Amplification of Quantum Transfer and Quantum Ratchet

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How to amplify the quantum transfer and make it directed?
The simplest model of quantum transport is the dynamics of the 2×2 density matrix

$$\frac{d}{dt}\rho(t) = -i[H, \rho(t)], \quad H = \begin{pmatrix} E_1 & J \\ J & E_2 \end{pmatrix}.$$

Eigenvalues and eigenvectors of the Hamiltonian are

$$E_{\pm} = E \pm \sqrt{J^2 + \Delta^2}, \quad E_1 + E_2 = 2E, \quad E_1 - E_2 = 2\Delta,$$

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2\left(J^2 + \Delta^2 \pm \Delta\sqrt{J^2 + \Delta^2}\right)}} \begin{pmatrix} \Delta \pm \sqrt{J^2 + \Delta^2} \\ J \end{pmatrix}.$$

For $E_1 \neq E_2$ evolution will not lead to a complete transition of the wave function

$$\langle 2|e^{-itH}|1\rangle = \frac{J}{2\sqrt{J^2+\Delta^2}} e^{-itE_+} \left(1 - e^{2it\sqrt{J^2+\Delta^2}}\right), \qquad (1)$$

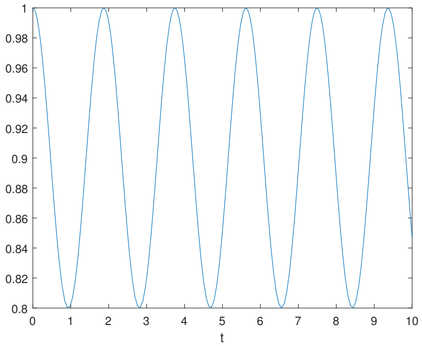
$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Decreasing of Δ enhances the transfer (transfer is effective when Δ is less than J).

For the Hamiltonian

$$H = \begin{pmatrix} 3 & 0.75 \\ 0.75 & 0 \end{pmatrix}$$

population oscillations for $\rho_{11}(t)$ are shown — the population transition of 20%.



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More complex model of transport — time dependence of the Hamiltonian, dissipation and sink are added

$$\frac{d}{dt}\rho(t) = -i[H(t), \rho(t)] + \mathcal{L}(\rho(t)) + \mathcal{S}(\rho(t)), \tag{2}$$

$$H(t) = \begin{pmatrix} E_1 + \mathbf{u} \cdot \mathbf{q}(t) & J \\ J & E_2 + \mathbf{v} \cdot \mathbf{q}(t) \end{pmatrix}, \tag{3}$$

$$\mathbf{q}(t) = \mathbf{w} \sin(\omega t). \tag{4}$$

Example: charge separation in quantum photosynthesis in the presence of vibrons $\mathbf{q}(t)$ described classically. The excitations are created by the absorption of light, the excitation is the $|1\rangle$ level of the system. The charge separation corresponds to the transition from the $|1\rangle$ level to the $|2\rangle$ level.

Decoherence and dissipation are described by the GKSL term

$$\mathcal{L}(\rho) = \gamma^{+}\left(\langle 2|\rho|2\rangle|1\rangle\langle 1| - \frac{1}{2}\{\rho, |2\rangle\langle 2|\}\right) +$$

$$+\gamma^{-}\left(\langle 1|\rho|1\rangle|2\rangle\langle 2| - \frac{1}{2}\{\rho, |1\rangle\langle 1|\}\right), \qquad (5)$$

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Here $\gamma^{+}/\gamma^{-} = e^{-\beta(E_1 - E_2)}$, E_1 and E_2 ($E_1 > E_2$) are energies of levels $|1\rangle$ and $|2\rangle$, β is the inverse temperature ($\beta^{-1} \approx 300K \approx 200$ cm^{-1} for room temperature), and $\{A, B\} := AB + BA$ denotes anticommutator.

Sink of excitations

$$\mathcal{S}(\rho) = -s_1\langle 1|\rho|1\rangle|1\rangle\langle 1| - s_2\langle 2|\rho|2\rangle|2\rangle\langle 2|, \quad s_1, s_2 > 0 \qquad (6)$$

Physical meaning: the second term $-s_2\langle 2|\rho|2\rangle|2\rangle\langle 2|$ describes the transfer of an electron along the charge transfer chain, the first term $-s_1\langle 1|\rho|1\rangle|1\rangle\langle 1|$ describes the recombination of excitons.
To make the work of quantum photosynthesis more efficient, it is necessary to minimize recombination through the first term of the sink operator (6). The exciton recombination is proportional to the effective time the system stays in the $|1\rangle$ state, i.e.

$$\bar{T} = \int_0^\infty \rho_{11}(t)dt, \qquad (7)$$

where $\rho(t)$ is a solution of (2) with the initial condition $|1\rangle\langle 1|$.

Quantum ratchet. The following mechanism is proposed to enhance the quantum transfer in the model (2) and to make it directional, that is, the speed of the direct transition $|1\rangle \to |2\rangle$ should exceed the speed of the reverse transition $|2\rangle \to |1\rangle$. Such a mechanism (quantum ratchet) includes two elements:

1) Resonance of transition with the vibron. Let the transition frequency be in resonance with the vibration frequency of the vibron $\mathbf{q}(t)$, then for the direct transition $|1\rangle \to |2\rangle$ the vibron oscillation reduces the energy difference and increases the transition amplitude. When the system reaches the level $|2\rangle$ the vibron oscillates in the opposite direction and the energy level difference increases, decreasing the amplitude of the reverse transition. This effect can be compared with the formula (1) where the value Δ will be different for the forward and reverse transitions.

2) Tuning of decoherence. When the decoherence time coincides with the transition time, the forward transition works (approximately) in a coherent mode (with increased efficiency), and the reverse transition performs incoherently (with reduced efficiency), which increases the directionality of the transition. Such a regime can be discussed as the collapse of the wave function at the moment of transition.

Both of these transition parameter tunings (transition resonance with the vibron and decoherence rate tuning) have been discussed for quantum photosynthesis [1], [2], [3].

Simulation. We choose the Hamiltonian (3) as

$$H(t) = \begin{pmatrix} 3 & 0.75 \\ 0.75 & 2\sin(3.35t) \end{pmatrix}. \qquad (8)$$

Such a Hamiltonian is intended to describe PSII-RC (photosystem II reaction center), energy and frequency are given in hundreds of inverse centimeters (in fact, these are 300, 75 and 340). Also

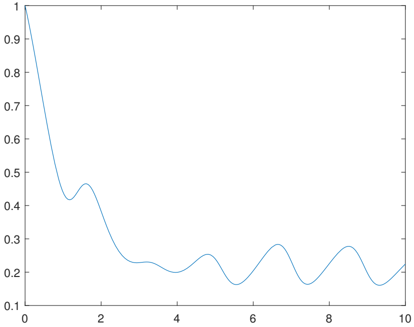
$$s_2 = 0.1, \quad \gamma^- = 0.5, \quad \gamma^+/\gamma^- = 0.22, \quad \gamma^+ = 0.11. \qquad (9)$$

The vibron frequency 340 cm^{-1} corresponds to almost exact resonance

$$2\sqrt{(E_1 - E_2)^2/4 + J^2} = 335.$$

The decoherence time is close to the transition half-period.

Simulation result for element $\rho_{11}(t)$ of the density matrix with the initial condition $\rho(0) = |1\rangle\langle 1|$ is shown in Figure below (here $s_1 = 0$; the time unit is 100 fs).
The system performs a fast transition $|1\rangle \rightarrow |2\rangle$ and reverse transitions are suppressed. The directionality effect of the transition is actually important for the first two oscillations.



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Let us consider simulation with successive approximation to the model parameters.

Fig. 1. The friction is reduced $\gamma^- = 0.2$, the vibrons are disabled.
Fig. 2. The friction is reduced $\gamma^- = 0.2$, the vibrons are $\sin(3t)$.
Fig. 3. The friction $\gamma^- = 0.4$, the vibrons are $1.5 \sin(3t)$.
Fig. 4. The friction $\gamma^- = 0.5$, the vibrons are $2 \sin(3.35t)$.

The simulation shows an improvement in quantum transfer performance and a decrease in recombination (area under the curve) with tuning of parameters. The tail beyond the first few oscillations is not important (these are forced oscillations under the influence of vibrons).

Fig. 1. The friction is reduced $\gamma^{-} = 0.2$, the vibrons are disabled.

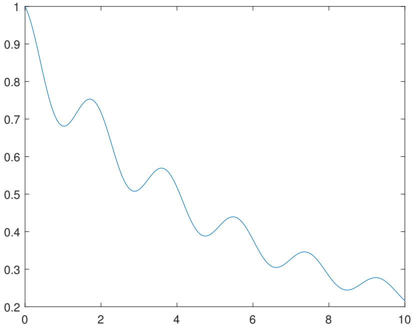

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Fig. 2. The friction is reduced $\gamma^- = 0.2$, the vibrons are $\sin(3t)$.

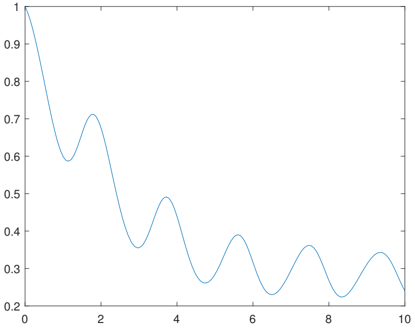

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Fig. 3. The friction $\gamma^{-} = 0.4$, the vibrons are $1.5\sin(3t)$.

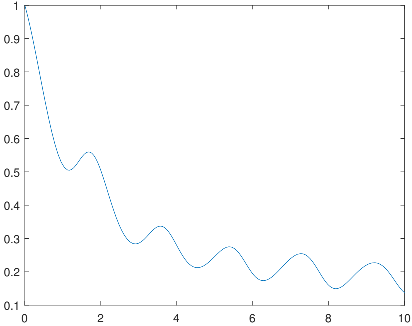

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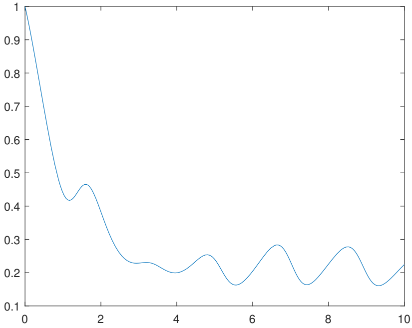
Fig. 4. The friction $\gamma^- = 0.5$, the vibrons are $2\sin(3.35t)$.



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Conclusions:
Application of the vibronic resonance with a transition and decoherence tuning makes it possible to enhance the quantum transfer and make it directional.
This mechanism is used in quantum photosynthesis.

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