Quantum ratchet

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Transport of electrons and excitons in quantum photosynthesis — presence of vibrons, transitions are directed. Contributions to evolution operator of tunneling transitions and dissipation are comparable. Vibrons — time dependence of the Hamiltonian (Landau–Zener mechanism) in presence of dissipation.
Out claim: model of quantum feedback control based on Landau–Zener mechanism with decoherence allows to describe directed transitions. Quantum ratchet.

S.V. Kozyrev, A.N. Pechen, Quantum feedback control in quantum photosynthesis, arXiv:2105.12128

Classical Maxwell's daemon, construction uses ratchet:

M. Smoluchowski, Experimentell nachweisbare, der ueblichen Thermodynamik widersprechende Molekularphaenomene, Phys. Z. 13, 1069–1080 (1912)

Landau–Zener formula. The dynamics with time dependent generator acting on states $|1\rangle$, $|2\rangle$ (called diabatic energy levels, eigenlevels $\psi_\pm(t)$ of the time dependent Hamiltonian $H(t)$ are called adiabatic levels)

$$\frac{d}{dt}\psi(t) = -iH(t)\psi(t),$$

$$H(t) = \begin{pmatrix} ut & J \\ J & vt \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Probability of transition between diabatic states will be equal to $1 - P$ where

$$P = e^{-2\pi\gamma}, \quad \gamma = \frac{J^2}{|u - v|}.$$

The transition occurs in vicinity of the avoided crossing point $t = 0$ where matrix elements at the diagonal of the generator are equal. Value of $1 - P$ is large for large interaction J or low difference $|u - v|$ of velocities of passage through the avoided crossing point at different slopes of the transition (adiabatic regime).

Landau–Zener formula with decoherence was discussed in:

Y.Gefen, E.Ben-Jacob, A.O.Caldeira, Zener transitions in dissipative driven systems, Phys. Rev. B, 36(5), 2770–2782 (1987).

P.Ao, J.Rammer, Influence of Dissipation on the Landau-Zener Transition, Phys. Rev. Lett., 62(25), 3004–3007 (1989).

P. Ao, J.Rammer, Quantum dynamics of a two-state system in a dissipative environment, Phys. Rev. B, 43(7), 5397–5418 (1991).

Measurements (projections) and Landau–Zener transitions

A.Pechen, A.Trushechkin, Measurement-assisted Landau-Zener transitions, Phys. Rev. A, 91:5 (2015), 052316, arXiv: 1506.08323

This approach is not valid if projection occurs at the avoided crossing.

Discussion by Landau — quasiclassical arguments: transition amplitude (expressed by T-exponent)

$$\langle 1|\, T e^{-i\int_{-\infty}^{+\infty} H(\tau)d\tau}|1\rangle = \langle \psi_+(+\infty)|\, T e^{-i\int_{-\infty}^{+\infty} H(\tau)d\tau}|\psi_-(-\infty)\rangle,$$

is approximated by the contour integral in complex plane

$$\langle \psi_+(+\infty)|e^{-i\int_C E_\pm(\tau)d\tau}|\psi_-(-\infty)\rangle.$$

$E_\pm(\tau)$ — eigenvalues of adiabatic eigenlevels $\psi_\pm(\tau)$, the contour is along the real axis with loop around imaginary branch point t where $E_+(t) = E_-(t)$. For transition probability P only integral along imaginary axis gives contribution

$$\exp\left(-\frac{2}{\hbar}\mathrm{Im}\int_0^t (E_+(\tau) - E_-(\tau))\, d\tau\right).$$

If the wave function is collapsed at the branch point t — direct and reverse transition probabilities are different and the transition is directed.

It might seem that the probability of collapse of the wave function in vicinity of the avoided crossing is small (since this vicinity is small) but if velocities u, v are low at avoided crossing (adiabatic regime) the system spends at vicinity of the avoided crossing considerable time and the probability of collapse can be large. In this case the transition probability depends on the direction of transition. This can be phenomenologically modeled by the quantum feedback control equation

$$\frac{d}{dt}\psi(t) = -iH(t)\psi(t),$$

$$H(t) = \begin{pmatrix} ut|\langle 1|\psi(t)\rangle|^2 & J \\ J & vt|\langle 2|\psi(t)\rangle|^2 \end{pmatrix}.$$

Squares of moduli of matrix elements describe measurements.
Quantum ratchet equation

How ratchet works: direct transition $|1\rangle \to |2\rangle$, then

$$|\langle 1|\psi(t)\rangle|^2 = 1, \quad |\langle 2|\psi(t)\rangle|^2 = 0,$$

$$H(t) = \begin{pmatrix} ut & J \\ J & 0 \end{pmatrix}, \quad P = e^{-2\pi\gamma}, \quad \gamma = \frac{J^2}{|u|}.$$

Reverse transition $|2\rangle \to |1\rangle$, in this case

$$|\langle 1|\psi(t)\rangle|^2 = 0, \quad |\langle 2|\psi(t)\rangle|^2 = 1,$$

$$H(t) = \begin{pmatrix} 0 & J \\ J & vt \end{pmatrix}, \quad P = e^{-2\pi\gamma}, \quad \gamma = \frac{J^2}{|v|}.$$

The ratchet utilizes friction (i.e. collapse of wave function) and low velocity of passage through the avoided crossing.

Applications of different models of quantum control to problems of quantum technologies

A. N. Pechen, D. J. Tannor, Are there traps in quantum control landscapes?, Phys. Rev. Lett., 106 (2011), 120402 , 3 pp.,

K. W. Moore, A. Pechen, X.-J. Feng, J. Dominy, V.J. Beltrani, H. Rabitz, Why is chemical synthesis and property optimization easier than expected?, Physical Chemistry Chemical Physics, 13:21 (2011), 10048–10070.

A. Pechen, A. Trushechkin, Measurement-assisted Landau-Zener transitions, Phys. Rev. A, 91:5 (2015), 052316 , 15 pp. arXiv: 1506.08323

J. Gough, M.R. James, Quantum Feedback Networks: Hamiltonian Formulation, Communications in Mathematical Physics, 287:3, 1109–1132 (2009), arXiv:0804.3442

Quantum photosynthesis

Charge separation in quantum photosynthesis is close to irreversible [1]. Time of electronic transitions $|1\rangle \to |2\rangle$ in [3] is approximately 100 fs which is close to the lifetime of electronic coherences — collapse of electronic wave function is possible in the process of transition.

By [3] charge separation in bacterial reaction center utilizes interaction of electronic states with two vibrons with energies 115 and 35 cm^{-1}. Vibron with energy 115 cm^{-1} is generated when exciton state is created and oscillates along the reaction coordinate for transition between exciton state and charge separation state causing a transition to the charge separation state. Vibron with energy 35 cm^{-1} is generated after this transition and prevents recombination of the charge transfer state providing directionality of the process of charge separation.

Excitons generate vibrons as vibrations of nuclei in the field of exciton according to the (semiclassical) Franck–Condon principle.

[1] *C. D. van der Weij-de Wit, J. P. Dekker, R. van Grondelle, I. H. M. van Stokkum, Charge Separation is Virtually Irreversible in Photosystem II Core Complexes with Oxidized Primary Quinone Acceptor, J. Phys. Chem. A (2011), 115, 16, 3947–3956.*

[2] *E. Romero, V.I. Novoderezhkin, R. van Grondelle, Quantum design of photosynthesis for bio-inspired solar-energy conversion, Nature, V. 543, 356 (2017)*

[3] *F. Ma, E. Romero, M.R. Jones, V.I. Novoderezhkin, R. van Grondelle, Both electronic and vibrational coherences are involved in primary electron transfer in bacterial reaction center, Nature Communications (2019) 10:933*

[4] *P. Maly, V.I. Novoderezhkin, R. van Grondelle, T. Mancal, Electron-vibrational coupling decreases trapping by low-energy states in photosynthesis, Chemical Physics 522 (2019) 69–76.*

Semiclassical Franck–Condon principle: vibrons are switched on by transitions between electronic states: landscape of potential energy for nuclei changes abruptly when exciton is excited, at this new energy landscape positions of nuclei are non-equilibrium and nuclei begin to oscillate around new minima of potential energy. Excitation of the exciton $|1\rangle$ generates the vibron $\mathbf{q}^{(1)}(t)$ and transition to the charge separation state $|2\rangle$ generates also the second vibron $\mathbf{q}^{(2)}(t)$. Corresponding Landau–Zener generator is

$$\begin{pmatrix} \mathbf{h}_1 \cdot \mathbf{q}^{(1)}(t)\rho_{11}(t) & J \\ J & \mathbf{h}_2 \cdot \left(\mathbf{q}^{(1)}(t) + \mathbf{q}^{(2)}(t)\right)\rho_{22}(t) \end{pmatrix},$$

where all vibrons as functions of time should be continuous and have continuous first derivatives (a vibron after excitation starts moving from some initial position and zero velocity).

Landau–Zener with friction for $\mathbf{h}_1 = -\mathbf{h}_2 = \mathbf{h}$.
Phenomenological quantum feedback control equation

$$\frac{d}{dt}\psi(t) = -iH(\psi, t)\psi(t), \quad \psi(t) = \begin{pmatrix} \langle 1|\psi(t)\rangle \\ \langle 2|\psi(t)\rangle \end{pmatrix}, \tag{1}$$

$$H(\psi, t) =$$

$$= \begin{pmatrix} \mathbf{h}\cdot\mathbf{q}^{(1)}(t)|\langle 1|\psi(t)\rangle|^2 & J \\ J & -\mathbf{h}\cdot\left(\mathbf{q}^{(1)}(t) + \mathbf{q}^{(2)}(t)\right)|\langle 2|\psi(t)\rangle|^2 \end{pmatrix}. \tag{2}$$

Quantum feedback model (1), (2) has cubic nonlinearity as for nonlinear Schroedinger equation. This model allows to obtain different probabilities of transitions for direct $|1\rangle \to |2\rangle$ and reverse $|2\rangle \to |1\rangle$ transitions (hence it describes *quantum ratchet*) although the Landau–Zener formula predicts equal probabilities for direct and reverse transitions.

The direct move of the quantum ratchet — transition $|1\rangle \to |2\rangle$ where $\langle 1|\psi(t)\rangle = 1$ and $\langle 2|\psi(t)\rangle = 0$. The generator:

$$\begin{pmatrix} \mathbf{h}\cdot\mathbf{q}^{(1)}(t) & J \\ J & 0 \end{pmatrix}.$$

Avoided crossing point for the direct move of the quantum ratchet

$$\mathbf{h}\cdot\mathbf{q}^{(1)}(t) = 0.$$

Vibronic oscillations can be linearized in vicinity of the avoided crossing point. Transition probability for one passage through the avoided crossing by Landau–Zener formula equals $1 - P$,

$$P = e^{-2\pi\gamma}, \quad \gamma = \frac{J^2}{|\mathbf{h}\cdot\mathbf{v}|},$$

and $\mathbf{v}$ is velocity of the vibron in the moment of the passage. By deceleration of the vibron at the moment of the passage it is possible to make the transition probability close to one $1 - P \simeq 1$.

The reverse move of the quantum ratchet — transition $|2\rangle \to |1\rangle$ where $\langle 1|\psi(t)\rangle = 0$ and $\langle 2|\psi(t)\rangle = 1$. The generator:

$$\begin{pmatrix} 0 & J \\ J & -\mathbf{h}\cdot\left(\mathbf{q}^{(1)}(t)+\mathbf{q}^{(2)}(t)\right) \end{pmatrix}.$$

The avoided crossing point satisfies

$$\mathbf{h}\cdot\left(\mathbf{q}^{(1)}(t)+\mathbf{q}^{(2)}(t)\right)=0.$$

Instead of single vibron $\mathbf{q}^{(1)}(t)$ this transition is driven by the sum of two vibrons. It might happen that the above equation has no solutions and the transition probability is close to zero $1-P\simeq 0$.

The problem of quantum control for the model (1), (2) of the quantum ratchet: find parameters for vibrons $\mathbf{q}^{(1)}(t)$ and $\mathbf{q}^{(2)}(t)$ to make transition probability for the direct move $|1\rangle \to |2\rangle$ of the ratchet close to one and transition probability for the reverse move $|2\rangle \to |1\rangle$ of the ratchet make close to zero.

A model of the quantum ratchet

The ansatz for the first vibron

$$\mathbf{q}^{(1)}(t) = \mathbf{q}_0 + \theta(t - t_1)\mathbf{v}_1 \left(\cos \omega_1 (t - t_1) - 1\right), \tag{3}$$

where θ is the step function: when the vibron is switched on at time moment t_1 (when exciton is excited) it begins to oscillate along vector $\mathbf{v}_1$ with frequency ω_1, with zero initial velocity starting from the initial position $\mathbf{q}_0$ (which corresponds to the stationary nuclear coordinates in the ground state $|0\rangle$ of the electron).
The ansatz for the second vibron

$$\mathbf{q}^{(2)}(t) = \theta(t - t_2)\mathbf{v}_2 \left(\cos \omega_2 (t - t_2) - 1\right), \tag{4}$$

i.e. the vibron is switched on at time moment t_2 and oscillates with frequency ω_2 along vector $\mathbf{v}_2$, initial displacement and initial velocity are equal to zero.

Equation of the avoided crossing point for the direct move

$$\mathbf{h} \cdot [\mathbf{q}_0 + \mathbf{v}_1 (\cos \omega_1 (t - t_1) - 1)] = 0 \qquad (5)$$

can be satisfied if $2\mathbf{h} \cdot \mathbf{v}_1 \geq \mathbf{h} \cdot \mathbf{q}_0$ (where scalar products are positive). To elevate transition probability one has to decrease velocity of the vibron $\mathbf{q}^{(1)}(t)$ in the moment of passage through the avoided crossing point (5) i.e. to make $2\mathbf{h} \cdot \mathbf{v}_1 \approx \mathbf{h} \cdot \mathbf{q}_0$ — the amplitude of the vibron is minimal which allows existence of solution of equation (5) of the crossing point.

The energy difference between adiabatic levels (eigenlevels of the time dependent Hamiltonian) in the initial point $t = t_1$ of the vibron is close to $\mathbf{h} \cdot \mathbf{q}_0$ (at $t = t_1$ adiabatic levels are close to diabatic levels $|1\rangle$, $|2\rangle$) and in the avoided crossing point it equals almost zero (since J is small), i.e. in the adiabatic regime energy of the vibron matches the energy difference between the levels. Approximate coincidence of energy of the vibron and energy difference of levels coupled to this vibron was widely discussed in the literature, in particular in [1]–[4].

Equation of the avoided crossing point for the reverse move

$$\mathbf{h}\cdot[\mathbf{q}_0 + \mathbf{v}_1\left(\cos\omega_1(t-t_1)-1\right) + \mathbf{v}_2\left(\cos\omega_2(t-t_2)-1\right)] = 0. \quad (6)$$

Solvability of this equation can be easily broken. In the adiabatic regime $2\mathbf{h}\cdot\mathbf{v}_1 \approx \mathbf{h}\cdot\mathbf{q}_0$ the sum of the first two terms in (6) will hardly cross zero. Let the third term in (6) gives a non-negative contribution in the scalar product with $\mathbf{h}$ (i.e. the scalar product $\mathbf{h}\cdot\mathbf{v}_2$ should be negative) then this contribution will be close to zero at time moments when the sum of the first two terms is positive. In this regime equation of the avoided crossing point (6) for the reverse move of the quantum ratchet will not have solutions and reverse transitions will be effectively forbidden.

Time parameter t_1 in (3) is the initial condition for (1), (2) (a moment of creation of exciton). Parameter t_2 in (4) is a moment of transition between diabatic states $|1\rangle$, $|2\rangle$ i.e. this time moment is related to a solution of (1). For simplicity let us make t_2 equal to the time moment when population of the level $|2\rangle$ in (1), (2) will exceed some threshold (if we start from the level $|1\rangle$ and only the first vibron $\mathbf{q}^{(1)}(t)$ is present in the generator). This definition is analogous to the definition of classical probability theory of the moment when the Brownian motion reaches a certain boundary (in general, random variables of this kind are called Markov moments).

Remark. Our approach to irreversibility of charge separation was based on application of two vibrons in generator (2) of the dynamics. We put $\mathbf{h}_1 = -\mathbf{h}_2 = \mathbf{h}$ in this formula, if we do not make this assumption, it is possible to obtain irreversibility even for the case of single vibron, if $\mathbf{h}_1$ and $\mathbf{h}_2$ are non-parallel and also $\mathbf{q}_0$ and $\mathbf{v}_1$ are non-parallel in the definition of the vibron.

Remark. To make charge transfer faster vibron (3) operates in the adiabatic regime: the amplitude of the vibron has the minimal value which allows to satisfy equation (5) of the avoided crossing point (energy of the vibron is close to Bohr frequency of the transition). In this regime the vibron is "fragile" — perturbations of parameters of the vibron related to mutations can break the solvability of (5) and block charge transfer.

In [3] mutations in photosynthetic reaction center were investigated: the YM210W mutation which causes small changes in geometry and potential in the reaction center modifies the operation of the vibron with energy 115 cm^{-1} and slows charge separation by two orders of magnitude. One can discuss this observation as a proof that vibron with energy 115 cm^{-1} works in the adiabatic regime (velocity of the vibron in the avoided crossing point is slow).

The GM203L mutation which removes the second vibron (with energy 35 cm^{-1}) slows charge separation by only one order of magnitude [3].

Summary. We considered a model of charge separation transition in quantum photosynthesis based on quantum feedback control equation. This quantum feedback control model is explained as follows: for Landau–Zener transition with friction and transitions close to adiabatic (the vibron is slow at avoided crossing) collapse of electronic wave function should occur at the avoided crossing point. This can be modeled by quantum feedback which allows to make probabilities of direct and reverse transitions different (the transition becomes directed). Taking in account excitation of two vibrons it is possible to make this transition maximally irreversible (i.e. to make probability of direct transition maximal and of reverse transition minimal). To make probability of the direct transition maximal energy of the vibron should be close to the Bohr frequency of the transition (which is observed in experiments).