Non-Markovianity boosts the efficiency of bio-molecular switches

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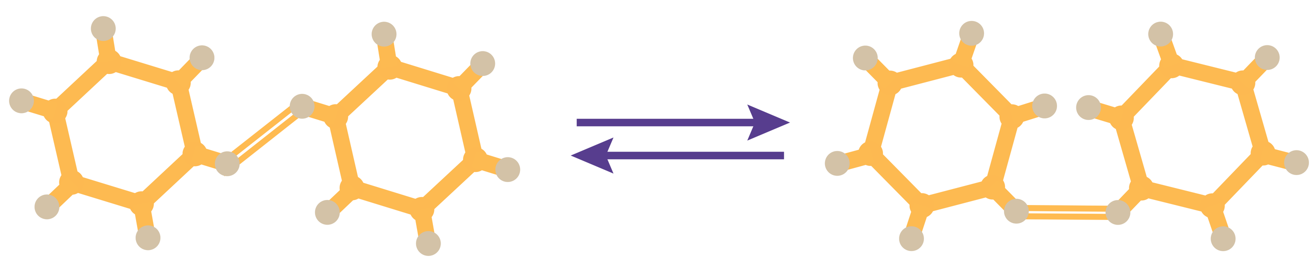
molecular switches and photoisomerization

Photoisomerization: change in the geometrical arrangement of a molecule, induced by photoexcitation.

Photoisomers can be reversibly switched between stable configurations.

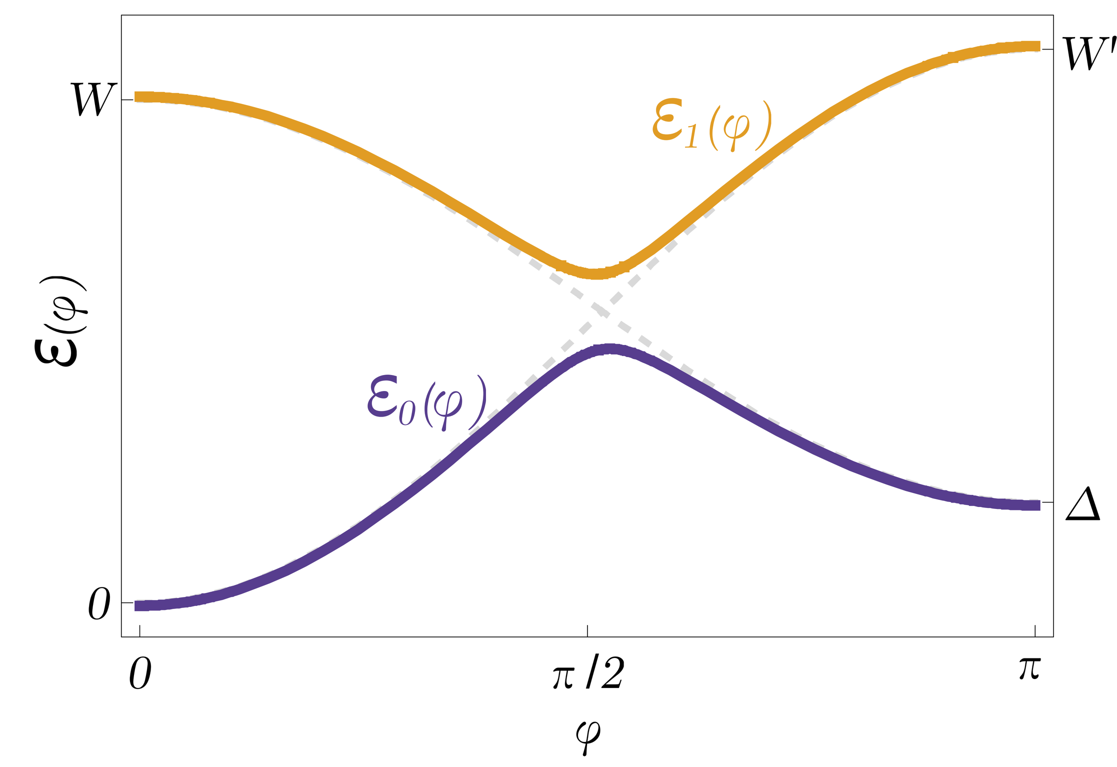
This phenomenon is the chemical basis of vision in humans, and can be artificially exploited in molecular machines and/or energy storage (e.g. solar thermal fuels).



The two stable configurations are separated by an energy barrier. However, a photoswitch can absorb a photon and then rotate while in contact with its environment.
The probability of switching configuration is called photoisomerization yield.

Exact dynamics too complicated, and the mechanisms involved are not entirely clear. Can resource theories help?

Q: Do memory effects (non-Markovianity) play a role in assisting photoisomerization?



thermodynamics as a quantum resource theory

Allowed operations on a system S:
a) contact with a thermal bath B
b) global energy-preserving unitary on S+B
c) thermal bath is traced out

Non-equilibrium states of S are then singled out as thermodynamical resources.

thermal operations

$$\mathcal{T}(\rho) = \mathrm{tr}_B\left[U\rho\otimes\frac{e^{-\beta H_B}}{Z_B}U^\dagger\right]$$

$$[U, H_S + H_B] = 0$$

Thermal operations (TO) commute with the free evolution of S (time-translation covariance).
As a consequence, the action of TO does not couple different modes of coherence.

time-translation covariance

$$\mathcal{T}\circ\mathcal{U}_t = \mathcal{U}_t\circ\mathcal{T} \quad \forall\mathcal{T}\in\mathsf{TO}$$

$$\mathcal{T}\left(\rho^{(\omega)}\right) = \mathcal{T}\left(\rho\right)^{(\omega)} \quad \forall\omega$$

The action of TO on quasiclassical states is fully characterized as that of Gibbs-stochastic (GS) matrices mapping the initial populations to the final ones.

Gibbs-stochastic matrices

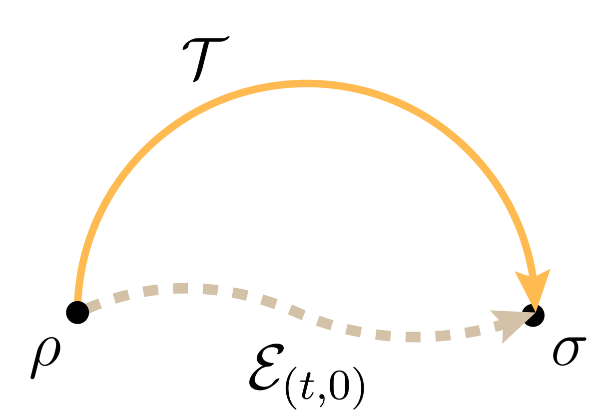
$$G\in\mathsf{GS} \iff \sum_i G_{ij} = 1 \text{ and } Ge^{-\beta H} = e^{-\beta H}$$

A criterion for the existence of a GS matrix connecting the population vectors of two states, can be given in terms of a partial order called thermomajorization.

thermomajorization

$$\rho \xrightarrow{\mathsf{GS}} \sigma \iff \rho \succ_{\mathrm{th}} \sigma$$

memoryless thermodynamics



A quantum channel can be implemented without using an external memory if its action can be reproduced by an underlying continuous-time Markovian dynamical map.

We define Markovianity in terms of the CP-divisibility of the map

CP-divisibility

$\mathcal{E}_{(t,0)}$ is CP-divisible if, for any $0\le s\le t$, it can be decomposed as

$$\mathcal{E}_{(t,0)} = \mathcal{E}_{(t,s)}\circ\mathcal{E}_{(s,0)}$$

with $\mathcal{E}_{(t,s)}$ a CP map.

memoryless thermal operations

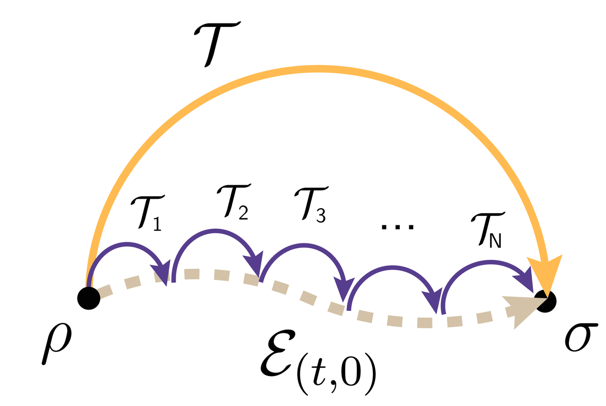
$\mathcal{T}\in\mathsf{TO}$ is memoryless if there exist a continuous family of generators $\mathcal{L}(\tau)$ such that $\forall s\ge r$ the map

$$\mathcal{E}_{(s,r)} = \mathsf{T}\exp\left(\int_r^s\mathcal{L}(\tau)d\tau\right)$$

defines a thermal operation and $\mathcal{E}_{(t,0)} = \mathcal{T}$.

CP-divisible maps are the one generated by (possibly time-dependent) Lindblad generators, with non-negative rates.

The absence of memory reflects itself in the possibility of splitting a TO into infinitesimal intermediate TOs.



the model

By fixing an initial state for the system, we construct a yield function on the set TO, which maps an operation to the yield that it produces in the final state

$$\rho_i \longmapsto \mathcal{T}(\rho_i)\,, \quad \gamma(\mathcal{T}) := \langle\mathcal{E}_0(\pi)|\,\mathcal{T}(\rho_i)|\mathcal{E}_0(\pi)\rangle$$

What is the maximum yield allowed by TO?
Can one reach the same yield in MTO, i.e. without exploiting memory?

Thanks to time-translation covariance we can reduce the problem to that of a GS mapping between population vectors

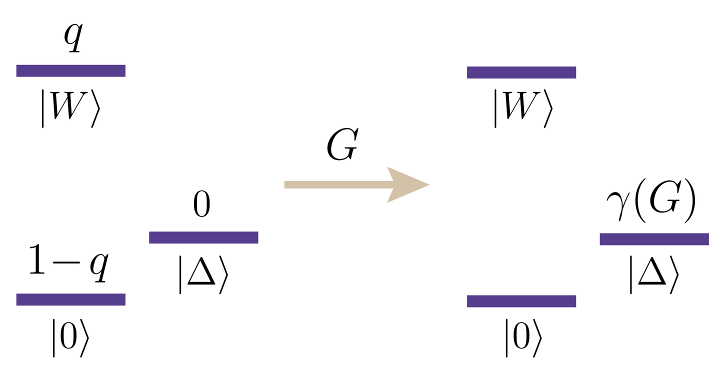
yield optimization

$$\gamma^* = \sup_{\mathcal{T}\in\mathsf{TO}}\gamma(\mathcal{T}) = \sup_{G\in\mathsf{GS}}\gamma(G)$$

$$\gamma_{\mathcal{M}} = \sup_{\mathcal{T}\in\mathsf{MTO}}\gamma(\mathcal{T}) = \sup_{G\in\mathsf{MGS}}\gamma(G)$$

By focusing on the stable cis/trans configurations only, and by ignoring the upermost level, we effectively reduce the photoisomer to a three-levels system.

Photoisomerization can then be seen as a GS mapping between population vectors of a qutrit

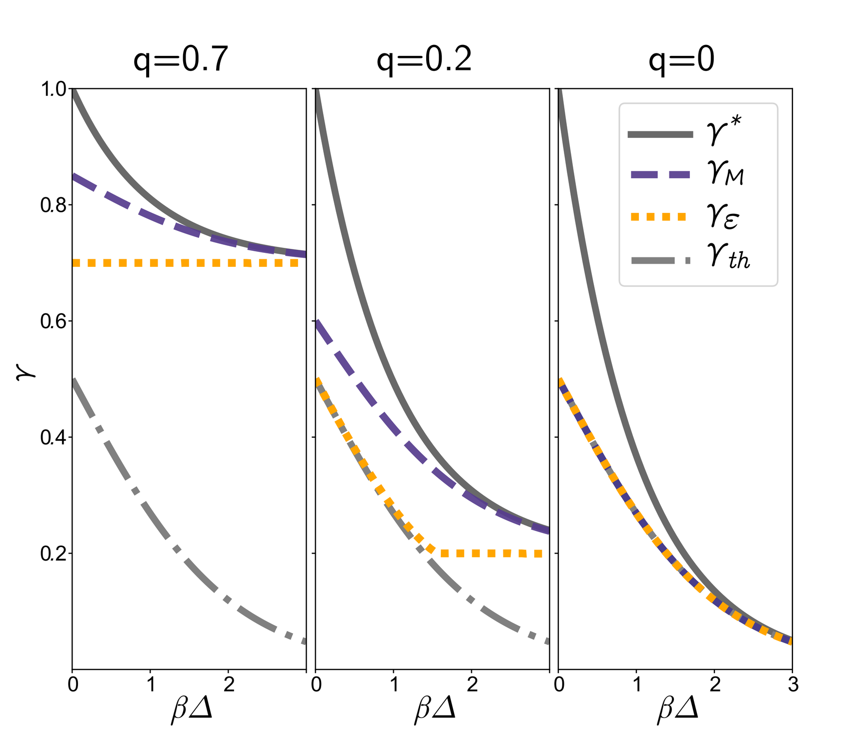


results

The problem can be solved exactly, and it is possible to find analytical expressions for the maximum yields that are achievable under TO and MTO.

$$\gamma^* = \begin{cases} q + (1-q)\left(e^{-\beta\Delta} - e^{-\beta W}\right) & \text{if } q \ge (1+e^{\beta W})^{-1}\,, \\ (1-q)e^{-\beta\Delta} & \text{if } q < (1+e^{\beta W})^{-1}\,, \end{cases}$$

$$\gamma_{\mathcal{M}} = \begin{cases} \left[q + (1-q)\frac{e^{-\beta\Delta}}{1+e^{-\beta\Delta}}\right]\frac{e^{-\beta\Delta}}{e^{-\beta\Delta}+e^{-\beta W}} & \text{if } q \ge (1+e^{\beta W})^{-1}\,, \\ \left[1 - q\frac{e^{-\beta W}}{e^{-\beta W}+e^{-\beta\Delta}}\right]\frac{e^{-\beta\Delta}}{1+e^{-\beta\Delta}} & \text{if } q < (1+e^{\beta W})^{-1}\,. \end{cases}$$



For large values of the cis-trans energy gap, the effects of memory on the photoisomerization yield are negligible.

On the other hand, for smaller gaps, memory significantly affects the achievable yield.

When q=0, MTO can at most thermalize the state.