Dark states and supertransport in quantum photosynthesis

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Photosynthesis — harvesting of photons,
generation of excitons,
transport of excitons to the reaction center,
absorption of excitons,
then further stages of photosynthesis
(transport of electrons, etc.).

We describe first stages of photosynthesis as a quantum thermodynamic machine (nonequilibrium quantum system with thermodynamic cycles) and discuss effects of supertransport and existence of quantum states with long lifetime.

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.

Naive model — enlarge the coupling constant —
exciton transport will be faster.
But in this case decoherence will also be faster (no photonic echo).

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

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

I. Ya. Aref'eva, I. V. Volovich, S. V. Kozyrev, Stochastic limit method and interference in quantum many-particle systems, Theoretical and Mathematical Physics, 2015, 183:3, 782–799.

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

M. Fleischhauer, M.D. Lukin, Dark-State Polaritons in Electromagnetically Induced Transparency, Phys. Rev. Lett. 2000, V.84, P.5094

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]

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

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, λ 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 Θ is a sum of

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

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

This generator can be obtained in the stochastic (weak coupling) limit approximation of weak coupling and long times

$$t \mapsto t/\lambda^2, \qquad \lambda \to 0.$$

The effect of small perturbations at large times — describes thermalization and decoherence, gives dissipative Lindblad generators.

L. Accardi, Lu Yun Gang, I. Volovich, Quantum theory and its stochastic limit, Springer-Verlag, Berlin, 2002

We will investigate the case where Θ is a sum of several θ which interact in a complicated way giving possibility to manipulate quantum states.

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,

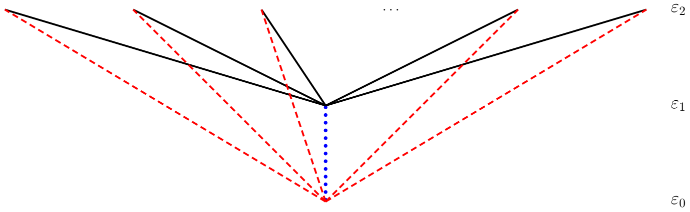
Degeneracy in the light-harvesting system,

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, ω_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 $\beta_{\rm em}^{-1} = 6000K$, $\beta_{\rm ph}^{-1} = 300K$, $\beta_{\rm sink}^{-1} = 0K$.

The full Hamiltonian

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

λ is the coupling constant.
The Hilbert space

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

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 χ belongs to the level ε_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 ψ belongs to the level ε_2.

χ **and** ψ **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)

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

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

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

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

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

γ 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)

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

The constants γ have the form

$$\gamma^{+}_{\mathrm{re},R} = \pi \int |g_R(k)|^2 \delta(\omega_R(k) - \varepsilon_2 + \varepsilon_0) N_R(k) dk,$$

$$\gamma^{-}_{\mathrm{re},R} = \pi \int |g_R(k)|^2 \delta(\omega_R(k) - \varepsilon_2 + \varepsilon_0)(N_R(k) + 1) dk,$$

$$\gamma^{+}_{\mathrm{im},R} = -\int |g_R(k)|^2 \, \mathrm{P.P.} \frac{1}{\omega_R(k) - \varepsilon_2 + \varepsilon_0} N_R(k) dk,$$

$$\gamma^{-}_{\mathrm{im},R} = -\int |g_R(k)|^2 \, \mathrm{P.P.} \frac{1}{\omega_R(k) - \varepsilon_2 + \varepsilon_0} (N_R(k) + 1) dk.$$

Here functions $N_R(k)$ describe thermal reservoirs

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

$R = \mathrm{em}, \mathrm{ph}, \mathrm{sink}$, $\beta_{\mathrm{em}}^{-1} = 6000K$, $\beta_{\mathrm{ph}}^{-1} = 300K$, $\beta_{\mathrm{sink}}^{-1} = 0K$.

The temperatures for different reservoirs are different:
$\beta_{\rm em}^{-1} = 6000K$, $\beta_{\rm ph}^{-1} = 300K$, $\beta_{\rm sink}^{-1} = 0K$.

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 of excitons describes the efficiency of this machine.
To improve the efficiency one has to increase the flow.

Let us discuss how our quantum thermodynamic machine works.

We also will discuss manipulations with quantum states — switch on and off different generators in the sum

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

Bright, dark and off-diagonal matrices: are defined for each Lindblad generator. Generator $\theta_{\rm em}$ (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 $\theta_{\rm em}$ — 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 $\theta_{\rm em}$ — 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 and dark spaces for photons and phonons in our model are different, this leads to excitation of quantum coherences.

Lindblad generators – quantum dissipative dynamics, relaxation and decoherence. Let us consider the example.

Dynamics for the transport (phononic) generator θ_{ph}.
Proposition *1) The dynamics generated by the equation*

$$\frac{d}{dt}\rho = \theta_{\mathrm{ph}}(\rho)$$

conserves each of the bright, dark and off–diagonal subspaces, moreover:
2) Dark matrices are stationary with respect to the dynamics.
3) Off–diagonal matrices exponentially decay to zero (if the coefficients γ are non–zero).

Proof Generator $\theta_{\rm ph}$ applied to bright matrices $|1\rangle\langle 1|$, $|\psi\rangle\langle\psi|$ maps this matrices again to the bright space.
Generator $\theta_{\rm ph}$ applied to dark matrices gives zero (actually each term in the generator gives zero).
Generator $\theta_{\rm ph}$ applied to an off–diagonal matrix gives

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

$$\left.-\gamma^+_{\rm re,ph}\{\rho,|1\rangle\langle 1|\}+i\gamma^+_{\rm im,ph}[\rho,|1\rangle\langle 1|]\right]$$

where $\gamma_{\rm re}$ are positive and at least one of anticommutators is non–zero. This implies exponential decay.

Dynamics in the bright subspace: supertransfer

Let us consider the bright matrix

$$\rho = \rho_1 |1\rangle\langle 1| + \rho_\psi |\widetilde{\psi}\rangle\langle\widetilde{\psi}|, \qquad \rho_1, \rho_\psi \geq 0.$$

Action of the transport generator in the bright space

$$\theta_{\mathrm{ph}}(\rho) = \|\psi\|^2 \left(2\gamma^-_{\mathrm{re,ph}}\rho_\psi - 2\gamma^+_{\mathrm{re,ph}}\rho_1\right)\left(|1\rangle\langle 1| - |\widetilde{\psi}\rangle\langle\widetilde{\psi}|\right).$$

The coefficient $\|\psi\|^2$ is proportional to the degeneracy N of the upper level (with the energy ε_2) (actually $0 \leq \|\psi\|^2 \leq N$). This corresponds to the **supertransport** phenomenon — coherent amplification of the transport in the bright subspace (the maximal amplification is achieved when $\|\psi\|^2 = N$).

This can be compared with the multislit experiment — amplification of transport by constructive interference

Decoherence (dynamics in the off–diagonal space) will also be amplified.

But the dark states will be stationary and will not decay!

This shows the possibility of existence of coherences with long lifetime in degenerate systems.

At the previous three slides we considered the dynamics only for the phononic generator.
But in this model the dynamics is given by joint action of three generators (light, phonons, sink).

Interaction of these generators creates some non–trivial quantum effects.

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

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

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

This means that for non–parallel $|\chi\rangle$, $|\psi\rangle$ some parts of the 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.

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: stage 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 θ_{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: stage 2. Switch off the light.

Apply to ρ_1 (obtained at the previous step) the dynamics generated by $\theta_{\rm ph} + \theta_{\rm sink}$ (transport and absorption, no light). Expansion of the bright photonic vector

$$\widetilde{\chi} = \widetilde{\chi}_0 + \widetilde{\chi}_1, \qquad \widetilde{\chi}_0 \| \widetilde{\psi}, \quad \widetilde{\chi}_1 \perp \widetilde{\psi}$$

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

In dynamics survives only the part of ρ_1 which is dark for the phononic generator $\theta_{\rm ph}$. We get for the limit of the dynamics

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

$\rho_{\chi\chi}$, $\rho_{\chi 0}$, $\rho_{0\chi}$ are as above (for ρ_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: stage 3. Switch on the light again.

Spectroscopy: apply to ρ_2 the dynamics generated by $i[\cdot, H_{\rm eff}]$ (ignore transport and absorption) and consider the dynamics of the off-diagonal part of ρ_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

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

Let us note that

$$1 - |\langle\widetilde{\psi}, \widetilde{\chi}\rangle|^2 = \sin^2\alpha,$$

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

Non–trivial contribution to spectroscopy is given by

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

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

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

$$\left(1 - |\langle\widetilde{\psi}, \widetilde{\chi}\rangle|^2\right)\left(|0\rangle\langle 0| - |\widetilde{\chi}|\rangle\langle\widetilde{\chi}|\right).$$

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.

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 vectors of bright states.
Bright photonic states can be dark phononic states.
Generation of non-decaying dark phononic states.
Relation to experiments with photonic echo — dark states give non-zero contribution in spectroscopy.