding remarks. The quantum mechanical approach suggested in the article is derived from first principles and allows us to reproduce the position of the EP PL peak. We also demonstrate that the vibration assisted evolution of polaritons is a complex process taking place in both coordinate and momentum spaces. In particular, we propose a mechanism for the emission of polaritons due to the exit of the wave packet beyond the geometric limits of the nanosystem.

The approach being fully analytic opens a way for calculation of the polariton PL spectra by means of the nonlinear optical spectroscopy theoretical method [31] and the Greens' function theories. Note, that in its general formulation, the equations of motion allows to account the multiple-polaritons states, and the quantum transitions between the upper and lower dispersion branches (see further publications).

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[32] $C^\dagger_q |\psi,\mu, M\rangle = |\psi,\mu + 1, M + 1\rangle$; $C_q |\psi,\mu, M\rangle = |\psi,\mu - 1, M - 1\rangle$;

[33] $c^\dagger |\sigma\rangle = \sigma^* |\sigma\rangle$, $c |\sigma\rangle = \sigma^* |\sigma\rangle$; completeness: $I = \int \frac{d^3 u}{|\sigma\rangle \langle \sigma|}$; the scalar product $\langle \sigma'|\sigma \rangle = e^{-|\sigma'| - \sigma|^2}$. 

[34] The eigenvectors $|\psi,\mu, M\rangle$ have explicit representation in the basis of $A_q$ and $B_q$ operators (Ref. 33). The action of operators: $Q^\dagger_q |\psi,\mu, M\rangle = \sqrt{\alpha + 1} |\psi,\mu + 1, M + 1\rangle$; $Q_q |\psi,\mu, M\rangle = \sqrt{\alpha} |\psi,\mu - 1, M - 1\rangle$; $P^\dagger_q |\psi,\mu, M\rangle = \sqrt{\alpha + 1} |\psi,\mu + 1, M + 1\rangle$; $P_q |\psi,\mu, M\rangle = \sqrt{\alpha} |\psi,\mu - 1, M - 1\rangle$.