# Dark states in quantum photosynthesis and quantum transport

S.V. Kozyrev, Steklov Mathematical Institute

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First stages of photosynthesis —
quantum thermodynamic machine
(nonequilibrium quantum system with thermodynamic cycles).

Thermodynamic cycle:

– Absorption of photons and generation of excitons

– Transport of excitons to the reaction center

– Absorption of excitons

Two observations:
1) Transport of excitons is more effective than expected (by one order of magnitude),
2) Photonic echo is observed for excitons, Coherencies for excitons decay slower than expected (by one order of magnitude)
— the effect of quantum photosynthesis.

G.S. Engel, T.R. Calhoun, E.L. Read, T.K.Ahn, T. Mancal, Y.C. Cheng, R.E. Blankenship, G.R. Fleming, Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. Nature, 2007, V.446. P.782–786.

G.D. Scholes, G.R. Fleming, A. Olaya-Castro, R. van Grondelle, Lessons from nature about solar light harvesting. Nature Chem., 2011, 3, 763–774.

Different mechanisms were proposed for quantum photosynthesis: vibrones, supertransport, corrections to quantum Markov models, holographic approach.

We discuss the second approach
(supertransport and superabsorption).
Can quantum coherences be observed in quantum thermodynamic machine performing supertransport?

Degeneracy (many light harvesting antennas) —
Supertransport effect (quantum amplification of transport).

Leaks in the quantum thermodynamic machine —
quantum states with long lifetime (dark states) —
the effect of quantum photosynthesis.

Manipulation of quantum states by Lindblad dissipative dynamics.

Exciton transport can be made made faster by quantum coherent amplification of transport in degenerate systems (the supertransfer effect)

R. Monshouwer, M. Abrahamsson, F. van Mourik and R. van Grondelle, Superradiance and Exciton Delocalization in Bacterial Photosynthetic Light-Harvesting Systems, *J. Phys. Chem.* **B101**, 7241–7248 (1997).

A. Olaya-Castro, C. F. Lee, F. F. Olsen and N. F. Johnson, Efficiency of energy transfer in a light-harvesting system under quantum coherence, *Phys. Rev.* **B78**, 085115 (2008).

S. Lloyd and M. Mohseni, Symmetry-enhanced supertransfer of delocalized quantum states, *New J. Phys.* **12**, 075020 (2010). arXiv:1005.2579

I. Ya. Aref'eva, I. V. Volovich, S. V. Kozyrev, Stochastic limit method and interference in quantum many-particle systems, *Theoretical and Mathematical Physics* **183** no 3, 782–799 (2015).

Non decaying "dark" states are widely discussed in quantum optics, quantum memory, light stopping ...

M. Fleischhauer and M.D. Lukin, Dark-State Polaritons in Electromagnetically Induced Transparency, *Phys. Rev. Lett.* **84**, 5094 (2000). arXiv:quant-ph/0001094

Experimental observation of quantum dark states in photosynthesis:

M. Ferretti, R. Hendrikx, E. Romero, J. Southall, R.J. Cogdell, V.I. Novoderezhkin, G.D. Scholes, R. van Grondelle, Dark States in the Light-Harvesting complex 2 Revealed by Two-dimensional Electronic Spectroscopy, *Scientific Reports* **6**, 20834 (2016).

How to obtain photonic echo in a degenerate model of quantum photosynthesis using dark states:

S.V. Kozyrev, I.V. Volovich, Dark states in quantum photosynthesis, arXiv:1603.07182 [physics.bio-ph]

I. V. Volovich and S. V. Kozyrev, Manipulation of States of a Degenerate Quantum System, *Proceedings of the Steklov Institute of Mathematics* **294**, 241–251 (2016).

## Dynamics of quantum open systems

Open system — system interacts with environment (the reservoir)

$$H = H_S + H_R + \lambda H_I.$$

Sum of Hamiltonians of the system, the reservoir and the interaction Hamiltonian, $\lambda$ is the coupling constant.
Dynamics of the reduced density matrix of the system (average over degrees of freedom of the reservoir)

$$\frac{d}{dt}\rho(t) = \Theta(\rho(t)),$$

the Lindblad (or GKSL) generator $\Theta$ is a sum of several

$$\theta(\rho) = -i[H_{\mathrm{eff}}, \rho] + L\rho L^* - \frac{1}{2}\{\rho, L^* L\}.$$

Here $[A, B]$ – commutator, $\{A, B\}$ – anticommutator.

## Dirac notations

$\mathcal{H}$ — Hilbert space with scalar product $\langle \cdot, \cdot \rangle$.
Let $x \in \mathcal{H}$. Then $x = |x\rangle$ is called Dirac notation (ket–vector).
$\langle y|$ for $y \in \mathcal{H}$ (bra–vector) is a functional acting as $\langle y||x\rangle = \langle y, x\rangle$.
$|z\rangle\langle y|$ is an operator acting as $|z\rangle\langle y||x\rangle = |z\rangle\langle y, x\rangle$.

**Model of quantum photosynthesis**:

One exciton approximation,

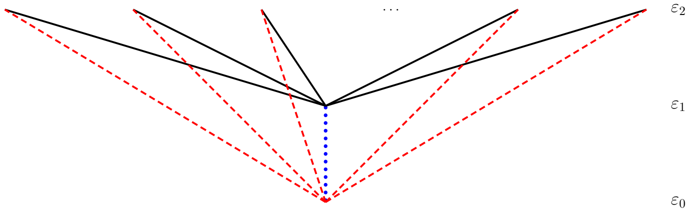
Degeneracy in the light-harvesting system,

Excitons in chromophores interact with three quantum fields (photons, phonons, sink).

Interaction with photons and phonons —
non-parallel vectors of "bright" states.

Generation of non-decaying "dark" states.

Relation to experiments with photonic echo.




**Degenerate 3–level system interacting with three reservoirs**

## Hamiltonian of light-harvesting system

$$H_S = \varepsilon_0|0\rangle\langle 0| + \varepsilon_1|1\rangle\langle 1| + \varepsilon_2\sum_{j=2}^{N}|j\rangle\langle j|.$$

$\varepsilon_0 < \varepsilon_1 < \varepsilon_2$,
$|0\rangle$ — state without excitons,
$|1\rangle$ is a state "exciton in the reaction center",
$|j\rangle$ — one-exciton states of chromophores in the "global" basis.

Transitions between the levels are related to Bose quantum fields (reservoirs) with Hamiltonians

$$H_R = \int_{\mathbb{R}^3}\omega_R(k)a_R^*(k)a_R(k)dk,$$

where $R = \mathrm{em}, \mathrm{ph}, \mathrm{sink}$ enumerate the reservoirs, $\omega_R$ is the dispersion of the Bose field $a_R$.

States of reservoirs — Gaussian states, quadratic correlator

$$\langle a_R^*(k) a_R(k') \rangle = N_R(k)\delta(k - k').$$

Temperature state

$$N_R(k) = \frac{1}{e^{\beta_R \omega_R(k)} - 1}.$$

Different reservoirs — different temperatures, for instance $\beta_{\mathrm{em}}^{-1} = 6000K$, $\beta_{\mathrm{ph}}^{-1} = 300K$, $\beta_{\mathrm{sink}}^{-1}$ depends on approximation (we take $300K$ for computation of transfer rate for excitons and $0K$ for the investigation of manipulation of quantum dark states).

**The full Hamiltonian**

$$H = H_S + H_{\mathrm{em}} + H_{\mathrm{ph}} + H_{\mathrm{sink}} + \lambda \left( H_{I,\mathrm{em}} + H_{I,\mathrm{ph}} + H_{I,\mathrm{sink}} \right),$$

$\lambda$ is the coupling constant.
The Hilbert space

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_{\mathrm{em}} \otimes \mathcal{H}_{\mathrm{ph}} \otimes \mathcal{H}_{\mathrm{sink}}.$$

**Interacting Hamiltonians:** different dipole Hamiltonians
**Light** (creation–annihilation of excitons):

$$H_{I,\mathrm{em}} = A_{\mathrm{em}}|\chi\rangle\langle 0| + A^*_{\mathrm{em}}|0\rangle\langle\chi|, \qquad A^*_{\mathrm{em}} = \int_{\mathbb{R}^3} g_{\mathrm{em}}(k)a^*_{\mathrm{em}}(k)dk,$$

the bright photonic vector $\chi$ belongs to the level $\varepsilon_2$,
$g_{\mathrm{em}}(k)$ — form–factor of the field.

**Phonons** (transport of excitons to the reaction center):

$$H_{I,\mathrm{ph}} = A_{\mathrm{ph}}|\psi\rangle\langle 1| + A^*_{\mathrm{ph}}|1\rangle\langle\psi|, \qquad A^*_{\mathrm{ph}} = \int_{\mathbb{R}^3} g_{\mathrm{ph}}(k)a^*_{\mathrm{ph}}(k)dk,$$

the bright phononic vector $\psi$ belongs to the level $\varepsilon_2$.

$\chi$ **and** $\psi$ **are non-parallel.**

**Sink** (absorption of excitons):

$$H_{I,\mathrm{sink}} = A_{\mathrm{sink}}|1\rangle\langle 0| + A^*_{\mathrm{sink}}|0\rangle\langle 1|, \qquad A^*_{\mathrm{sink}} = \int_{\mathbb{R}^3} g_{\mathrm{sink}}(k)a^*_{\mathrm{sink}}(k)dk.$$

**Dynamics** — sum of three generators (for three reservoirs)

$$\frac{d}{dt}\rho(t) = (\theta_{\rm em} + i[\cdot, H_{\rm eff}] + \theta_{\rm ph} + \theta_{\rm sink})(\rho(t)).$$

Different terms in the generator — different parts of the quantum thermodynamic cycle for photosynthesis.
The stochastic limit approximation
*L. Accardi, Lu Yun Gang, I. Volovich*, Quantum theory and its stochastic limit, Springer-Verlag, Berlin, 2002

**Light** (creation of excitons): generator in Lindblad form

$$L_{\rm em} = \theta_{\rm em} + i[\cdot, H_{\rm eff}],$$

$$H_{\rm eff} = s(|\chi\rangle\langle 0| + |0\rangle\langle\chi|), \qquad s \in \mathbb{R}.$$

$H_{\rm eff}$ describes coherent (laser) field (Rabi oscillations).

Dissipative (Lindblad) part of the generator

$$\theta_{\mathrm{em}}(\rho) = \|\chi\|^2 \Bigg[ 2\gamma^{-}_{\mathrm{re,em}} \left( \langle\widetilde{\chi}|\rho|\widetilde{\chi}\rangle |0\rangle\langle 0| - \frac{1}{2}\{\rho, |\widetilde{\chi}\rangle\langle\widetilde{\chi}|\} \right) -$$

$$-i\gamma^{-}_{\mathrm{im,em}}[\rho, |\widetilde{\chi}\rangle\langle\widetilde{\chi}|] +$$

$$+2\gamma^{+}_{\mathrm{re,em}} \left( \langle 0|\rho|0\rangle |\widetilde{\chi}\rangle\langle\widetilde{\chi}| - \frac{1}{2}\{\rho, |0\rangle\langle 0|\} \right) + i\gamma^{+}_{\mathrm{im,em}}[\rho, |0\rangle\langle 0|] \Bigg].$$

$\gamma$ are some constants
(called susceptibilities, depend on the states of the fields),
the normed bright photonic vector is given by

$$|\widetilde{\chi}\rangle = \frac{|\chi\rangle}{\|\chi\|}.$$

**Phonons** (transport of excitons):

$$\theta_{\rm ph}(\rho) = \|\psi\|^2 \Bigg[ 2\gamma^-_{\rm re,ph} \left( \langle\widetilde{\psi}|\rho|\widetilde{\psi}\rangle |1\rangle\langle 1| - \frac{1}{2}\{\rho, |\widetilde{\psi}\rangle\langle\widetilde{\psi}|\} \right) -$$

$$-i\gamma^-_{\rm im,ph}[\rho, |\widetilde{\psi}\rangle\langle\widetilde{\psi}|] +$$

$$+2\gamma^+_{\rm re,ph} \left( \langle 1|\rho|1\rangle |\widetilde{\psi}\rangle\langle\widetilde{\psi}| - \frac{1}{2}\{\rho, |1\rangle\langle 1|\} \right) + i\gamma^+_{\rm im,ph}[\rho, |1\rangle\langle 1|] \Bigg].$$

The normed bright phononic vector $|\widetilde{\psi}\rangle = |\psi\rangle / \|\psi\|$.

**Sink** (absorption of excitons)

$$\theta_{\rm sink}(\rho) = 2\gamma^-_{\rm re,sink} \left( \langle 1|\rho|1\rangle |0\rangle\langle 0| - \frac{1}{2}\{\rho, |1\rangle\langle 1|\} \right) - i\gamma^-_{\rm im,sink}[\rho, |1\rangle\langle 1|] +$$

$$+2\gamma^+_{\rm re,sink} \left( \langle 0|\rho|0\rangle |1\rangle\langle 1| - \frac{1}{2}\{\rho, |0\rangle\langle 0|\} \right) + i\gamma^+_{\rm im,sink}[\rho, |0\rangle\langle 0|].$$

The constants $\gamma$ have the form (note that $\gamma^{+}_{\mathrm{re},R}/\gamma^{-}_{\mathrm{re},R} = e^{-\beta_R \omega_R}$)

$$\gamma^{+}_{\mathrm{re},R} = \pi \int |g_R(k)|^2 \delta(\omega_R(k) - \omega_R) N_R(k) dk,$$

$$\gamma^{-}_{\mathrm{re},R} = \pi \int |g_R(k)|^2 \delta(\omega_R(k) - \omega_R)(N_R(k) + 1) dk,$$

$$\gamma^{+}_{\mathrm{im},R} = -\int |g_R(k)|^2 \,\mathrm{P.P.}\, \frac{1}{\omega_R(k) - \omega_R} N_R(k) dk,$$

$$\gamma^{-}_{\mathrm{im},R} = -\int |g_R(k)|^2 \,\mathrm{P.P.}\, \frac{1}{\omega_R(k) - \omega_R} (N_R(k) + 1) dk.$$

Here functions $N_R(k)$ describe thermal reservoirs

$$N_R(k) = \frac{1}{e^{\beta_R \omega_R(k)} - 1},$$

$R = \mathrm{em}, \mathrm{ph}, \mathrm{sink}$, $\beta_{\mathrm{em}}^{-1} = 6000K$, $\beta_{\mathrm{ph}}^{-1} = \beta_{\mathrm{sink}}^{-1} = 300K$,

$$\omega_{\mathrm{em}} = \varepsilon_2 - \varepsilon_0, \quad \omega_{\mathrm{ph}} = \varepsilon_2 - \varepsilon_1, \quad \omega_{\mathrm{sink}} = \varepsilon_1 - \varepsilon_0.$$

The temperatures for different reservoirs are different:
$\beta_{\rm em}^{-1} = 6000K$, $\beta_{\rm ph}^{-1} = 300K$, $\beta_{\rm sink}^{-1} = 300K$.

Thus our model is an example of nonequilibrium quantum system.

Since there are thermodynamic cycles

(absorption of photons and creation of excitons –
transport of excitons to the reaction center –
absorption of excitons)

the model describes a **quantum thermodynamic machine** (which transforms light to absorbed excitons).
The flow (transfer rate) of excitons describes the efficiency of this machine. To improve the efficiency one has to increase the flow.

Let us discuss how this quantum thermodynamic machine works.

## Flow for the case of parallel bright vectors

Let us denote $\alpha$ the angle between bright photonic and phononic vectors $|\chi\rangle$, $|\psi\rangle$. Let $\alpha = 0$ (bright vectors are parallel).
Transport of excitons runs in the subspace of matrices

$$\rho = \rho_{00}|0\rangle\langle 0| + \rho_{11}|1\rangle\langle 1| + \rho_{\psi\psi}|\widetilde{\psi}\rangle\langle\widetilde{\psi}|.$$

The stationary state of dynamics from this subspace

$$\frac{d}{dt}\rho(t) = \left(\theta_{\rm em} + \theta_{\rm ph} + \theta_{\rm sink}\right)\left(\rho(t)\right) = 0.$$

(Nonequilibrium environment, no laser, parallel bright vectors).

# Dynamics — relaxation to nonequilibrium Stationary state

$$\rho_{\psi\psi} = \frac{\gamma^{+}_{\mathrm{re,em}}\gamma^{+}_{\mathrm{re,ph}}\|\chi\|^2\|\psi\|^2 + \gamma^{+}_{\mathrm{re,em}}\gamma^{-}_{\mathrm{re,sink}}\|\chi\|^2 + \gamma^{+}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,sink}}\|\psi\|^2}{\Delta};$$

$$\rho_{11} = \frac{\gamma^{+}_{\mathrm{re,em}}\gamma^{-}_{\mathrm{re,ph}}\|\chi\|^2\|\psi\|^2 + \gamma^{-}_{\mathrm{re,em}}\gamma^{+}_{\mathrm{re,sink}}\|\chi\|^2 + \gamma^{-}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,sink}}\|\psi\|^2}{\Delta};$$

$$\rho_{00} = \frac{\gamma^{-}_{\mathrm{re,em}}\gamma^{+}_{\mathrm{re,ph}}\|\chi\|^2\|\psi\|^2 + \gamma^{-}_{\mathrm{re,em}}\gamma^{-}_{\mathrm{re,sink}}\|\chi\|^2 + \gamma^{-}_{\mathrm{re,ph}}\gamma^{-}_{\mathrm{re,sink}}\|\psi\|^2}{\Delta};$$

$$\Delta = \left(\gamma^{+}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,em}} + \gamma^{-}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,em}} + \gamma^{+}_{\mathrm{re,ph}}\gamma^{-}_{\mathrm{re,em}}\right)\|\chi\|^2\|\psi\|^2 +$$
$$+ \left(\gamma^{+}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,sink}} + \gamma^{-}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,sink}} + \gamma^{-}_{\mathrm{re,ph}}\gamma^{-}_{\mathrm{re,sink}}\right)\|\psi\|^2 +$$
$$+ \left(\gamma^{+}_{\mathrm{re,em}}\gamma^{-}_{\mathrm{re,sink}} + \gamma^{-}_{\mathrm{re,em}}\gamma^{+}_{\mathrm{re,sink}} + \gamma^{-}_{\mathrm{re,em}}\gamma^{-}_{\mathrm{re,sink}}\right)\|\chi\|^2.$$

Transfer rate of excitons to sink is equal

$$F = 2\gamma^{-}_{\mathrm{re,sink}}\rho_{11} - 2\gamma^{+}_{\mathrm{re,sink}}\rho_{00}.$$

For the stationary density matrix the flow reduces to

$$F = \frac{2\|\chi\|^2\|\psi\|^2\gamma^{-}_{\mathrm{re,em}}\gamma^{+}_{\mathrm{re,ph}}\gamma^{+}_{\mathrm{re,sink}}}{\Delta}\left(e^{\left(\beta_{\mathrm{ph}}-\beta_{\mathrm{em}}\right)(\varepsilon_2-\varepsilon_0)} - 1\right).$$

1) Coefficient $\|\chi\|^2$ in the numerator describes the effect of superabsorption – coherent amplification of absorption (the inverse effect to superradiance.
2) Coefficient $\|\psi\|^2$ describes the effect of supertransfer – coherent amplification of transfer.
3) The numerator of expression for the flow contains the product of three coefficients $\gamma$ (related to each of three reservoirs), and the denominator contains a linear combination of products of $\gamma$ for pairs of reservoirs. Thus the dependence of the flow on $\gamma_{\mathrm{re},R}$ for $R = \mathrm{em}, \mathrm{ph}, \mathrm{sink}$ has saturating form — for small $\gamma_{\mathrm{re},R}$ (corresponding to low intensity of the corresponding interaction, in particular for $R = \mathrm{em}$ small $\gamma_{\mathrm{re},\mathrm{em}}$ corresponds to low intensity of light) the dependence of the flow on $\gamma_{\mathrm{re},R}$ will be linear and for high $\gamma_{\mathrm{re},R}$ this dependence will tend to constant.
4) When the state of environment tends to equilibrium, i.e. $\beta_{\mathrm{em}} \to \beta_{\mathrm{ph}}$, the flow tends to zero. This corresponds to absence of thermodynamic flows in equilibrium systems.

## Flow for the case of non–parallel bright vectors

The flow of excitons (efficiency of the quantum thermodynamic photosynthetic machine) will be proportional to

$$|\langle\widetilde{\psi},\widetilde{\chi}\rangle|^2 = \cos^2\alpha,$$

In the first approximation the flow for non–parallel case is given by the flow for parallel case multiplied by $\cos^2\alpha$.
Hence for non–parallel $|\chi\rangle$, $|\psi\rangle$ some parts of the quantum thermodynamic machine (photonic and phononic generators) are not well fit together and some quantum states will leak.

This leakage of quantum dark states can be discussed as origin of quantum coherences observed in quantum photosynthesis.

**Quantum photosynthesis** – photonic echo in photosynthetic systems.

We will discuss manipulations with quantum states which imitate the experimental setup in Quantum photosynthesis — switch on and off different generators in the sum

$$\theta_{\rm em} + i[\cdot, H_{\rm eff}] + \theta_{\rm ph} + \theta_{\rm sink}.$$

Here the laser part of the generator $i[\cdot, H_{\rm eff}]$ is important. We will also use the approximation $\beta_{\rm sink}^{-1} = 0$ — absorption of excitons in the reaction center is irreversible.

Let us discuss properties of Lindblad generators for degenerate systems.

**Bright, dark and off-diagonal matrices**: are defined for each Lindblad generator. Generator $\theta_{\mathrm{em}}$ (light):
**Bright** matrices — linear combinations

$$|0\rangle\langle 0|, \quad |\chi\rangle\langle\chi|.$$

Dark matrices $B$ give zero when multiplied by any bright matrix $A$:

$$AB = BA = 0.$$

Off-diagonal matrices $C$ are orthogonal to all bright $A$ and dark $B$

$$\mathrm{tr}(CA) = \mathrm{tr}(CB) = 0.$$

**Dark** matrices for $\theta_{\mathrm{em}}$ — linear combinations of

$$|\phi\rangle\langle\phi'|, \quad |1\rangle\langle 1|, \quad |\phi\rangle\langle 1|, \quad |1\rangle\langle\phi|, \quad \phi\perp\chi, \phi'\perp\chi.$$

**Off-diagonal** matrices for $\theta_{\mathrm{em}}$ — linear combinations of

$$|\chi\rangle\langle 0|, \quad |\chi\rangle\langle\phi|, \quad |\chi\rangle\langle 1|, \quad |1\rangle\langle 0|, \quad |\phi\rangle\langle 0|, \quad \phi\perp\chi$$

and conjugated.

Generator $\theta_{\rm ph}$ (phonons):
Bright matrices — linear combinations of

$$|1\rangle\langle 1|, \quad |\psi\rangle\langle\psi|.$$

Dark matrices — linear combinations of

$$|\eta\rangle\langle\eta'|, \quad |0\rangle\langle 0|, \quad |\eta\rangle\langle 0|, \quad |0\rangle\langle\eta|, \quad \eta\perp\psi, \eta'\perp\psi.$$

Off–diagonal matrices — linear combinations of

$$|\psi\rangle\langle 1|, \quad |\psi\rangle\langle\eta|, \quad |\psi\rangle\langle 0|, \quad |0\rangle\langle 1|, \quad |\eta\rangle\langle 1|, \quad \eta\perp\psi$$

and conjugated.

Space of all matrices is an orthogonal sum of dark, bright and off–diagonal subspaces. Bright matrices — quantum transport; dark matrices — stationary (no dynamics, no transport, no dissipation, no decoherence); off–diagonal matrices — decoherence. Bright and dark spaces for photons and phonons in our model are different, this leads to excitation of quantum coherences.

## Manipulations with quantum states and experiments on quantum photosynthesis

Let us describe manipulations with quantum states in our model of quantum photosynthesis which imitate the scheme of experiments on photonic echo in quantum photosynthesis.

Manipulations by Lindblad dissipative dynamics in complex quantum system.

1) Prepare a state by application of laser.
Excitations of quantum coherences.

2) Switch off the laser and make system relax.
Part of coherences are destroyed by decoherence,
and part will survive –
by the effect of dark states
(coherent population trapping,
decoherence free subspace).

3) Spectroscopy — apply the laser again and observe a response.

**Manipulations with quantum states: step 1.**
**Switch on the light.**

Initial state — no excitons

$$\rho_0 = |0\rangle\langle 0|.$$

Apply dynamics given by the light generator $L_{\mathrm{em}} = \theta_{\mathrm{em}} + i[\cdot, H_{\mathrm{eff}}]$ (switch off other generators, strong light approximation), get

$$\rho_1 = \rho_{00}|0\rangle\langle 0| + \rho_{\chi\chi}|\widetilde{\chi}\rangle\langle\widetilde{\chi}| + \rho_{\chi 0}|\widetilde{\chi}\rangle\langle 0| + \rho_{0\chi}|0\rangle\langle\widetilde{\chi}|,$$

$$\rho_{00} = \frac{\gamma^{-}_{\mathrm{re,em}} - \frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)}{\gamma^{+}_{\mathrm{re,em}} + \gamma^{-}_{\mathrm{re,em}} - 2\frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)},$$

$$\rho_{\chi\chi} = \frac{\gamma^{+}_{\mathrm{re,em}} - \frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)}{\gamma^{+}_{\mathrm{re,em}} + \gamma^{-}_{\mathrm{re,em}} - 2\frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)},$$

$$\rho_{\chi 0} = \frac{is}{\|\chi\|\mu_{\chi 0}} \frac{\gamma^{-}_{\mathrm{re,em}} - \gamma^{+}_{\mathrm{re,em}}}{\gamma^{+}_{\mathrm{re,em}} + \gamma^{-}_{\mathrm{re,em}} - 2\frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)},$$

$$\rho_{0\chi} = -\frac{is}{\|\chi\|\mu_{0\chi}} \frac{\gamma^{-}_{\mathrm{re,em}} - \gamma^{+}_{\mathrm{re,em}}}{\gamma^{+}_{\mathrm{re,em}} + \gamma^{-}_{\mathrm{re,em}} - 2\frac{s^2}{\|\chi\|^2}\mathrm{Re}\left(\frac{1}{\mu_{\chi 0}}\right)},$$

where

$$\mu_{\chi 0} = \mu^{*}_{0\chi} = -\gamma^{-}_{\mathrm{re,em}} - \gamma^{+}_{\mathrm{re,em}} + i\gamma^{-}_{\mathrm{im,em}} + i\gamma^{+}_{\mathrm{im,em}}.$$

is (up to normalization) the eigenvalue for $\theta_{\mathrm{em}}$ acting on the off–diagonal matrix $|\chi\rangle\langle 0|$:

$$\theta_{\mathrm{em}}(|\chi\rangle\langle 0|) = \|\chi\|^2 \mu_{\chi 0} |\chi\rangle\langle 0|.$$

**Manipulations with quantum states: step 2. Switch off the light.**

Apply to $\rho_1$ (obtained at the previous step) the dynamics generated by $\theta_{\rm ph}+\theta_{\rm sink}$ (transport and absorption, no light)

$$\widetilde{\chi}=\widetilde{\chi}_0+\widetilde{\chi}_1,\quad \widetilde{\chi}_0\|\widetilde{\psi},\widetilde{\chi}_1\perp\widetilde{\psi},\quad \|\widetilde{\chi}_0\|=\cos\alpha,\|\widetilde{\chi}_1\|=\sin\alpha,$$

$$|\widetilde{\chi}_0\rangle=\langle\widetilde{\psi},\widetilde{\chi}\rangle|\widetilde{\psi}\rangle=|\widetilde{\psi}\rangle\langle\widetilde{\psi}||\widetilde{\chi}\rangle,\qquad |\widetilde{\chi}_1\rangle=(1-|\widetilde{\psi}\rangle\langle\widetilde{\psi}|)|\widetilde{\chi}\rangle.$$

In dynamics survives only the part of $\rho_1$ which is dark for the phononic generator $\theta_{\rm ph}$ (here it is important $\beta_{\rm sink}^{-1}=0$ – absorption of excitons is irreversible). Thus the dynamics of the density matrix reduces to substitution $|\widetilde{\chi}\rangle\mapsto|\widetilde{\chi}_1\rangle$. In the limit $t\to\infty$ of the dynamics

$$\rho_2=\rho_{00}|0\rangle\langle0|+\rho_{\chi\chi}|\widetilde{\chi}_1\rangle\langle\widetilde{\chi}_1|+\rho_{\chi0}|\widetilde{\chi}_1\rangle\langle0|+\rho_{0\chi}|0\rangle\langle\widetilde{\chi}_1|,$$

$\rho_{\chi\chi}$, $\rho_{\chi0}$, $\rho_{0\chi}$ are as above (for $\rho_1$) and

$$\rho_{00}=1-\|\widetilde{\chi}_1\|^2\rho_{\chi\chi}.$$

This state in our model **never decays** (when there are no light).

## Manipulations with quantum states: step 3. Switch on the light again.

Spectroscopy: apply to $\rho_2$ the dynamics generated by $i[\cdot, H_{\rm eff}]$ (ignore transport and absorption) and consider the dynamics of the off-diagonal part of $\rho_2$

$$\rho_{\chi 0}|\widetilde{\chi}_1\rangle\langle 0| + \rho_{0\chi}|0\rangle\langle\widetilde{\chi}_1|.$$

Contribution to this dynamics comes from $\widetilde{\chi}_2$ — projection of $\widetilde{\chi}_1$ to $\widetilde{\chi}$, equal to

$$|\widetilde{\chi}_2\rangle = \left(1 - |\langle\widetilde{\psi}, \widetilde{\chi}\rangle|^2\right)|\widetilde{\chi}\rangle = \sin^2\alpha|\widetilde{\chi}\rangle$$

where $\alpha$ is the angle between bright photonic and phononic vectors $|\chi\rangle$, $|\psi\rangle$.

Non–trivial contribution to spectroscopy is given by

$$\rho_3 = i[\rho_{\chi 0}|\widetilde{\chi}_2\rangle\langle 0| + \rho_{0\chi}|0\rangle\langle\widetilde{\chi}_2|, H_{\rm eff}].$$

In the limit $s \to \infty$ (i.e. for strong laser fields) we get

$$\lim_{s\to\infty}\rho_3 = -\frac{1}{2}\|\chi\|^2\pi\int|g_{\rm em}(k)|^2\delta(\omega_{\rm em}(k)-\varepsilon_2+\varepsilon_0)dk$$

$$\sin^2\alpha\left(|0\rangle\langle 0| - |\widetilde{\chi}|\rangle\langle\widetilde{\chi}|\right).$$

We observe here matrices which photosynthetic quantum thermodynamic machine was not able to transport.

**Quantum photosynthesis is the effect of leakage of quantum dark states in poorly developed quantum thermodynamic machine**.
Exciton transport (proportional to $\cos^2\alpha$) and photonic echo (proportional to $\sin^2\alpha$) are competing phenomena

$$\cos^2\alpha + \sin^2\alpha = 1.$$

**Summary:**

Model of quantum photosynthesis:
Degeneracy in the light-harvesting system,
Excitons in chromophores interact with three quantum fields (photons, phonons, sink).
Degeneracy may lead to the supertransport effect — coherent amplification of the transport.

Interaction with photons and phonons — non–parallel bright vectors ($\alpha$ is the angle between bright vectors). The flow of excitons is proportional to $\cos^2 \alpha$.
Bright photonic states can be dark phononic states.
Generation of non-decaying dark phononic states — proportional to $\sin^2 \alpha$.
Relation to experiments with photonic echo — dark states give non–zero contribution in spectroscopy.