# Exact characterization of entropy and free energy without thermodynamic limit or averaging

**Markus P. Müller**

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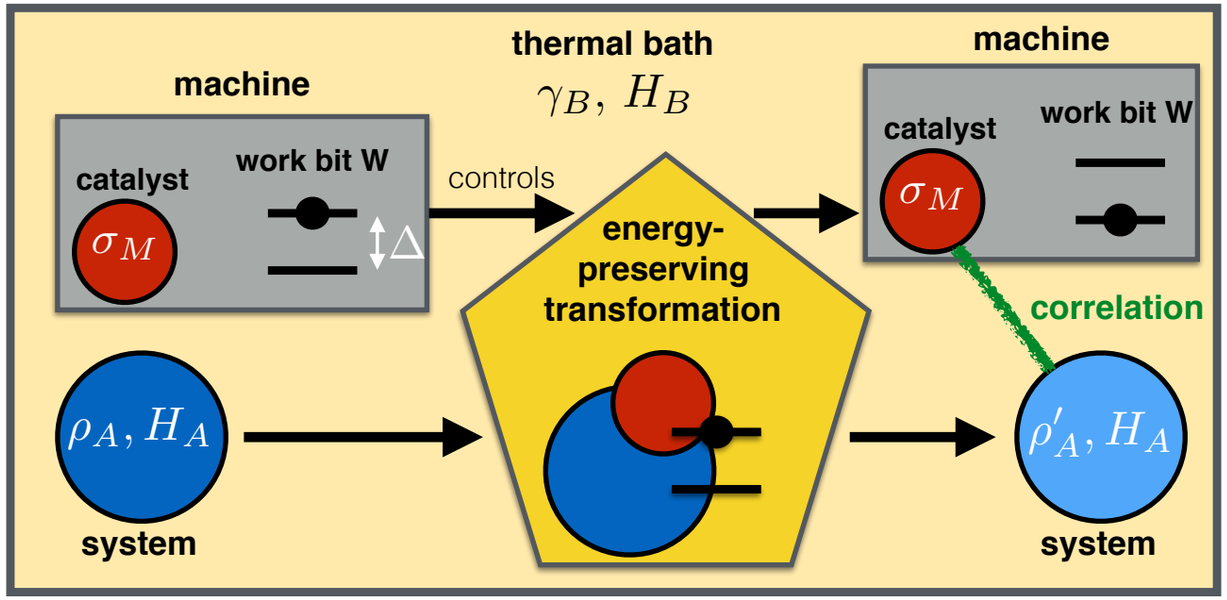
# Overview

1. Standard view: thermodynamic limit

2. Thermodynamics as a resource theory

3. Characterization of *F* and *S* without thermodynamic limit




4. How about coherence? A no-broadcasting theorem

5. Consequences for quantum information theory

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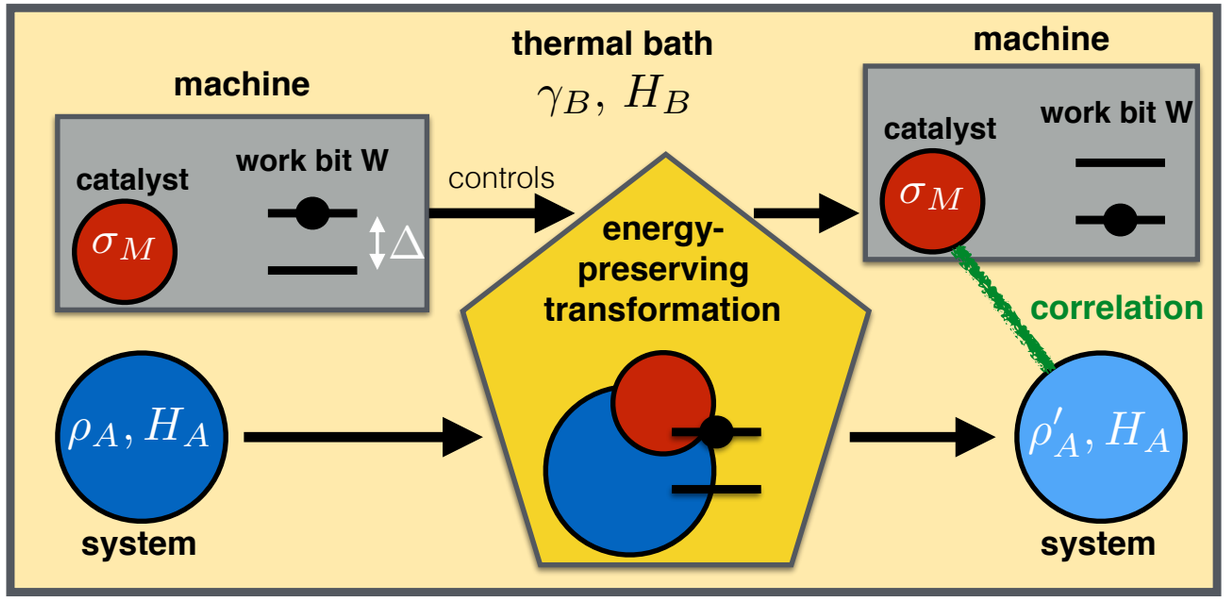

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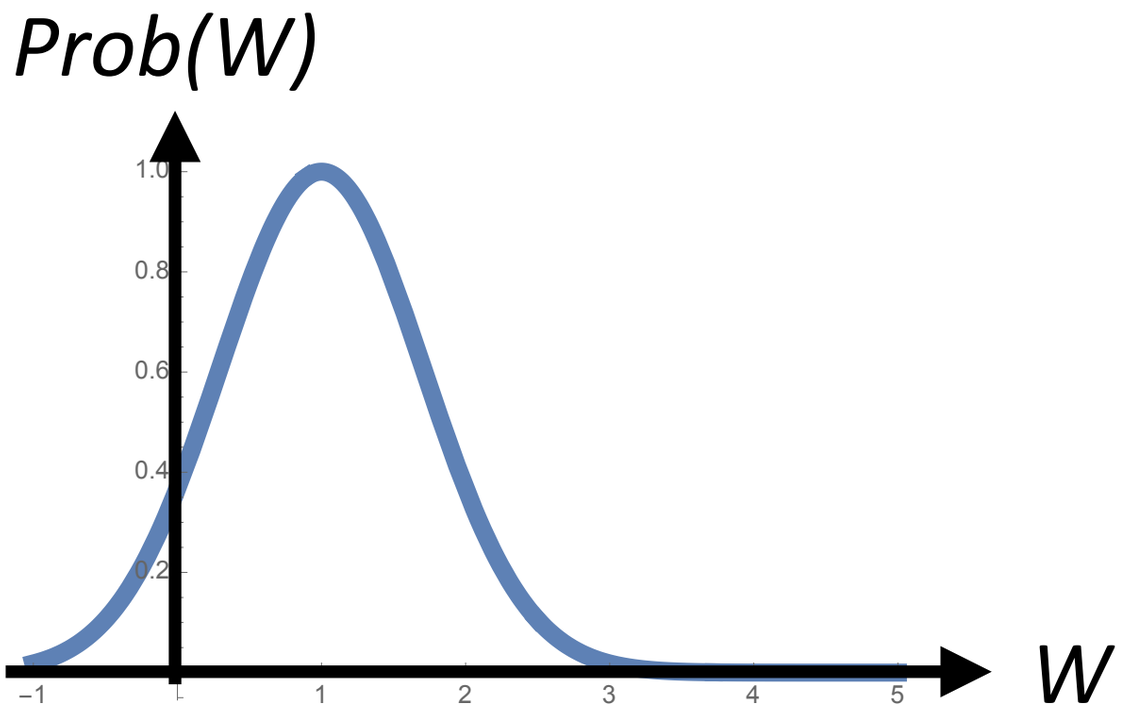
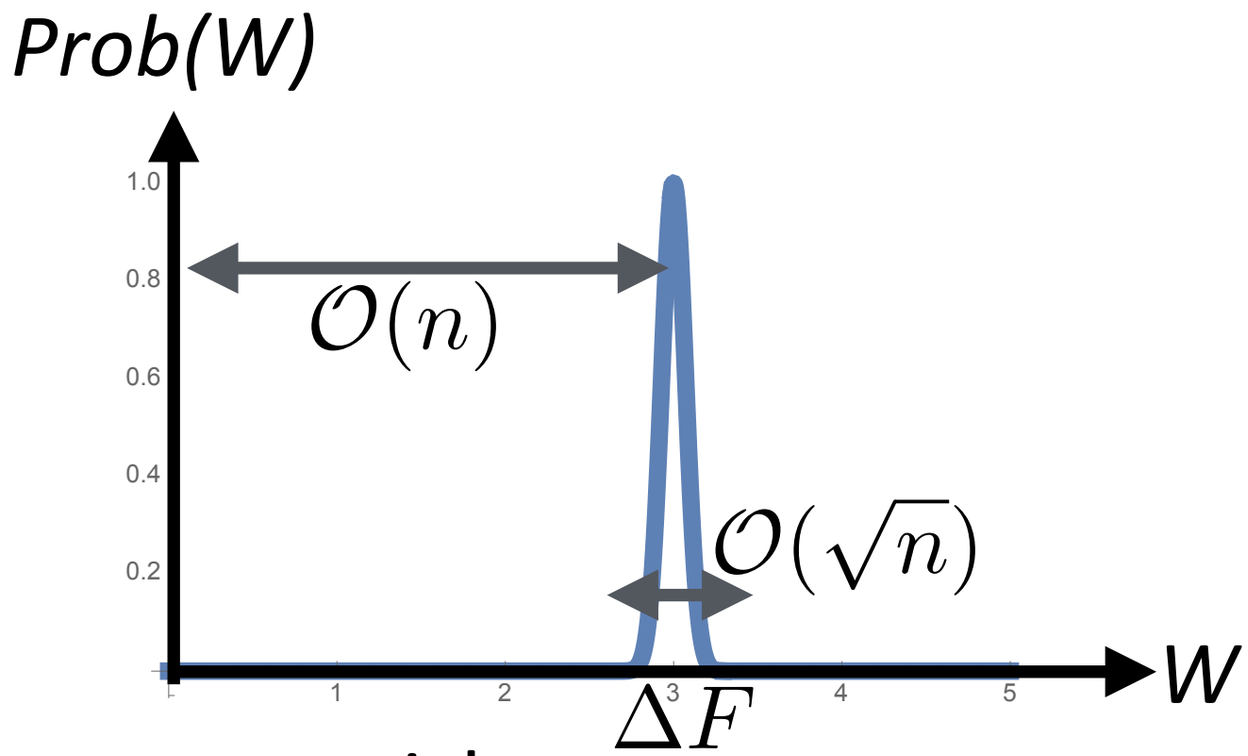
But this is a statement **on average**, since "work" is a random variable.

# Standard view: thermodynamic limit

Work is a **random variable** (for any given process):




small # of particles

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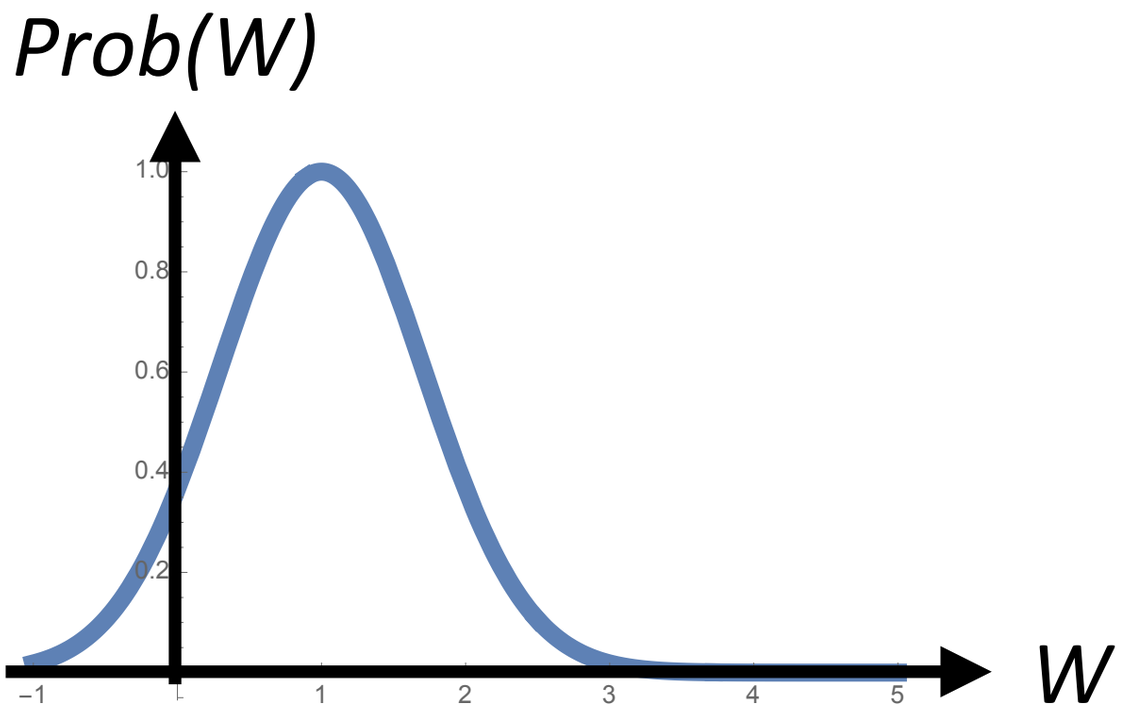


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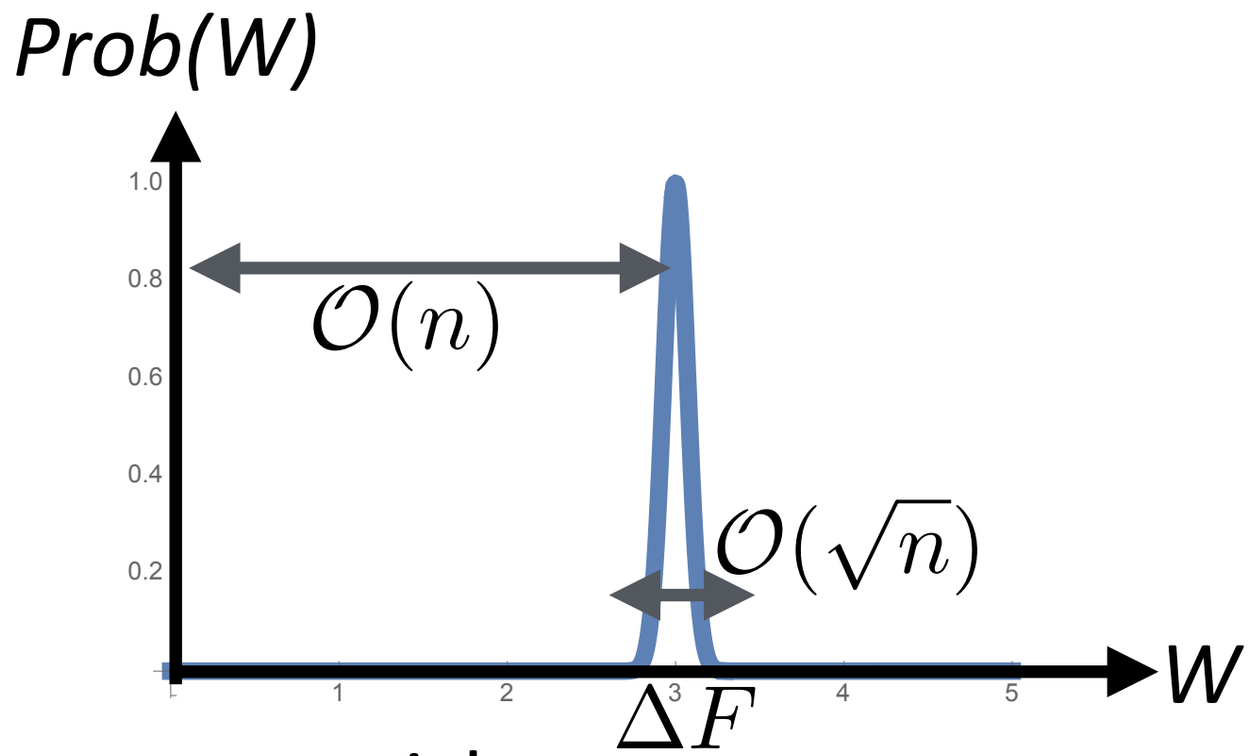


*n* particles

Reliably extractable work "is" $\Delta F$ :
only true in the thermodynamic limit $n \to \infty$
when fluctuations become irrelevant (law of large numbers).

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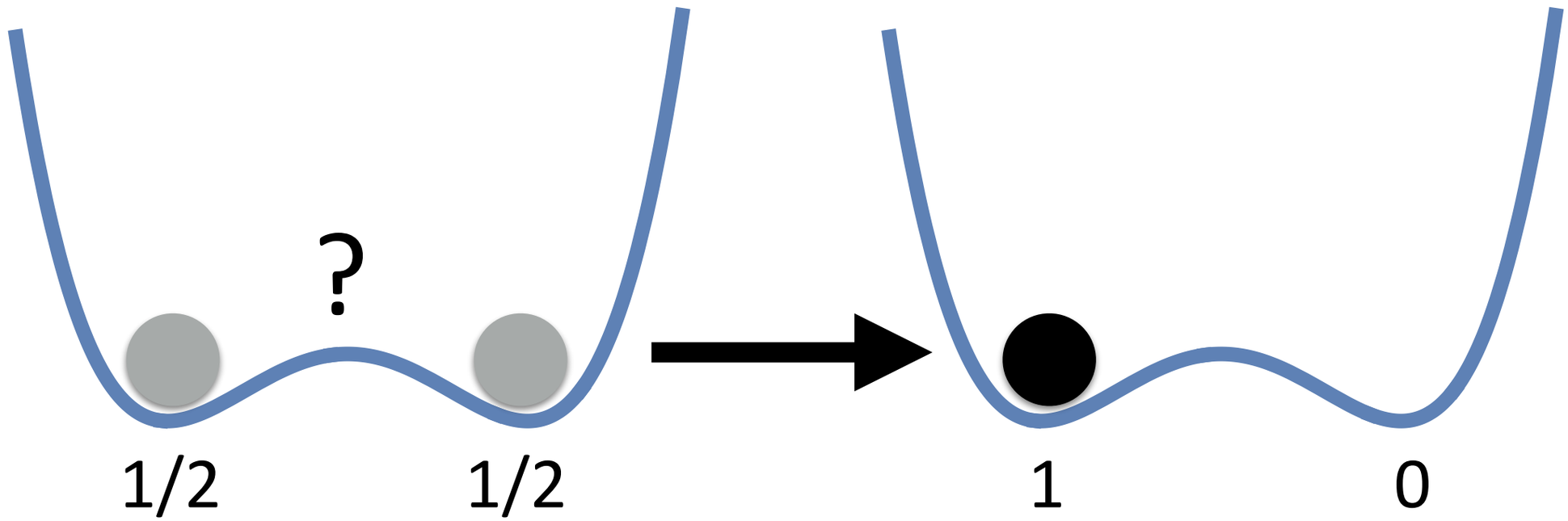


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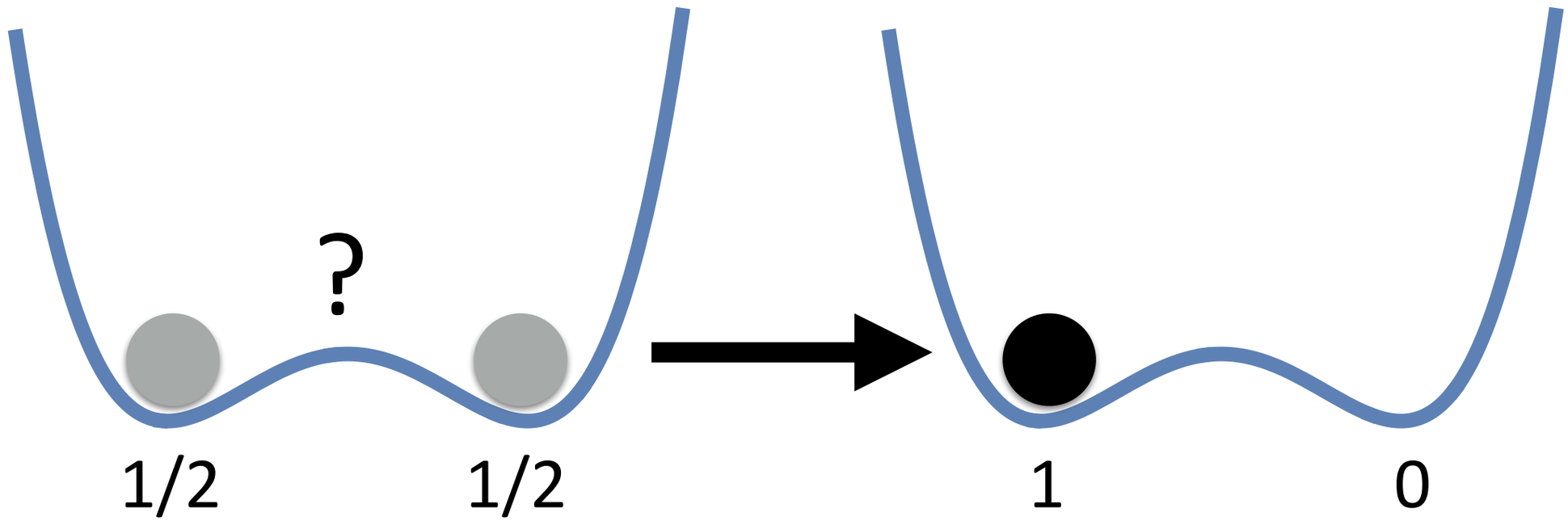


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**But: Bennett’s puzzle:**

$$\left(\frac{1}{2}, \frac{1}{2}, 0, \ldots, 0\right) \longrightarrow \left(1-\epsilon, \frac{\epsilon}{N}, \frac{\epsilon}{N}, \ldots, \frac{\epsilon}{N}\right)$$

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**Landauer erasure:**

Free energy *F* determines possibility of state transitions **only in the thermodynamic limit**. For “small” systems, resource theory formulation gives **additional constraints** (and dissolves Bennett’s puzzle). More soon.

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# Shannon / von Neumann entropy and data compression

**Schumacher compression:**

Given $n$ copies of a quantum state $\rho$, we would like to project into a smaller subspace (with projection $P^{(n)}$ ) such that

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Conventionally, F and S attain their operational meaning **only in the limit of very large ensembles**, due to version of the (statistical) law of large numbers.
But we would like to say more without this limit.

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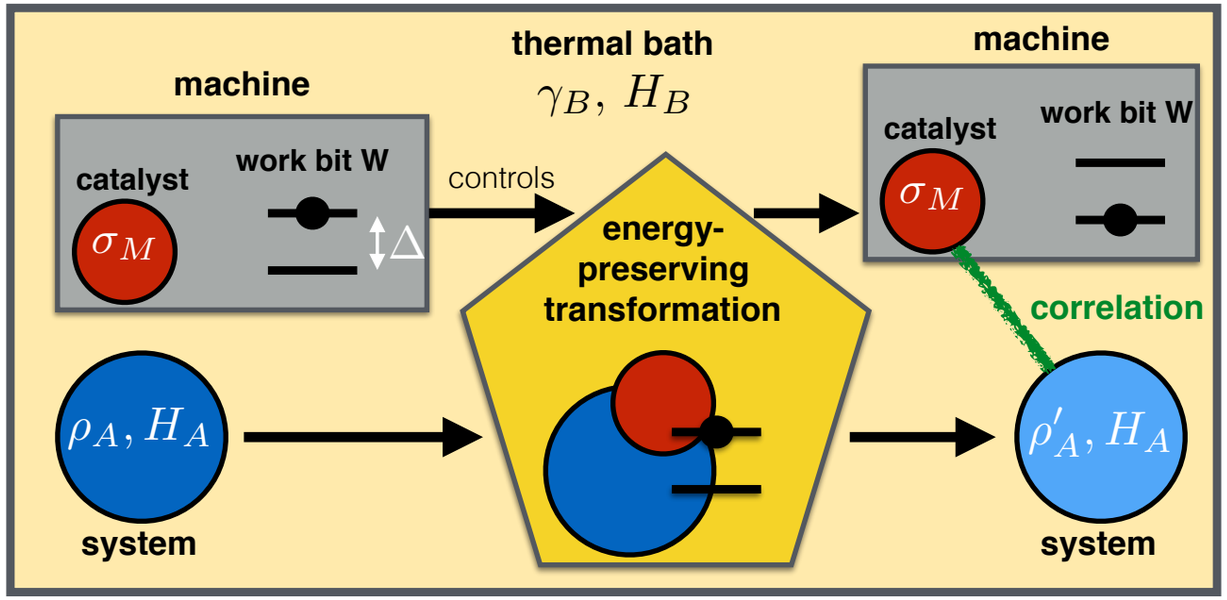

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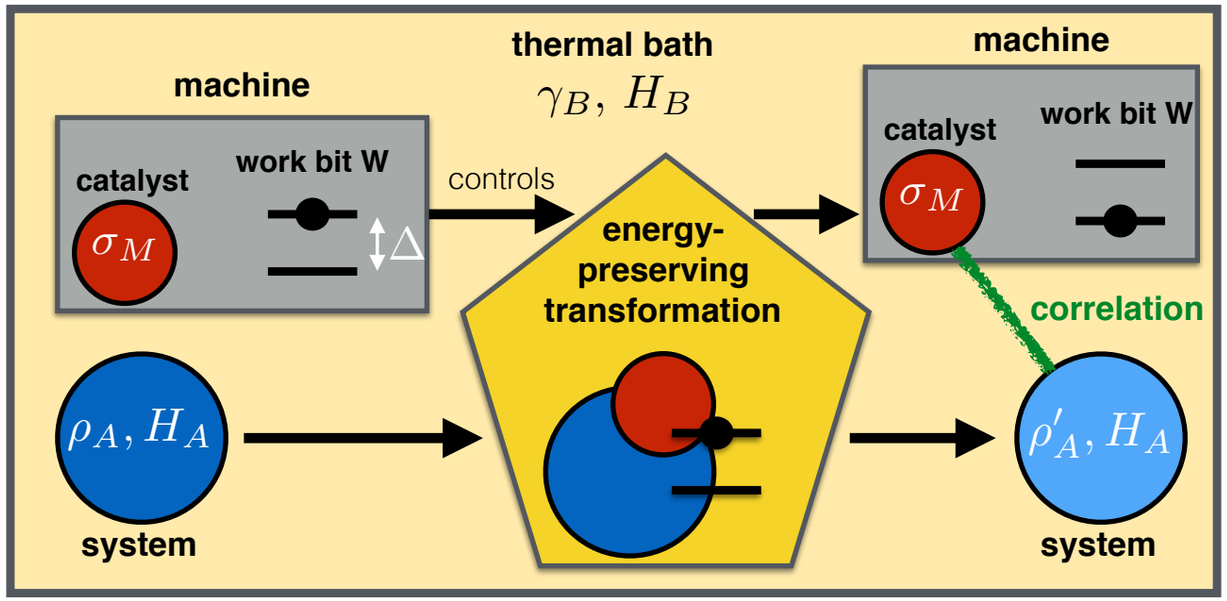


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# The second laws of quantum thermodynamics

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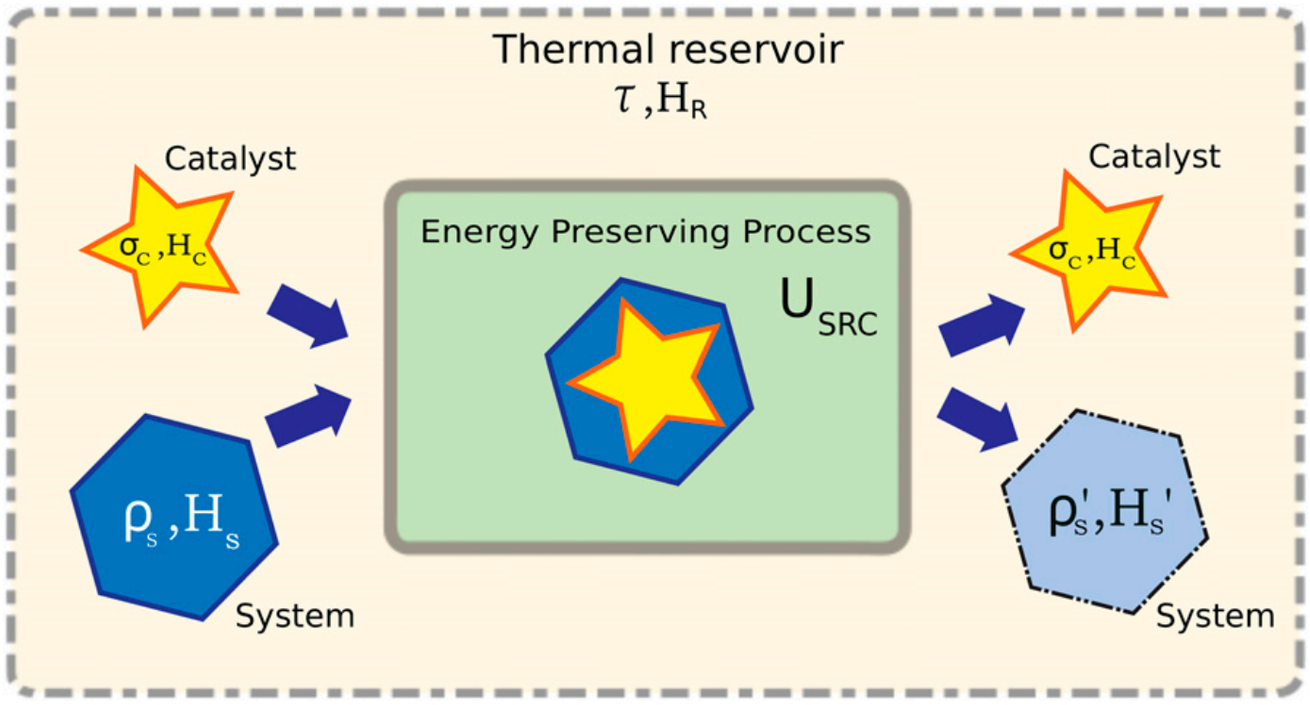

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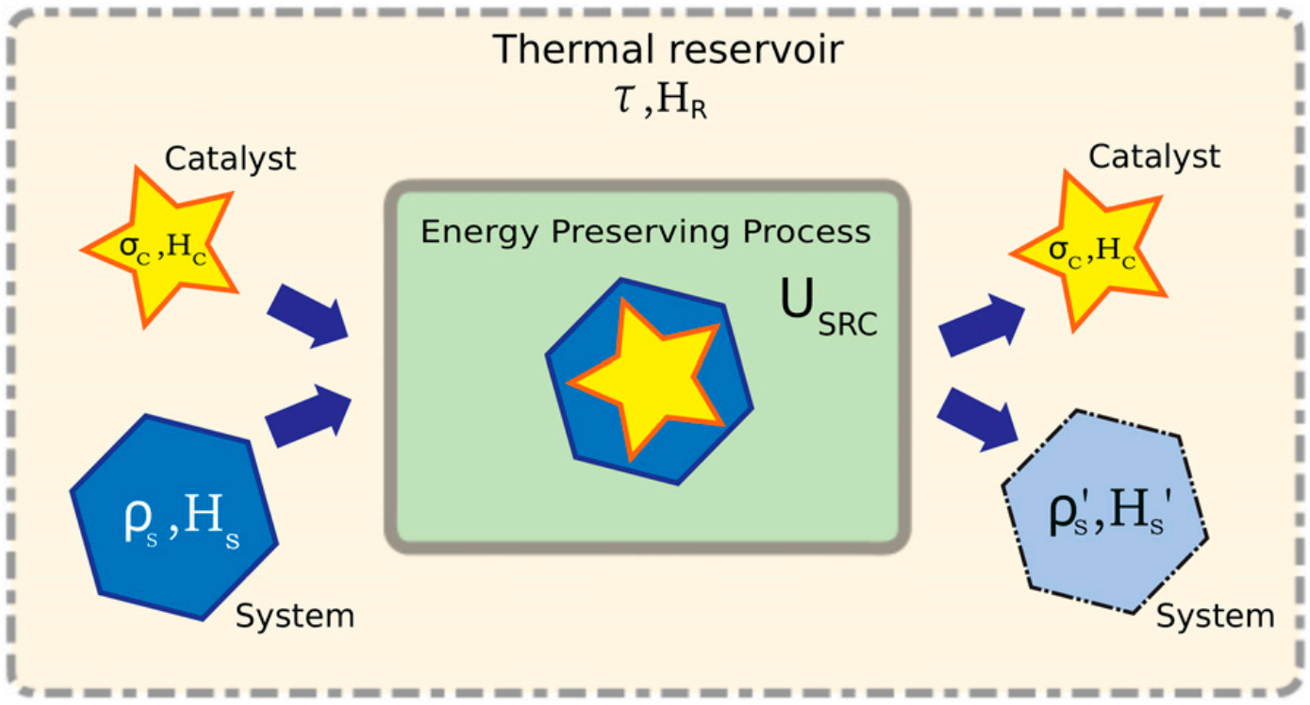


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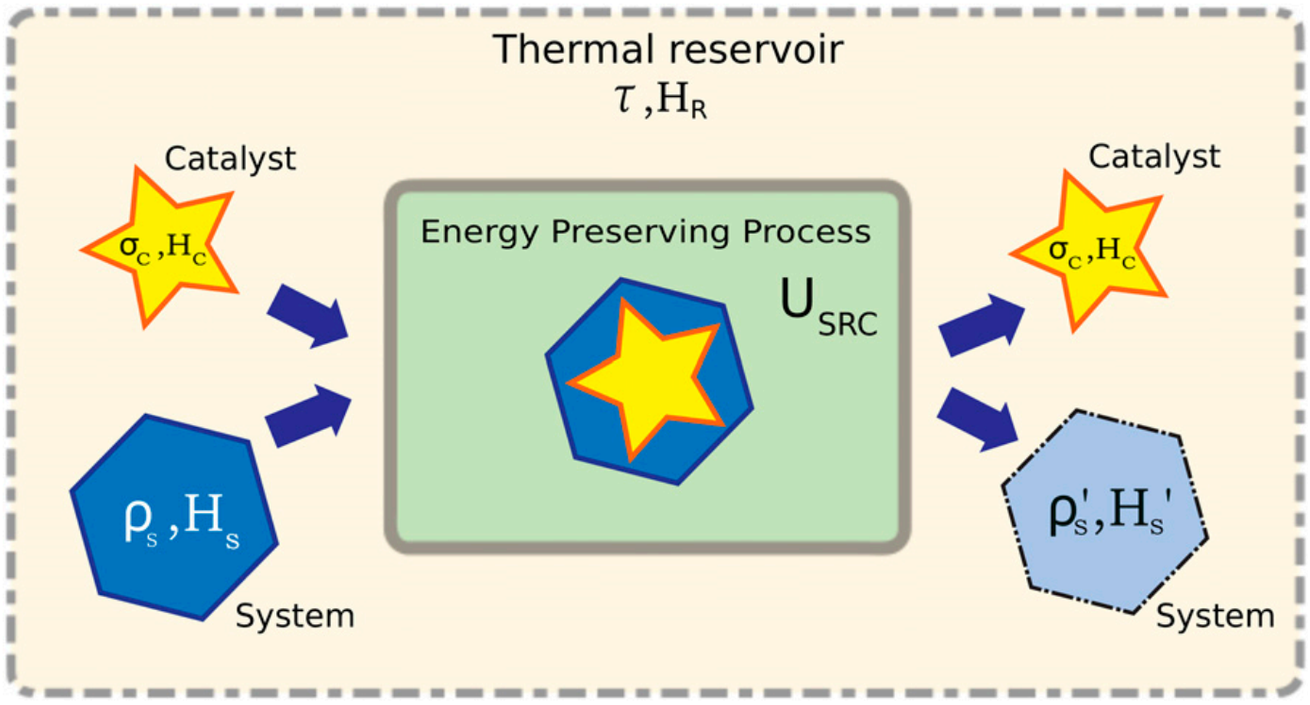


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$$[U_{SRC}, H_S + H_R + H_C] = 0$$

(energy strictly preserved).

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But other interpretations are possible, too.

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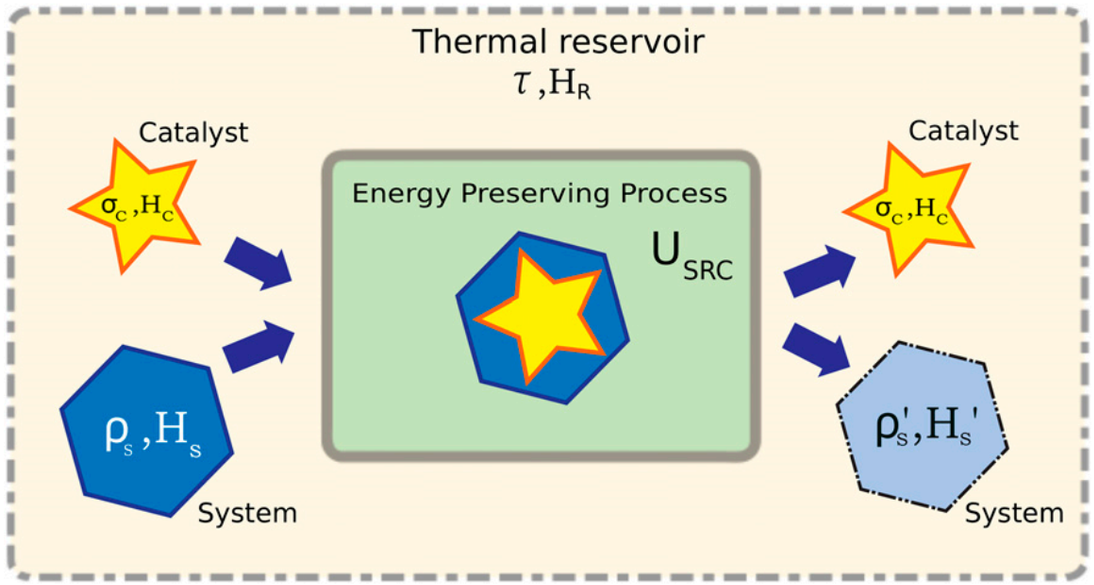

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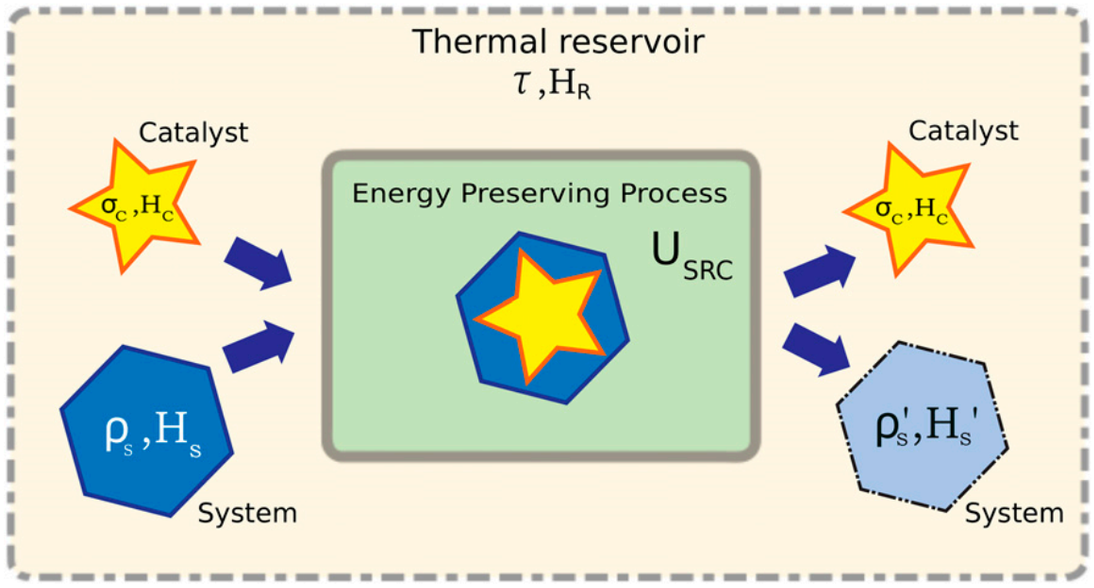


**Theorem:** For ("classical") states that are blockdiagonal in energy, $\rho \to \rho'$ is possible if and only if

$$F_\alpha(\rho) \geq F_\alpha(\rho') \text{ for all } \alpha$$

("Rényi-α-free energies").

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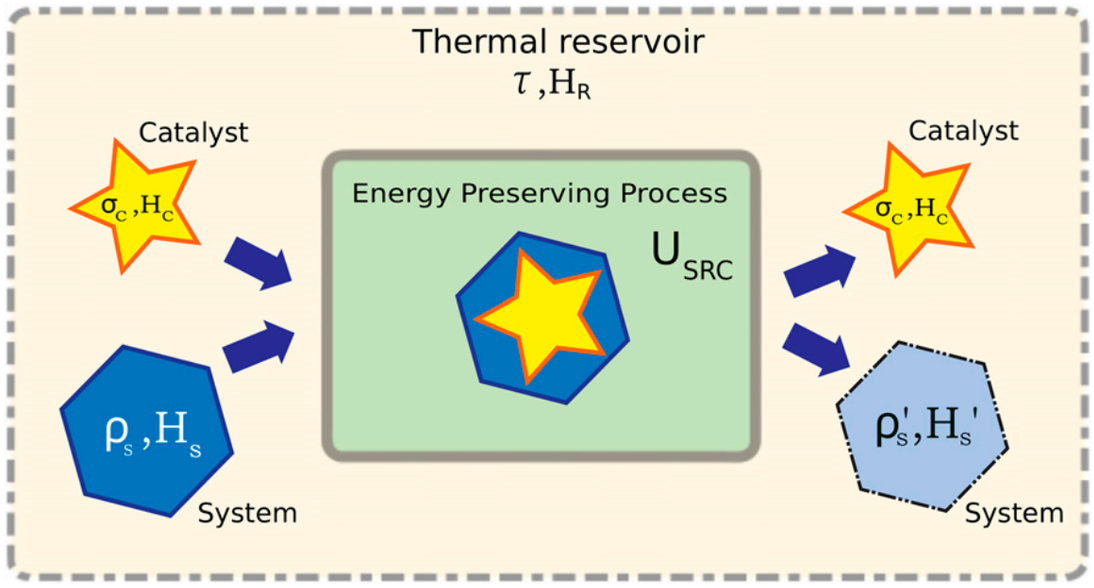


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$$F(\rho_A) \equiv F_1(\rho) = \mathrm{tr}(\rho_A H_A) - k_B T S(\rho_A),$$

$$F_\alpha(\rho) = k_B T S_\alpha(\rho \| \gamma) + F_\alpha(\gamma).$$

Rényi divergence

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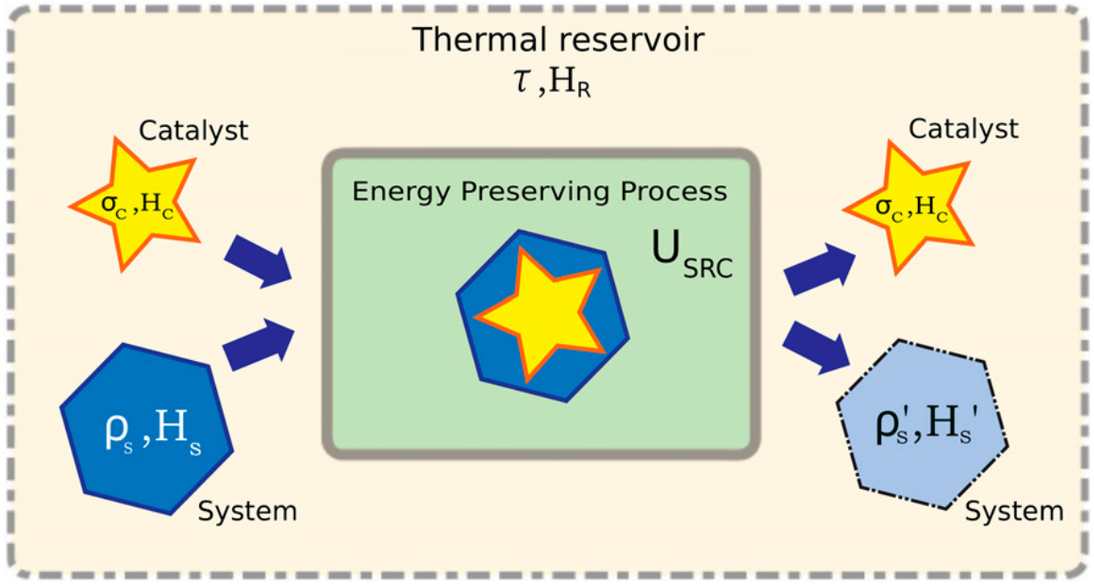


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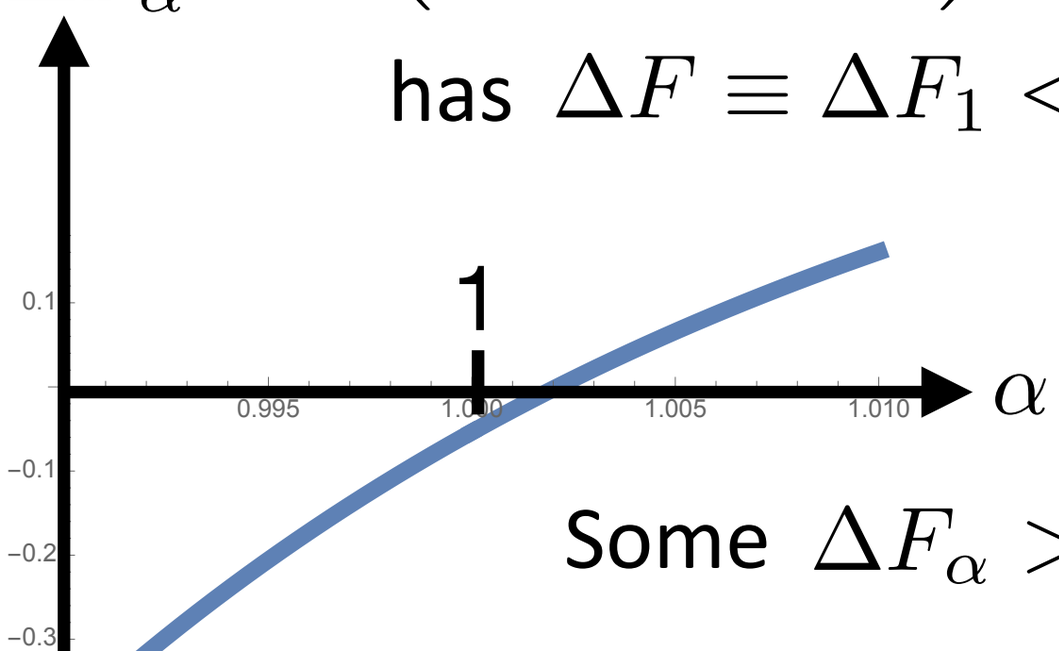
has $\Delta F \equiv \Delta F_1 < 0$ so why is this not possible?




$$\epsilon = \frac{1}{100}, \quad N = 10^{30}.$$

Some $\Delta F_\alpha > 0$, hence it **must be impossible.**

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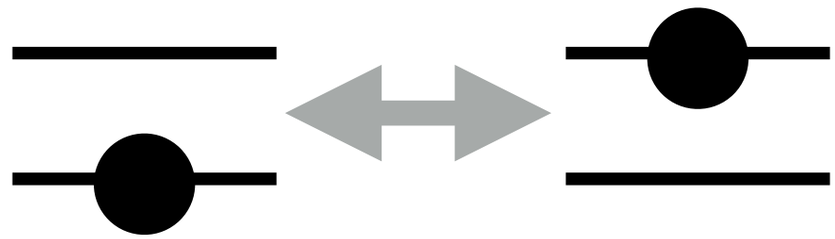

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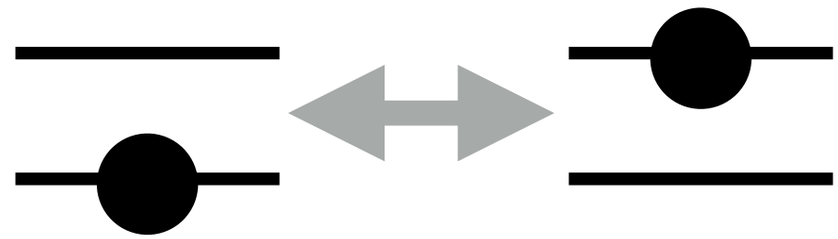

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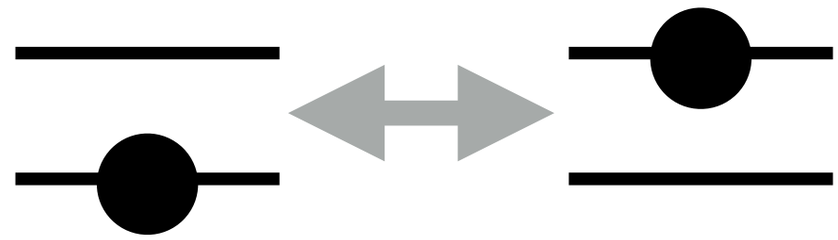

$F_0 \ll F \ll F_\infty.$ Fundamental irreversibility.

$$\lim_{n\to\infty} \frac{1}{n} F_{0/\infty}^\varepsilon(\rho^{\otimes n}) = F(\rho) \equiv \mathrm{tr}(\rho H) - k_B\, T\, S(\rho).$$

(Only) in the thermodynamic limit, (the rates of) extractable work and work cost become equal. **Emergent reversibility.**

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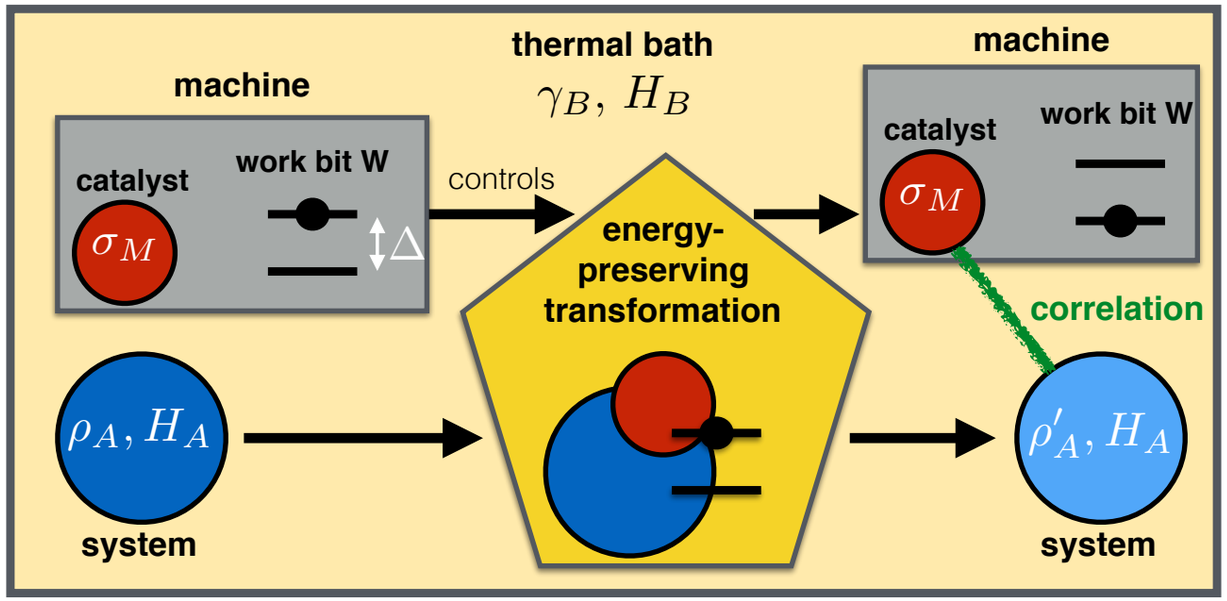


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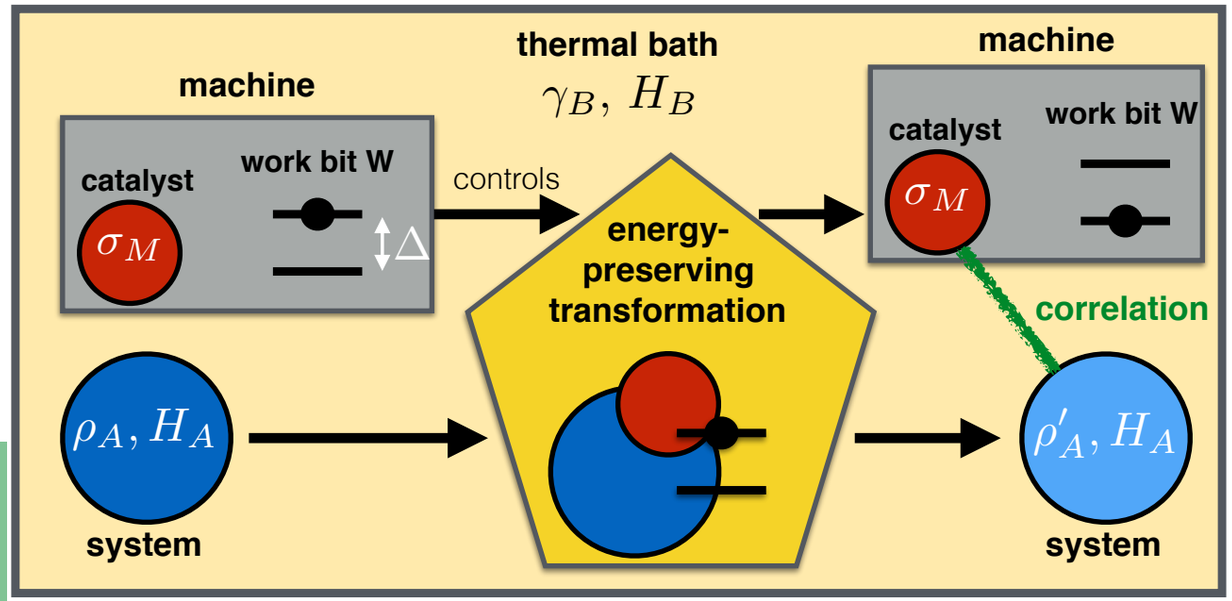


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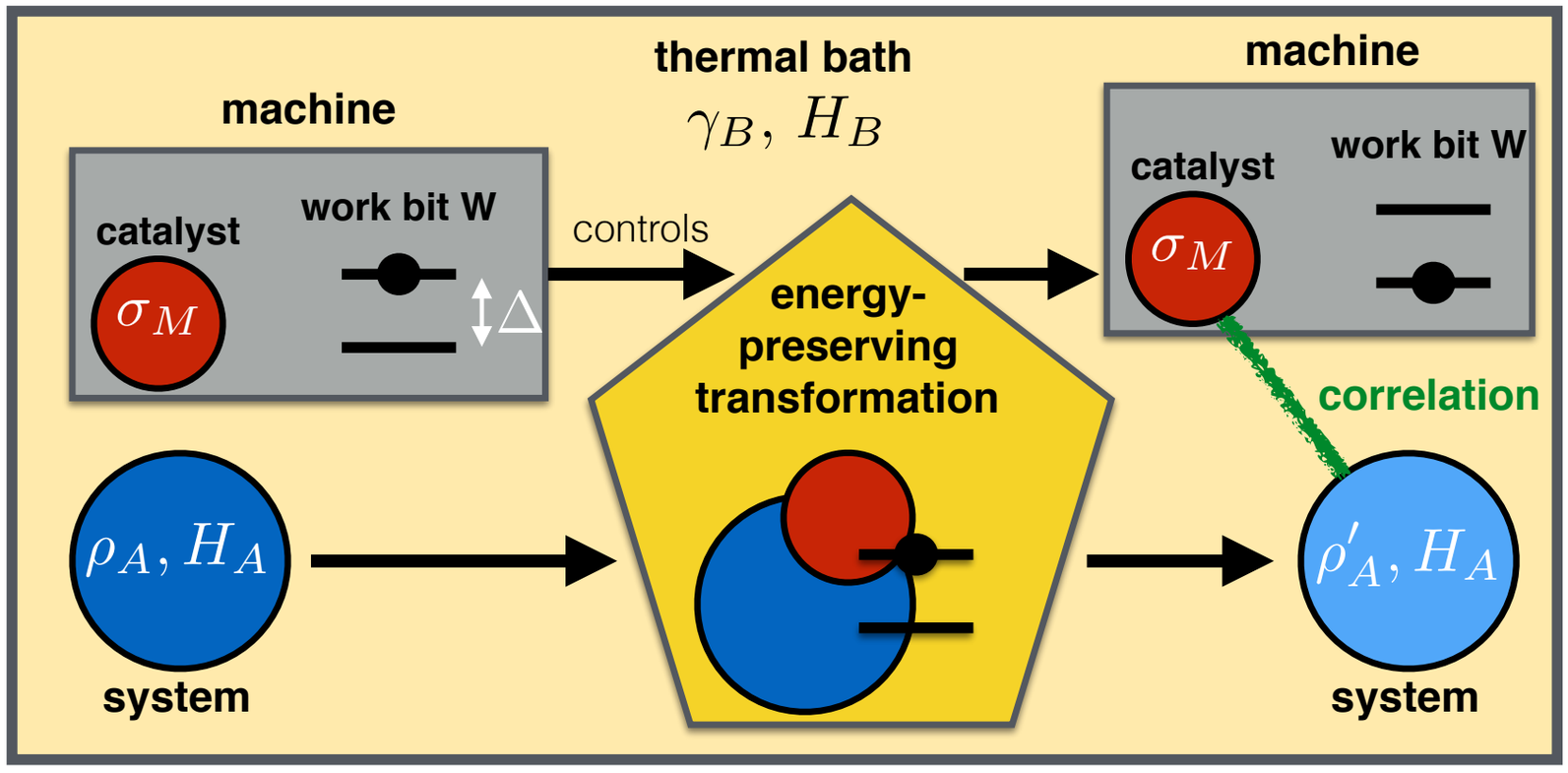


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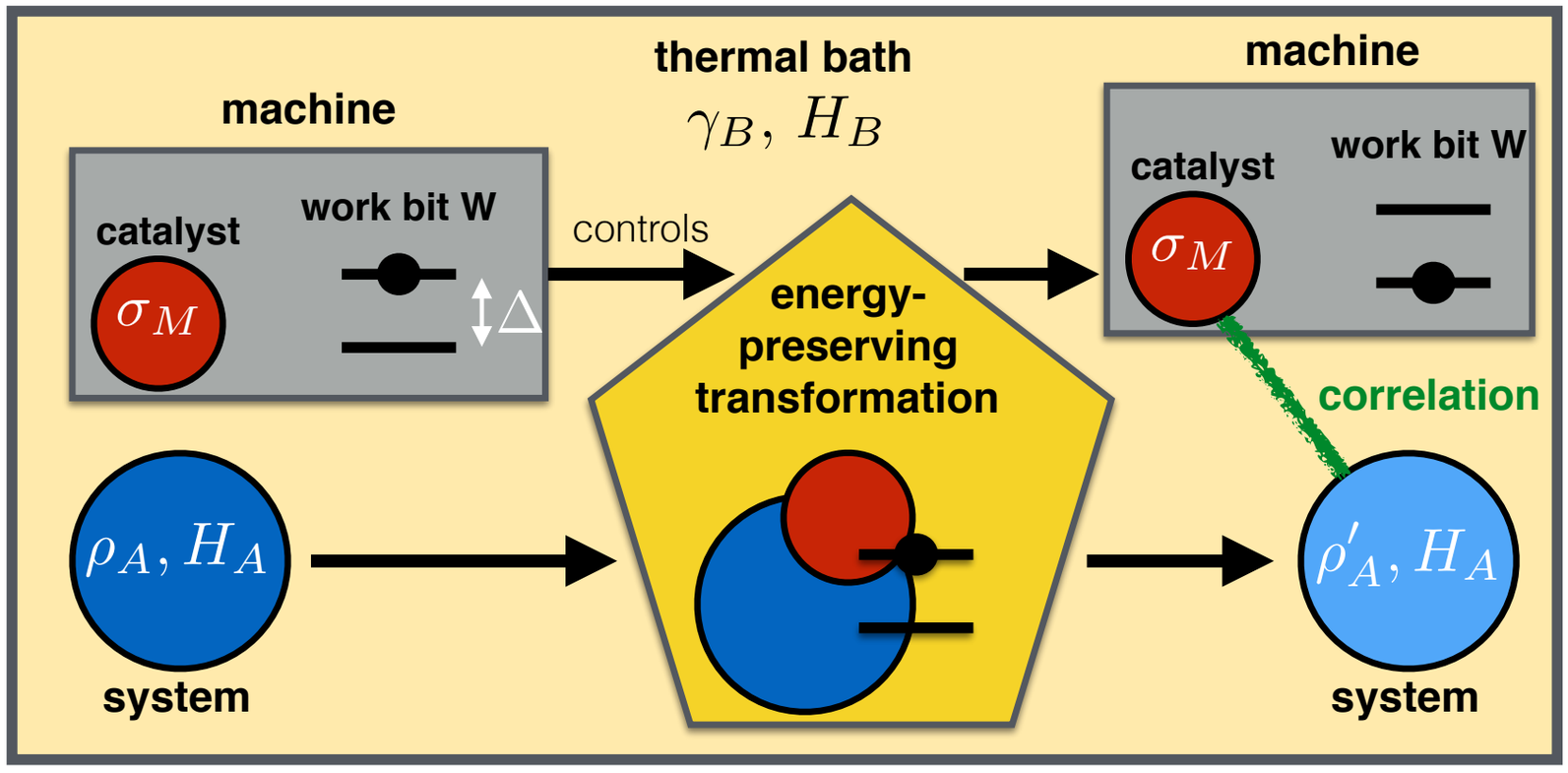


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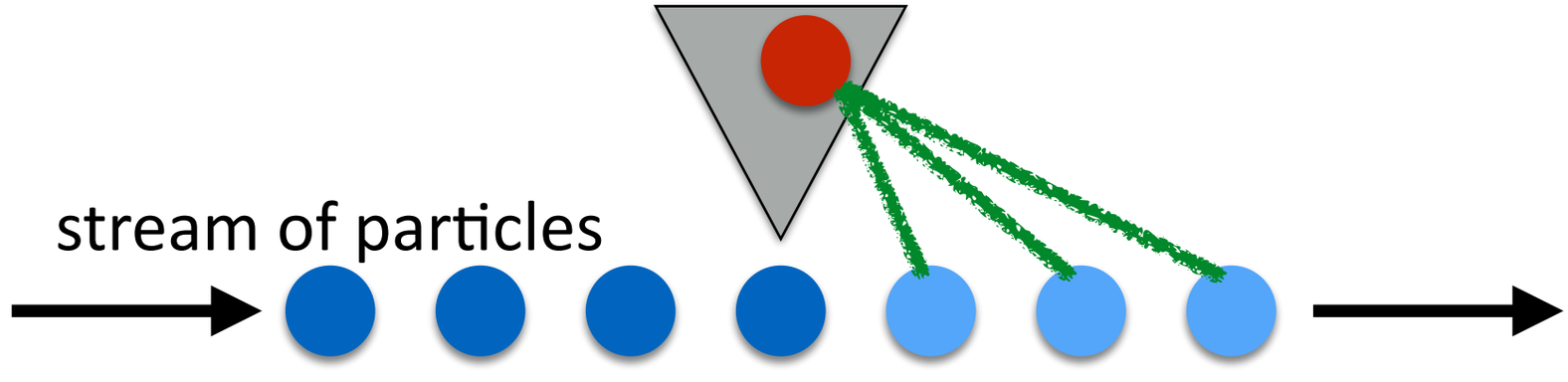
Okay for situations like these:

thermal machine,
acting on one system at a time,
**not** encountering systems again



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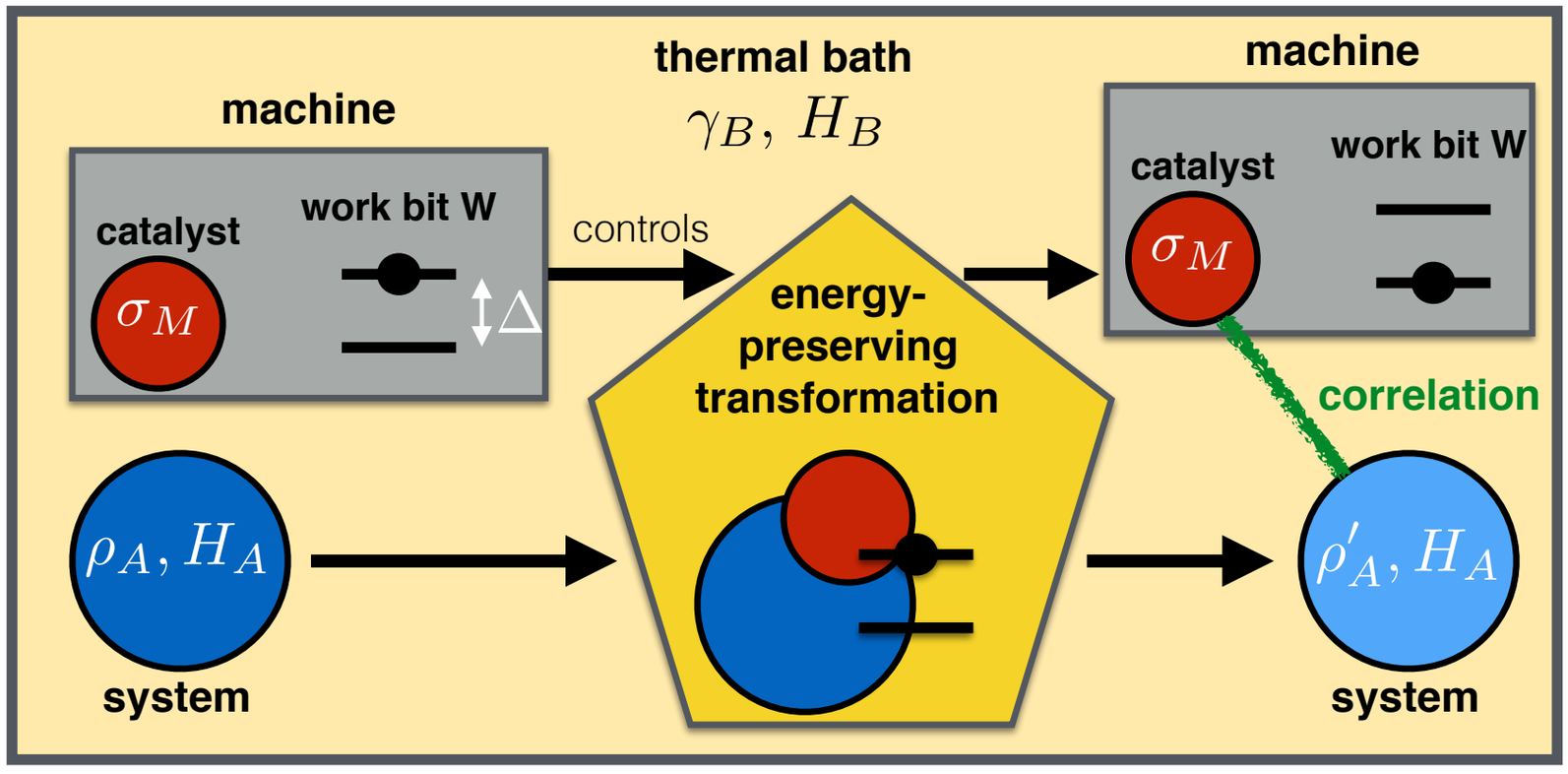


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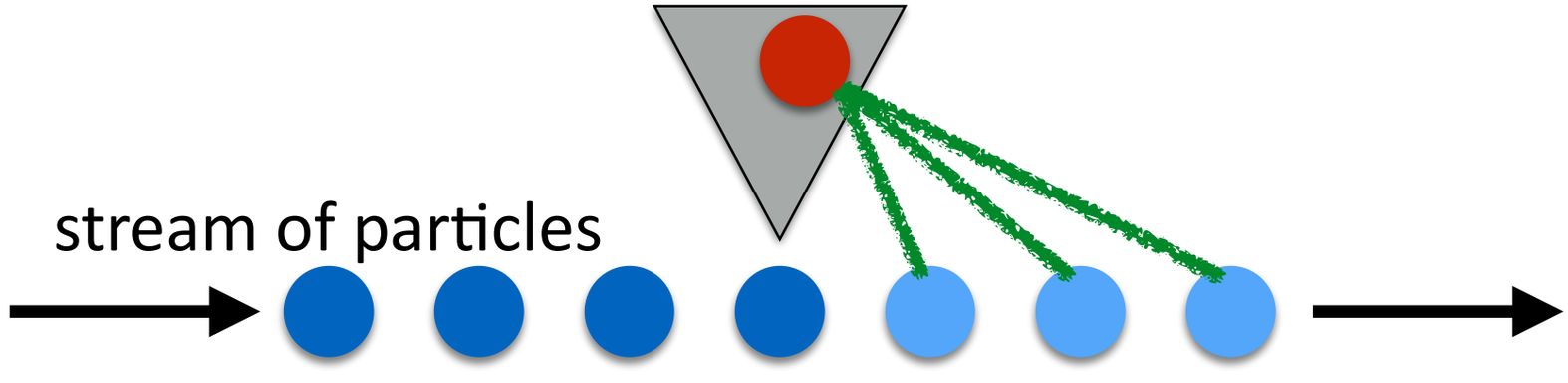


Can this help?
**Yes!**

# Creating correlations can help: **example**

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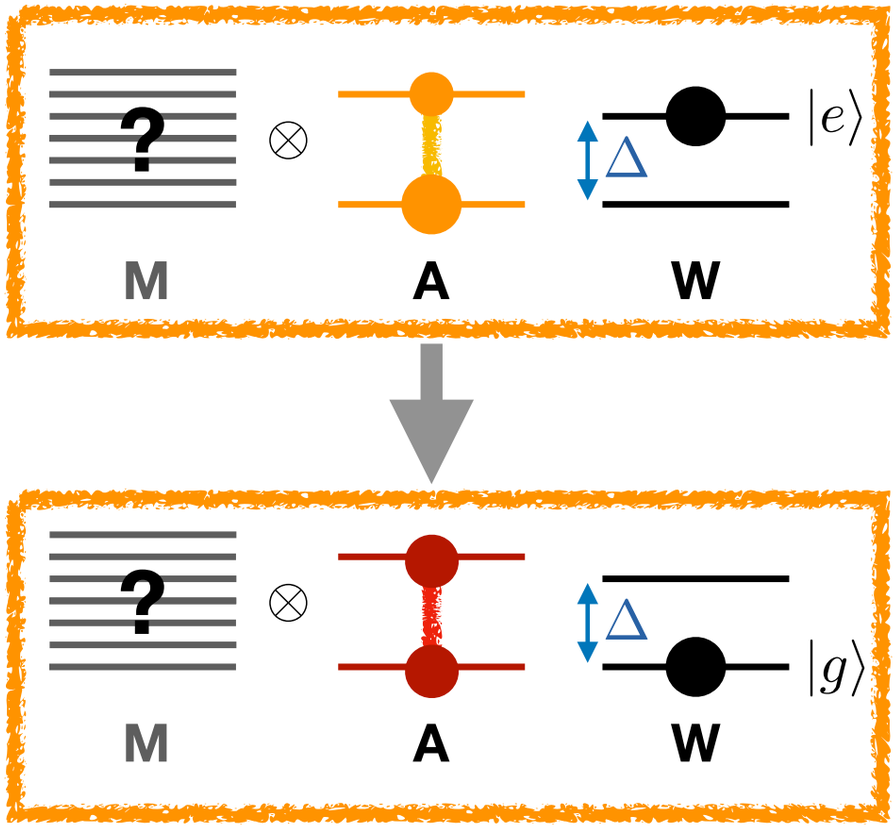

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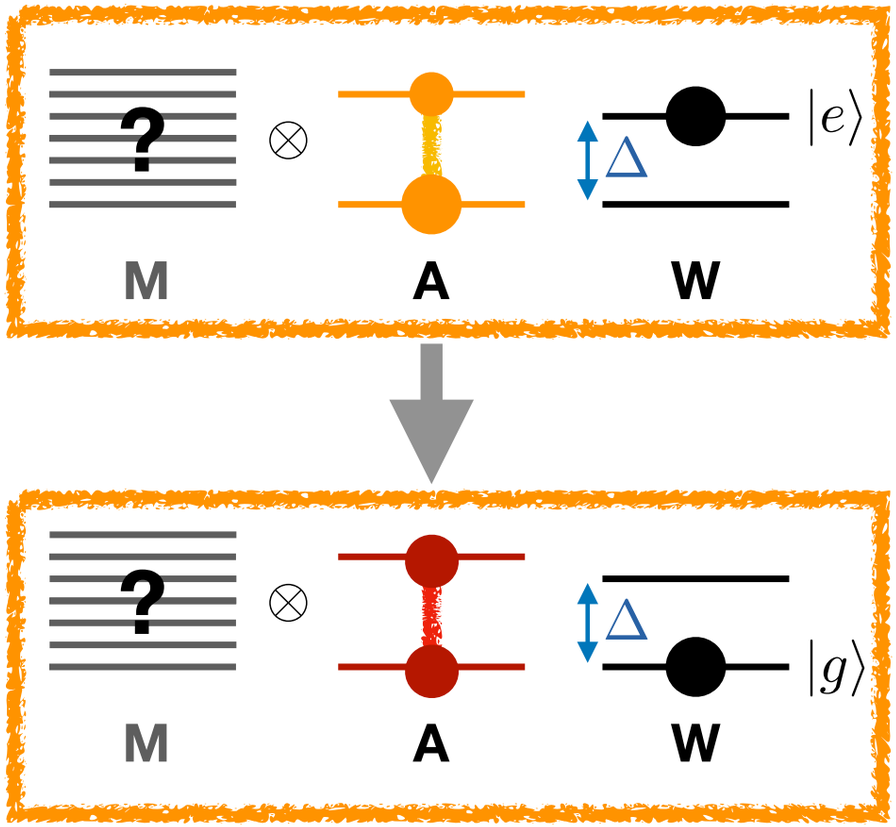


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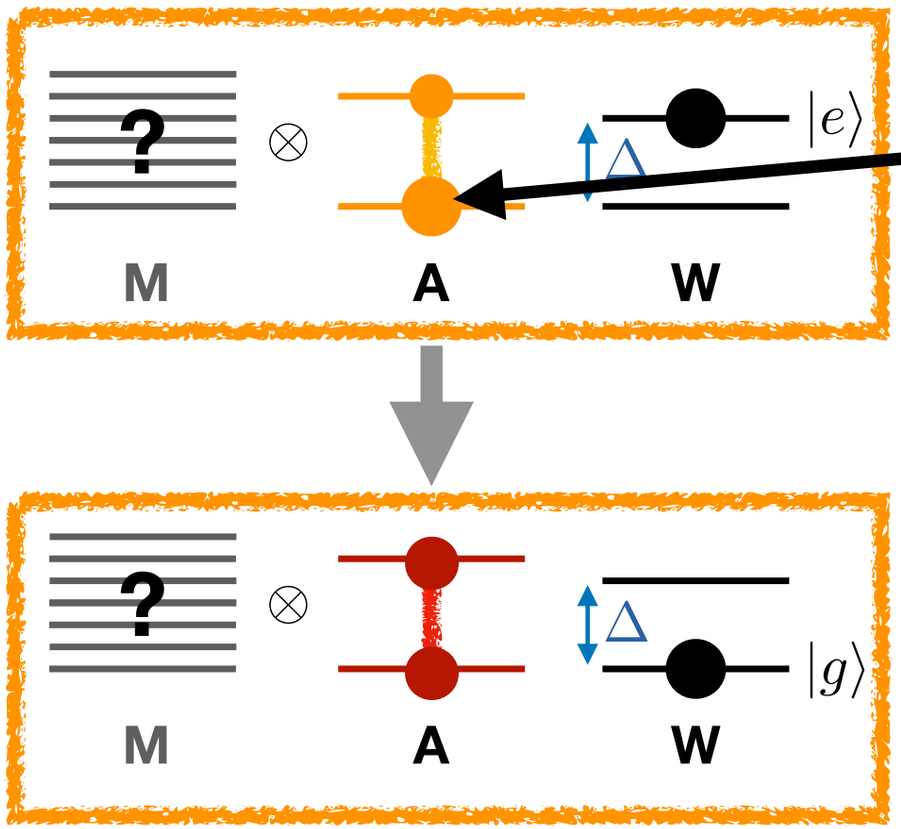


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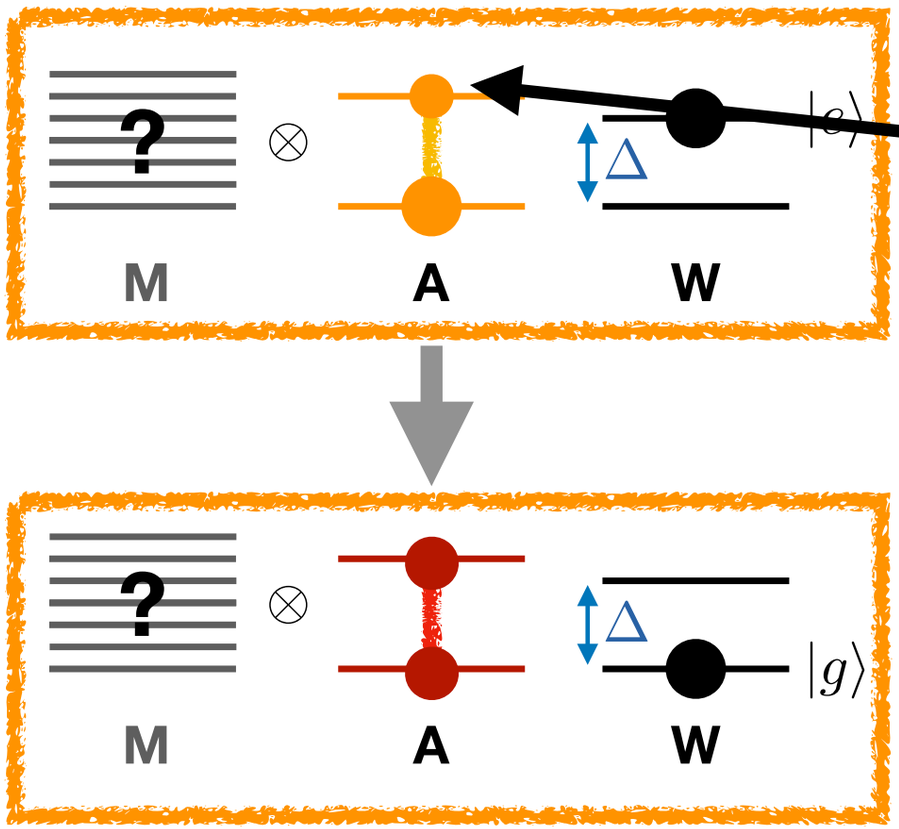


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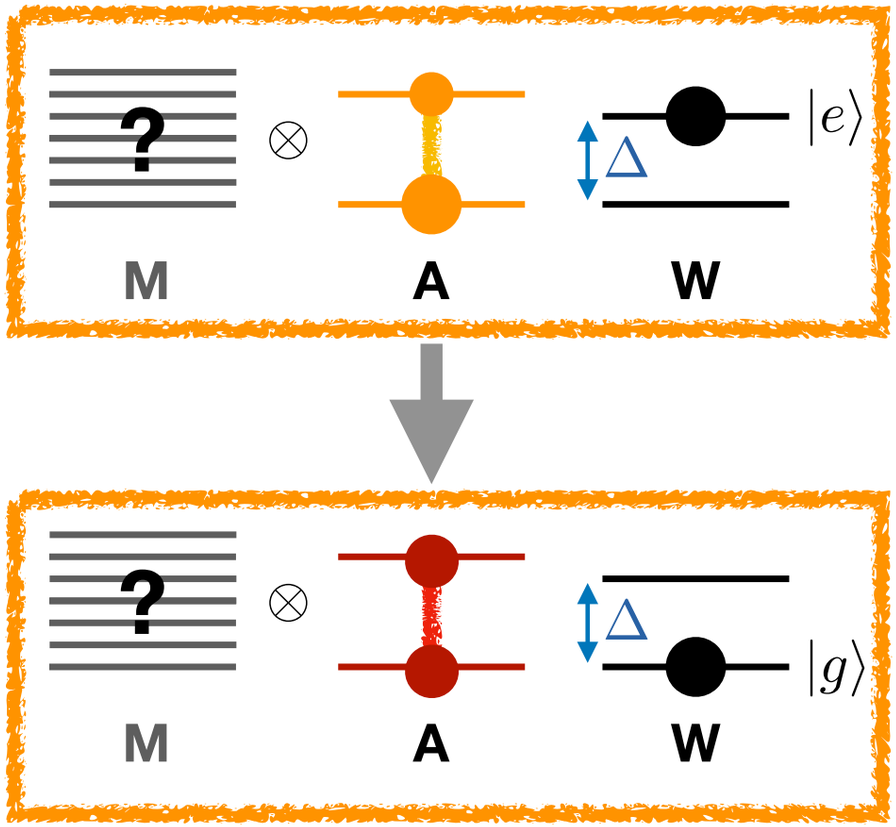


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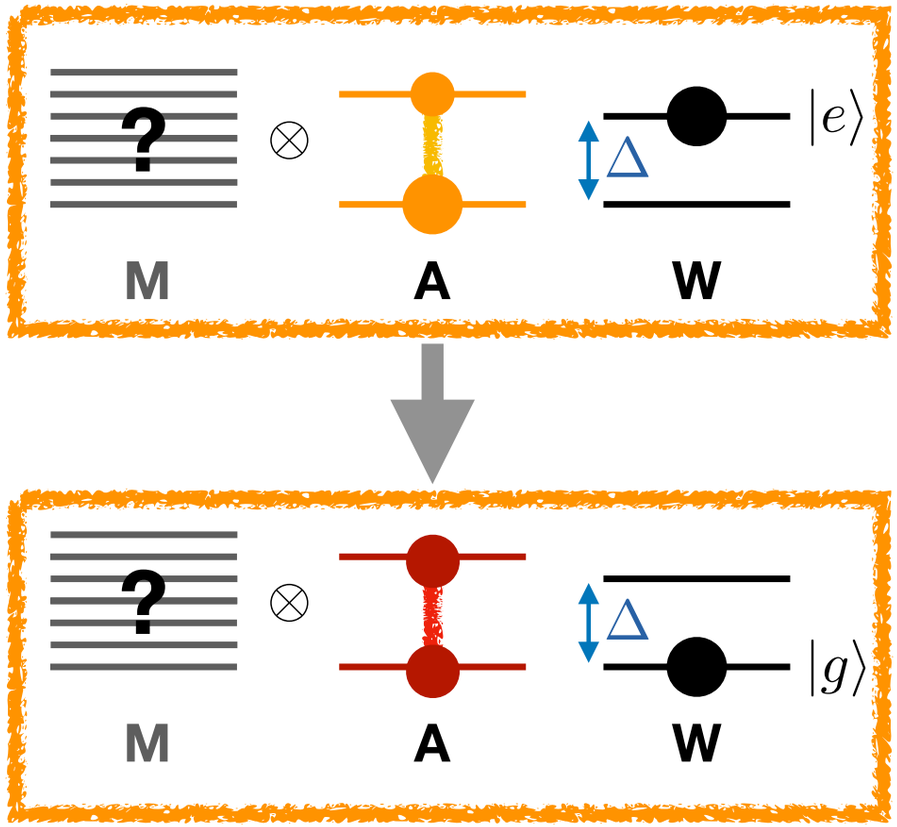


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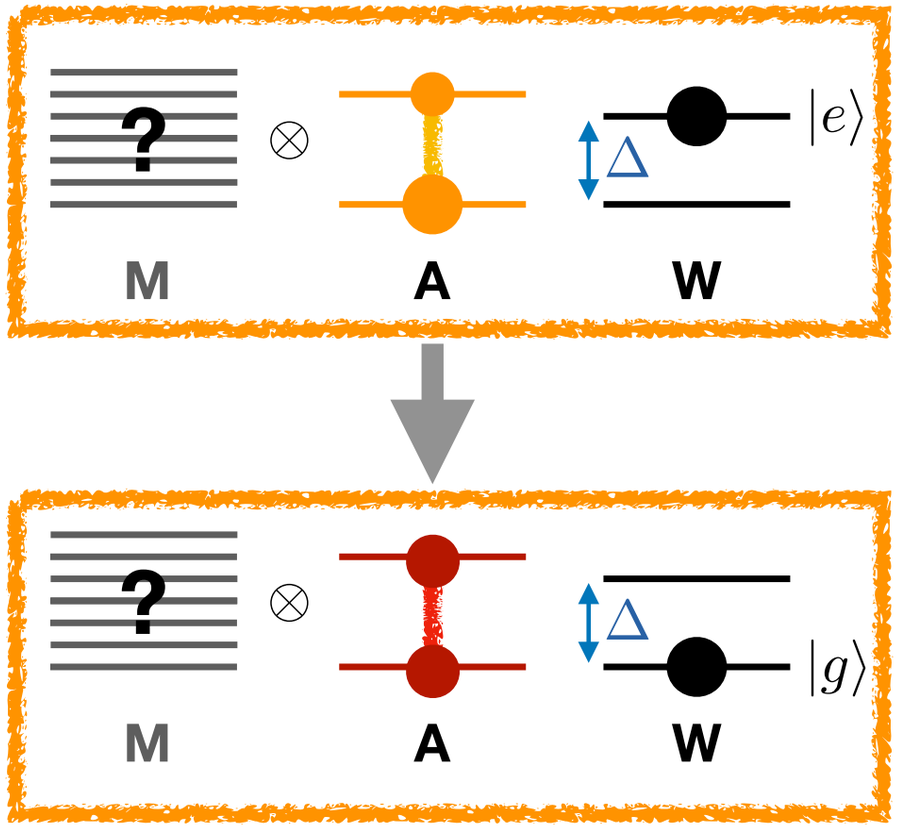


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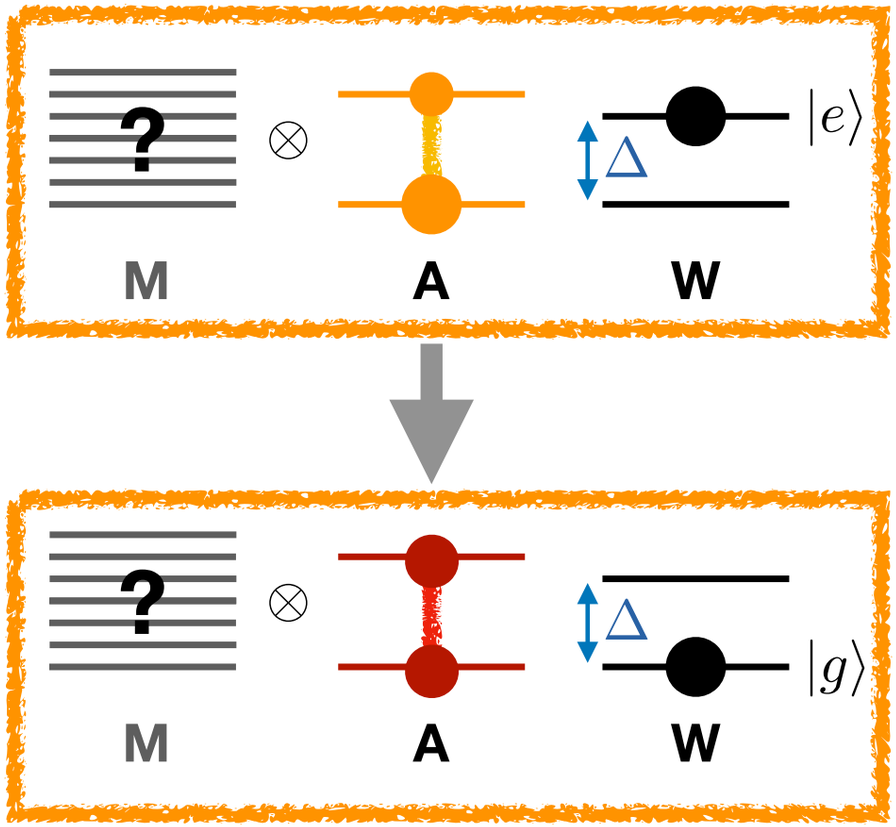


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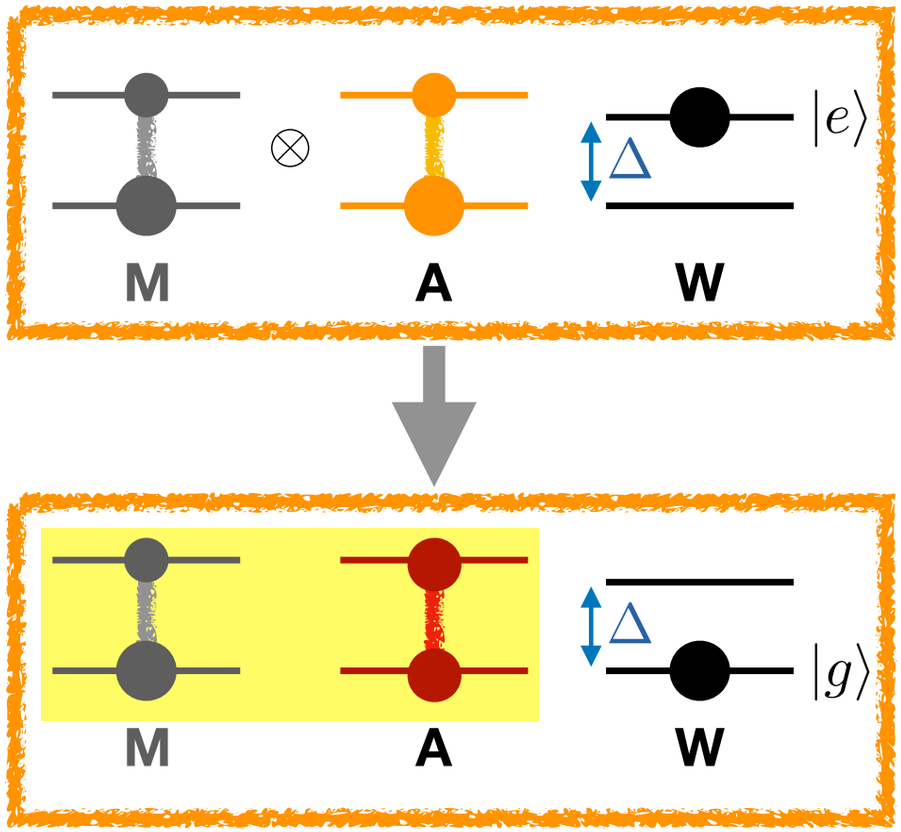


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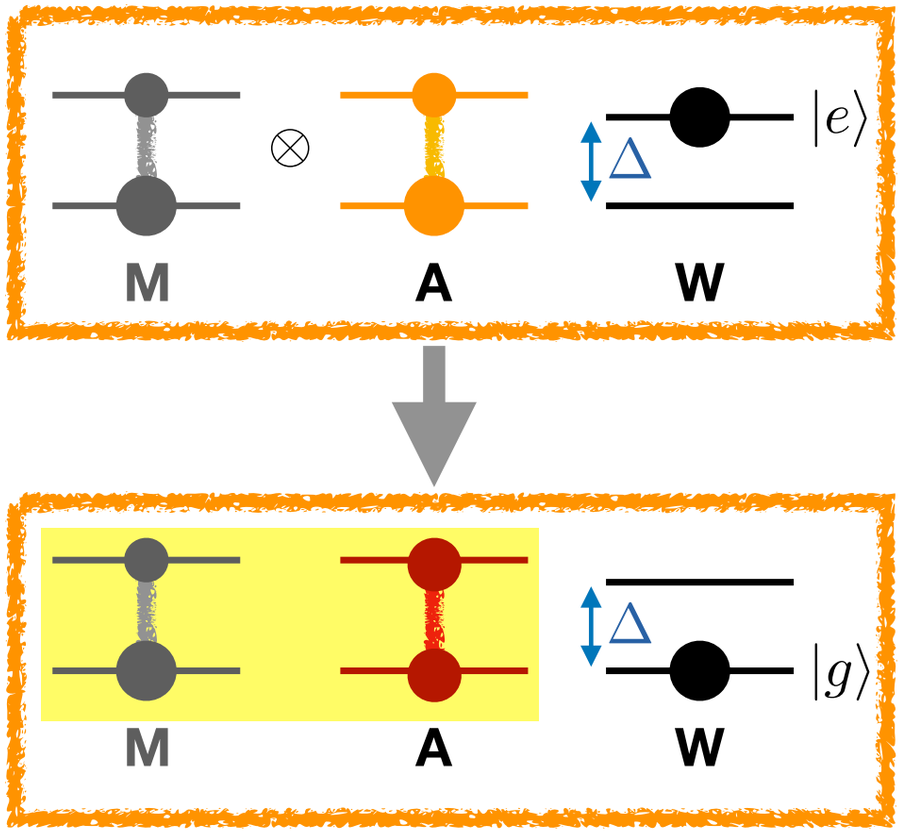


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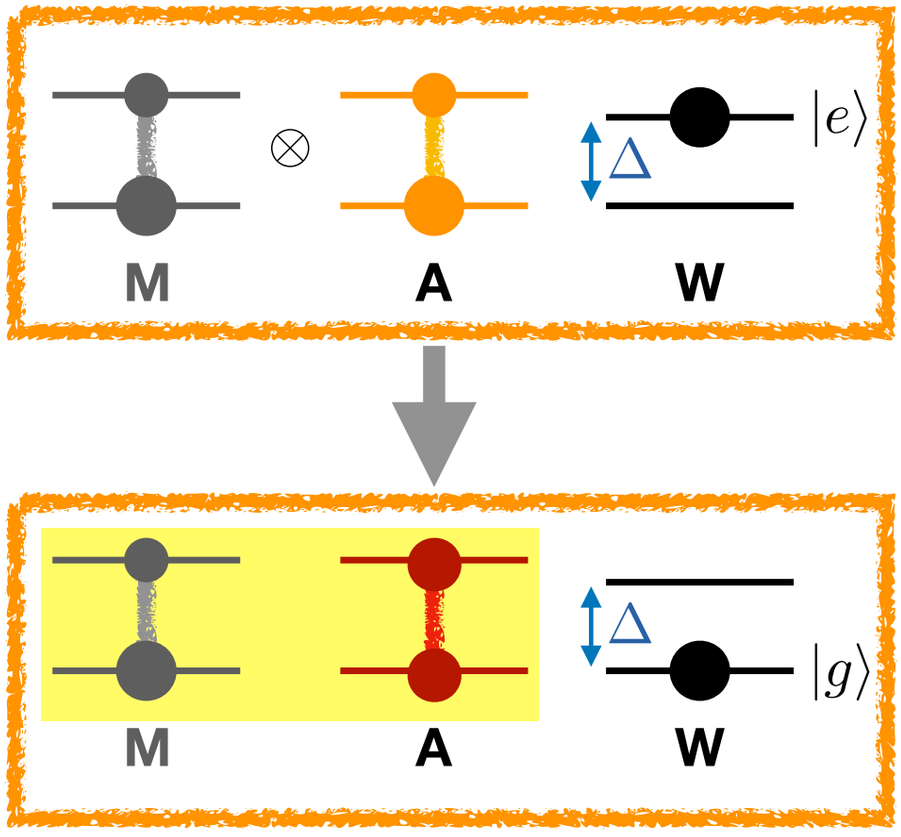


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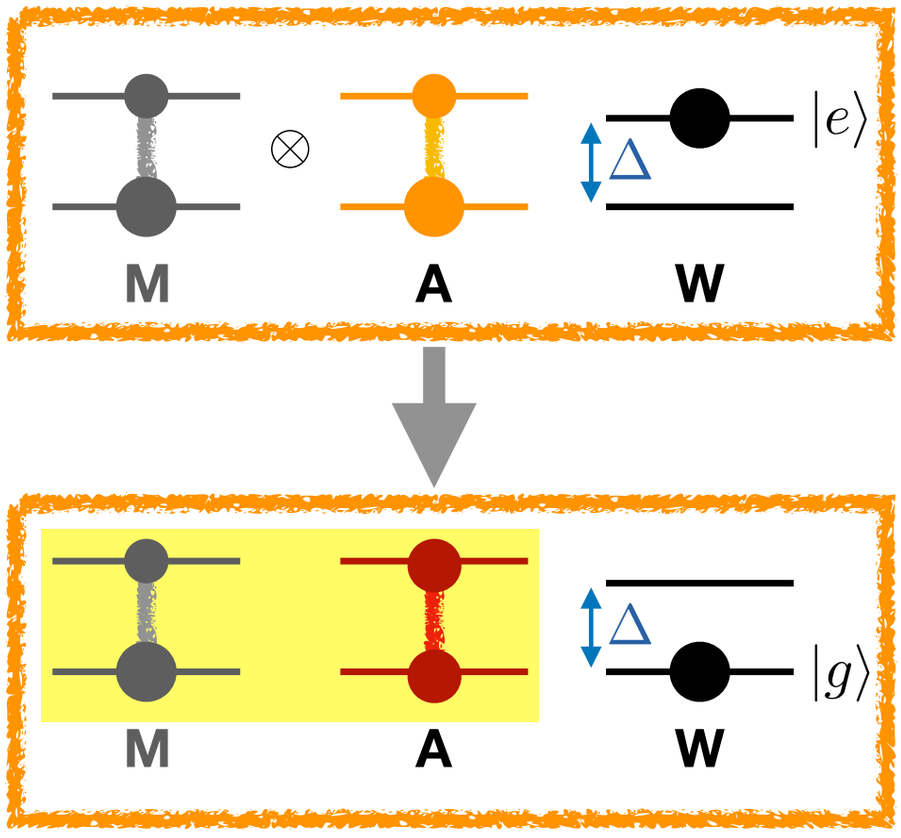


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Turns out: there is a thermal operation that achieves this transition, and it only needs $\Delta \geq .26 k_B T$ (before it was $.4 k_B T$ ).

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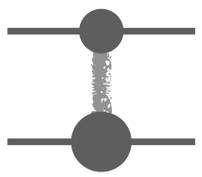


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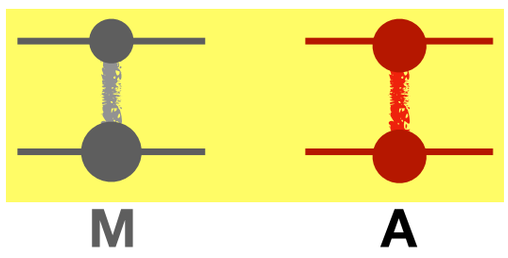


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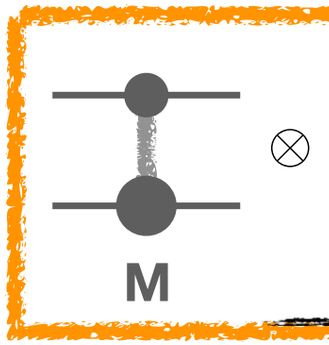


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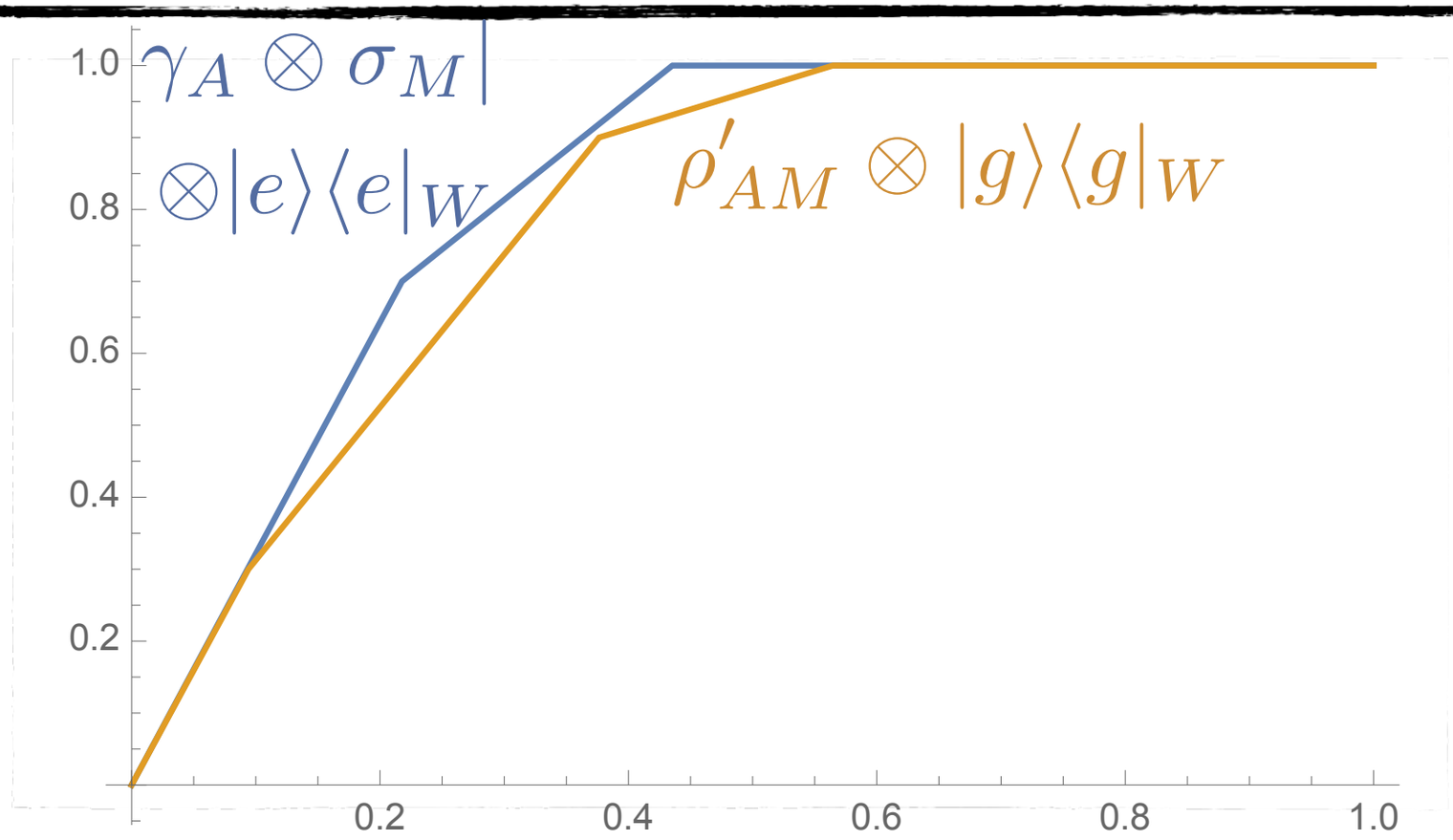


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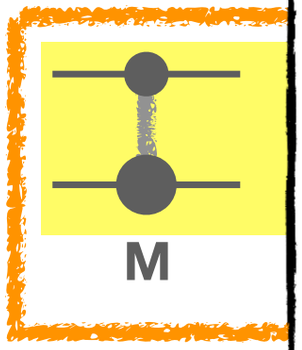


**Q:** Given arbitrary (larger) catalysts *M*, how far can we go?

**A:** Down to $\Delta F = .06 k_B T$, but not further!

$M$

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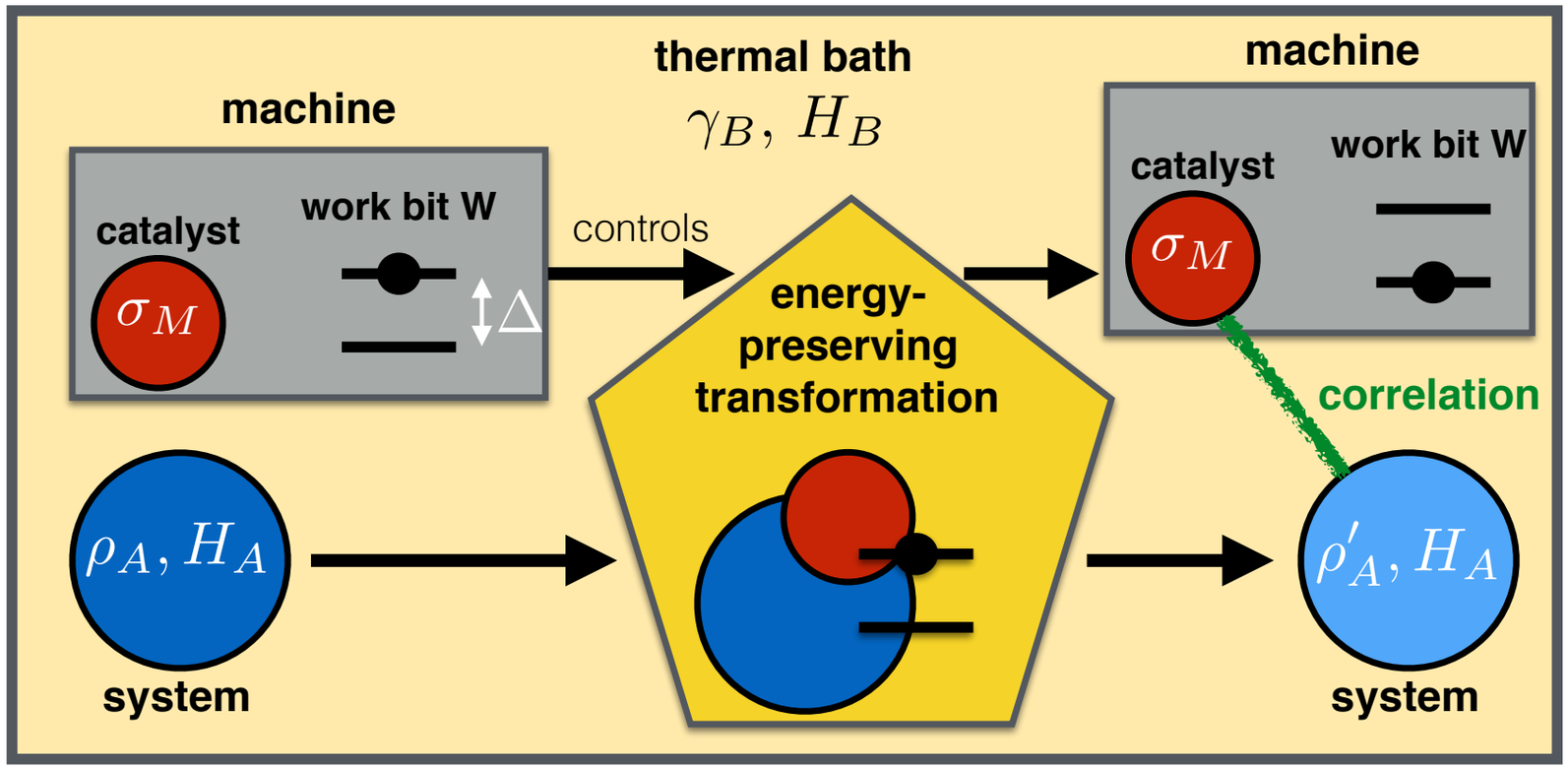


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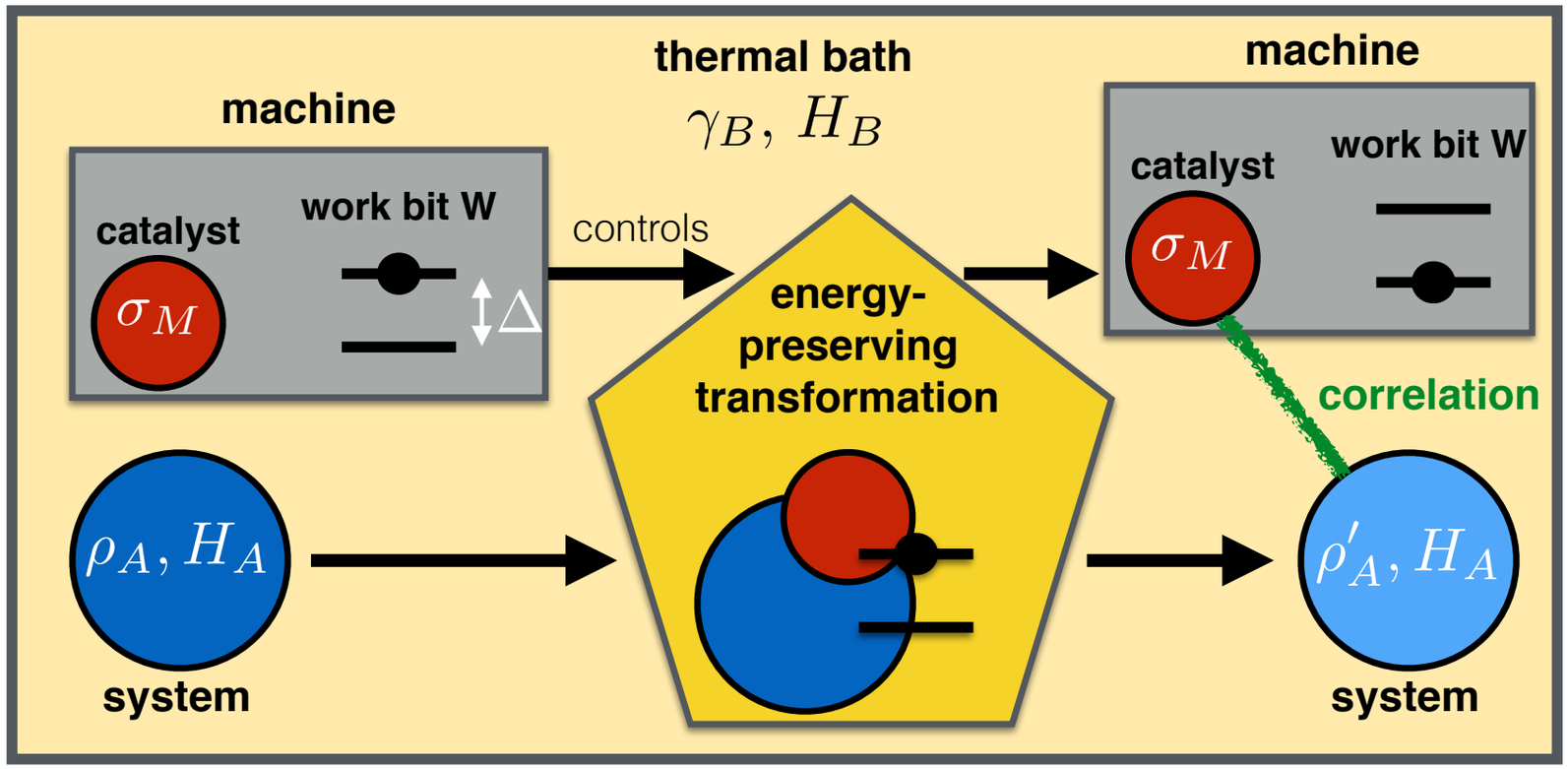


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**Theorem:** If the desired final state is block-diagonal in energy, then $\rho \to \rho'$ is possible (without the work bit) if and only if

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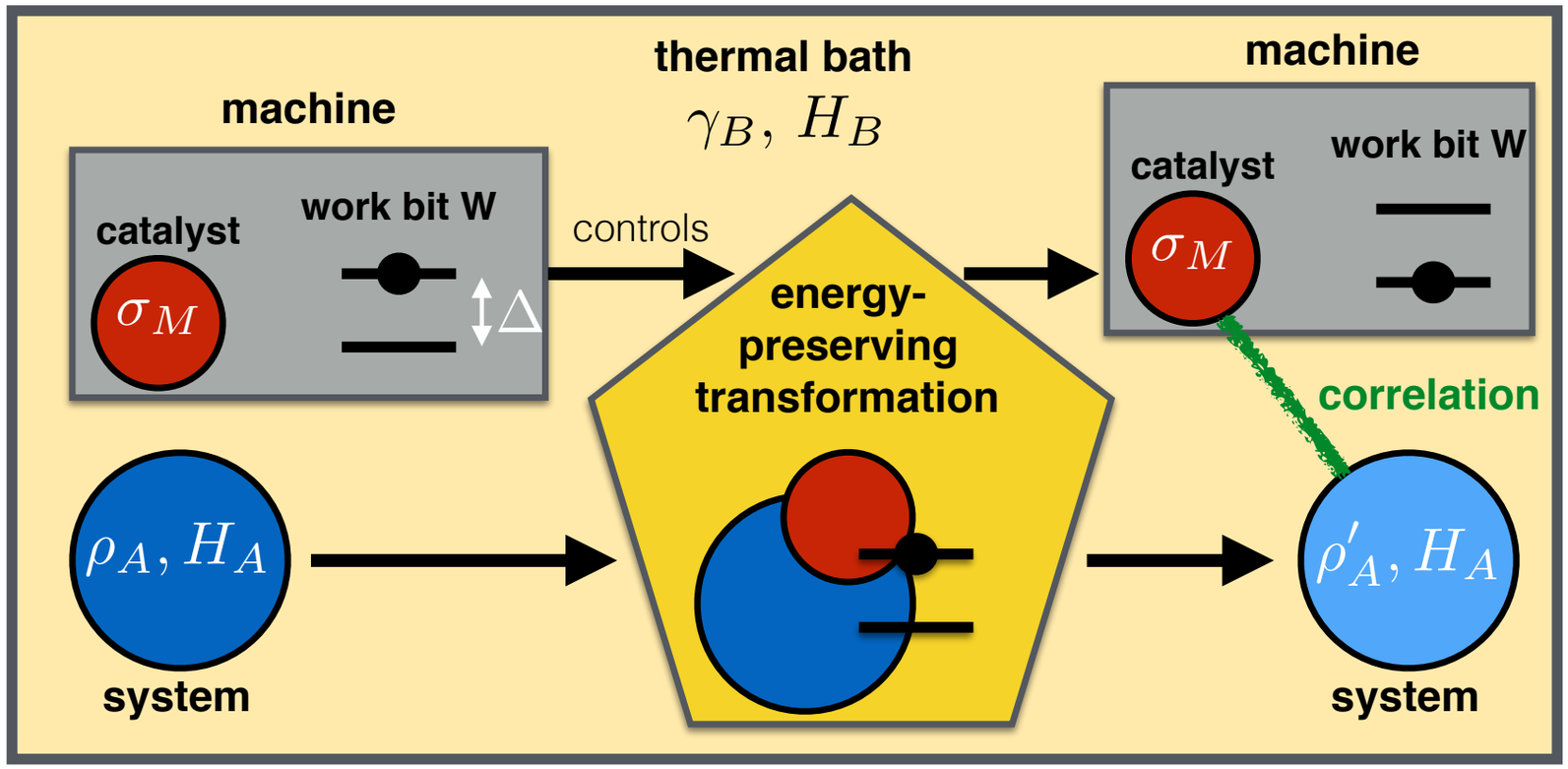


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With work bit W: The **work cost** is exactly $\Delta F = F(\rho') - F(\rho)$, resp. we can extract work arbitrarily close to $|\Delta F|$.

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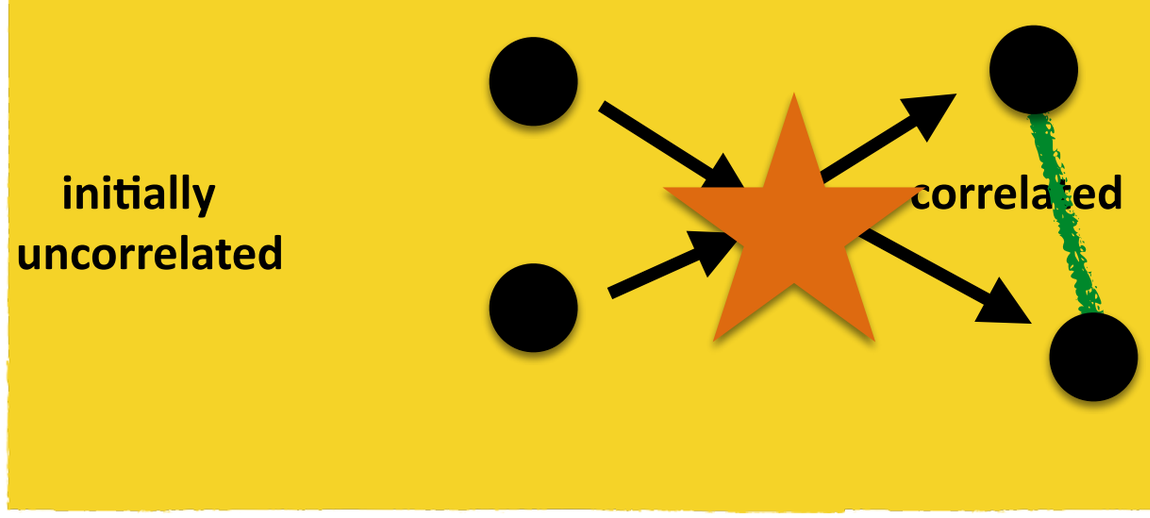


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Exact characterization of the Helmholtz free energy *F* without thermodynamic limit or averaging.

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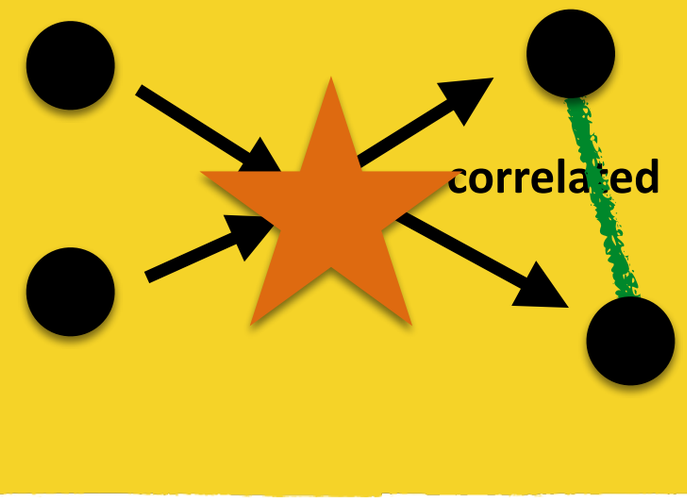


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**Question:** what happens in the case of **coherence** between the energy levels?

Exact

without thermodynamic limit or averaging.

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if and only if $H_0(p) \leq H_0(p')$ and $H(p) < H(p')$. Moreover, for every $\varepsilon > 0$, we can choose $Y$ and $p'_{XY}$ such that the mutual information is $I(X:Y) \equiv S(p'_{XY} \| p'_X \otimes p'_Y) < \varepsilon$.

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**Majorization:** prob. vectors $p = (p_1, \ldots, p_n), \;\; q = (q_1, \ldots, q_n)$

$$p \succ q \;\; \Leftrightarrow \;\; \sum_{i=1}^{k} p_i^{\downarrow} \geq \sum_{i=1}^{k} q_i^{\downarrow} \qquad (k = 1, \ldots, n).$$

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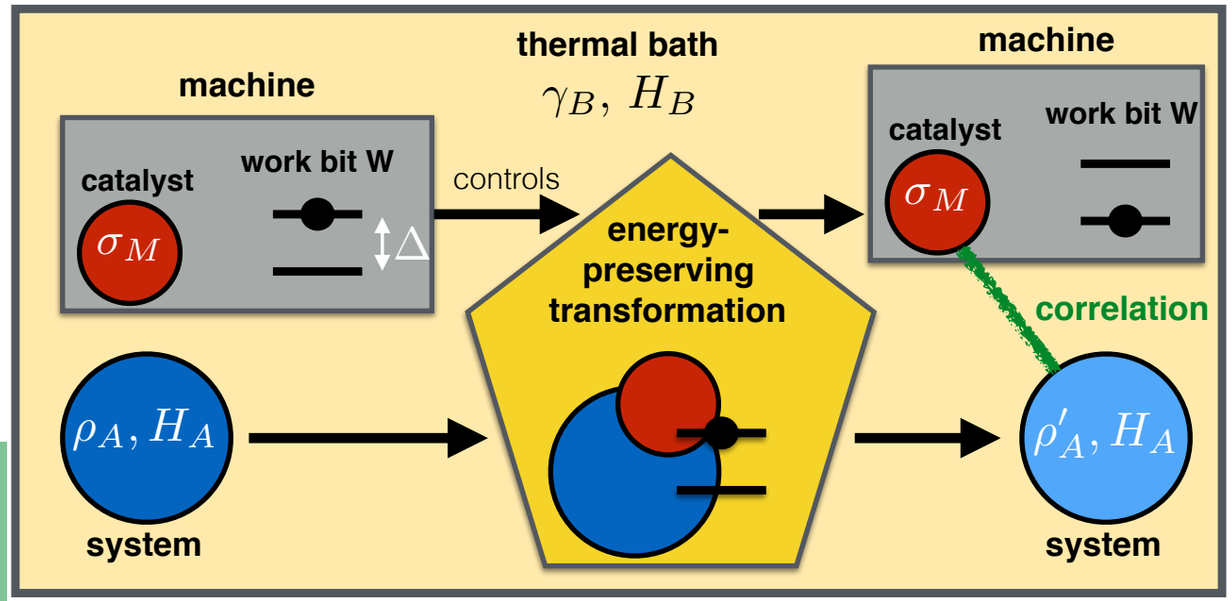
1. Standard view: thermodynamic limit

2. Thermodynamics as a resource theory

3. Characterization of *F* and *S* without thermodynamic limit




4. How about coherence? A no-broadcasting theorem

5. Consequences for quantum information theory

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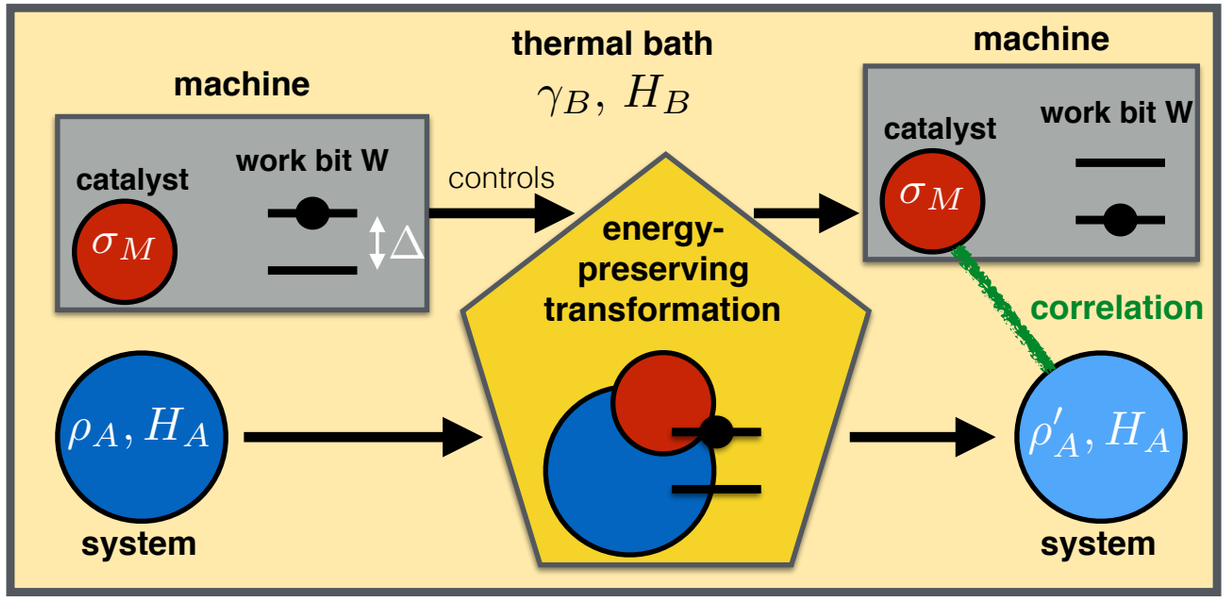


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## What if we have coherence between energy levels?

**Theorem.** Let $\rho_A, \rho'_A$ be block-diagonal states. Then, for every $\varepsilon > 0$, there is a thermal operation $\mathcal{T}_\varepsilon$, a state $\rho'_A(\varepsilon)$ with $\|\rho'_A - \rho'_A(\varepsilon)\| < \varepsilon$ and a finite-dimensional catalyst $\sigma_C$ such that

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Note that thermal operations are **time-translation-symmetric**:

$\mathcal{T}_\varepsilon(\mathcal{U}_t(\rho_{AC})) = \mathcal{U}_t(\mathcal{T}_\varepsilon(\rho_{AC}))$, where $\mathcal{U}_t = e^{-itH} \bullet e^{itH}$.

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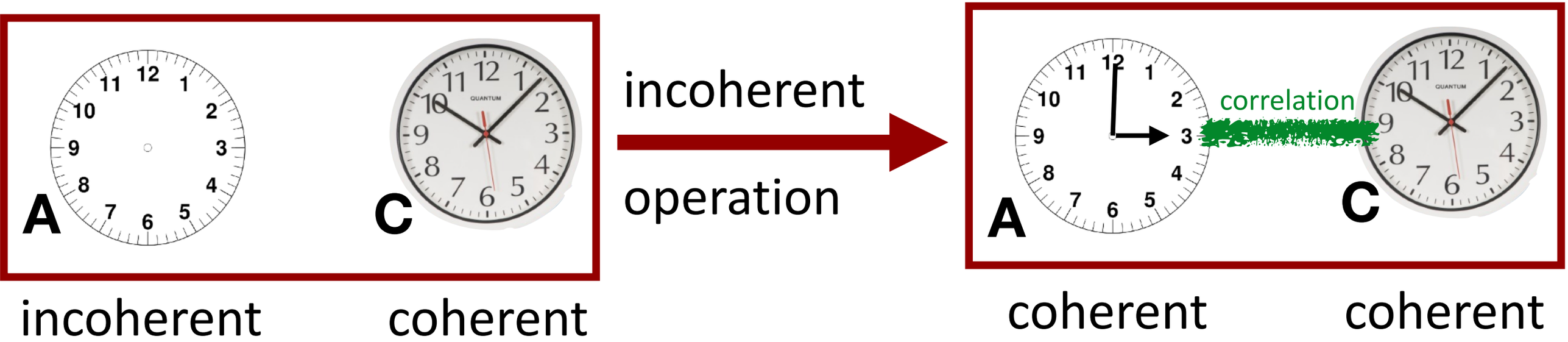

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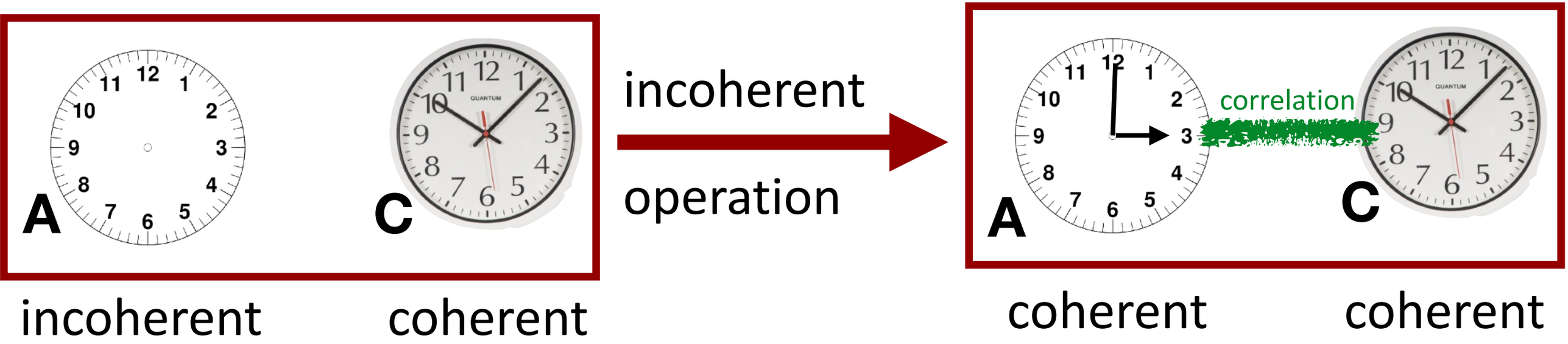


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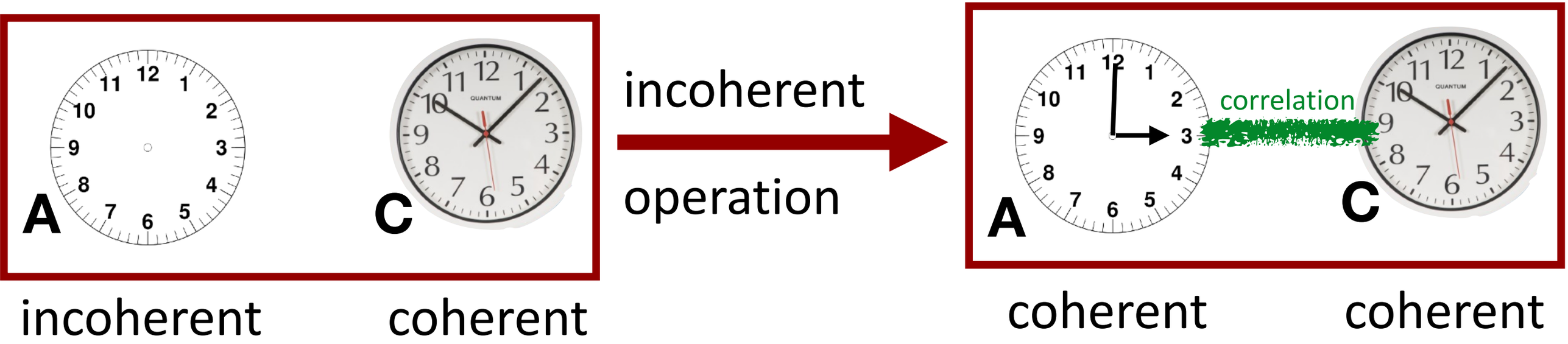


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**C** identical to before.

**Consequence:** The characterization of *F* that I've presented cannot remain valid in the presence of coherences between energy levels. 😕

incohere oherent

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PRL **113,** 150402 (2014) PHYSICAL REVIEW LETTERS week ending 10 OCTOBER 2014

## Catalytic Coherence

Johan Åberg*
*Institute for Physics, University of Freiburg, Hermann-Herder-Strasse 3, D-79104 Freiburg, Germany*
(Received 10 December 2013; revised manuscript received 30 July 2014; published 7 October 2014)

Because of conservation of energy we cannot directly turn a quantum system with a definite energy into a superposition of different energies. However, if we have access to an additional resource in terms of a system with a high degree of coherence, as for standard models of laser light, we can overcome this

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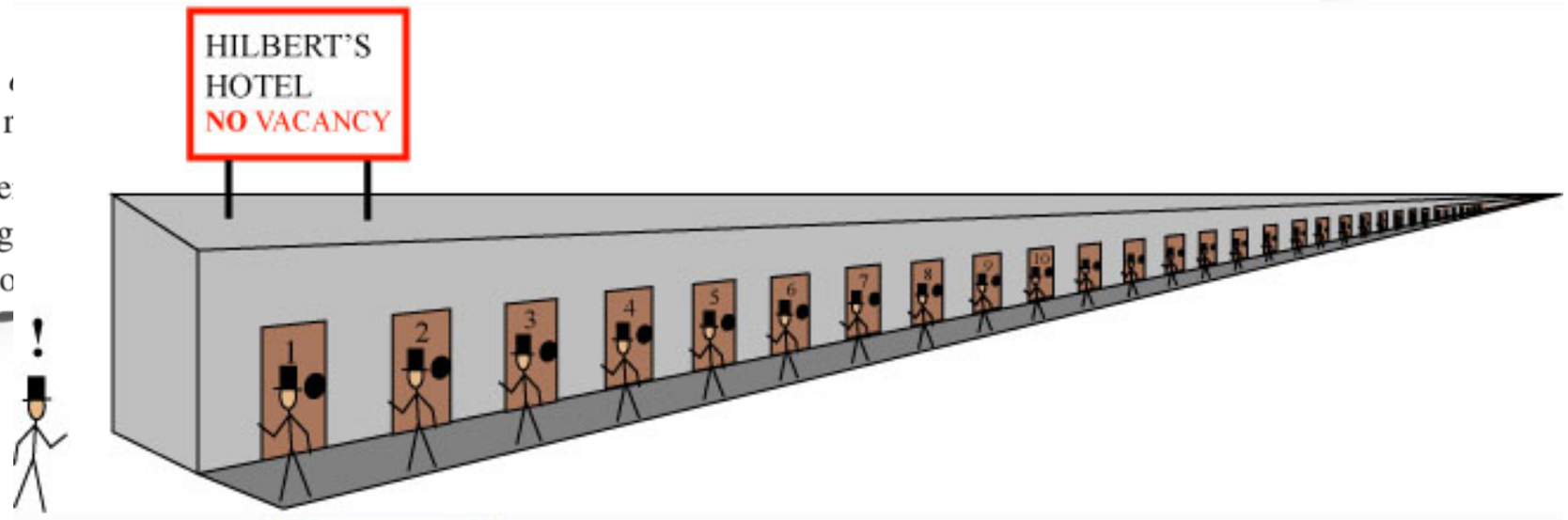


However, we showed that even this weak version is **impossible** for finite-dimensional catalysts.

# Overview

1. Standard view: thermodynamic limit

2. Thermodynamics as a resource theory

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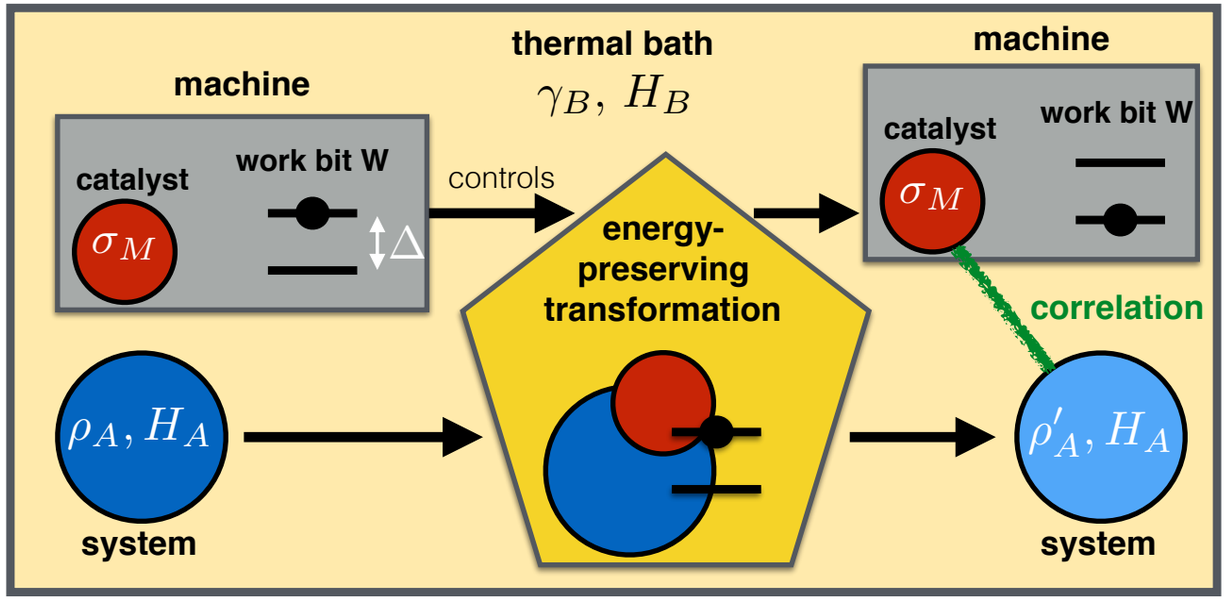


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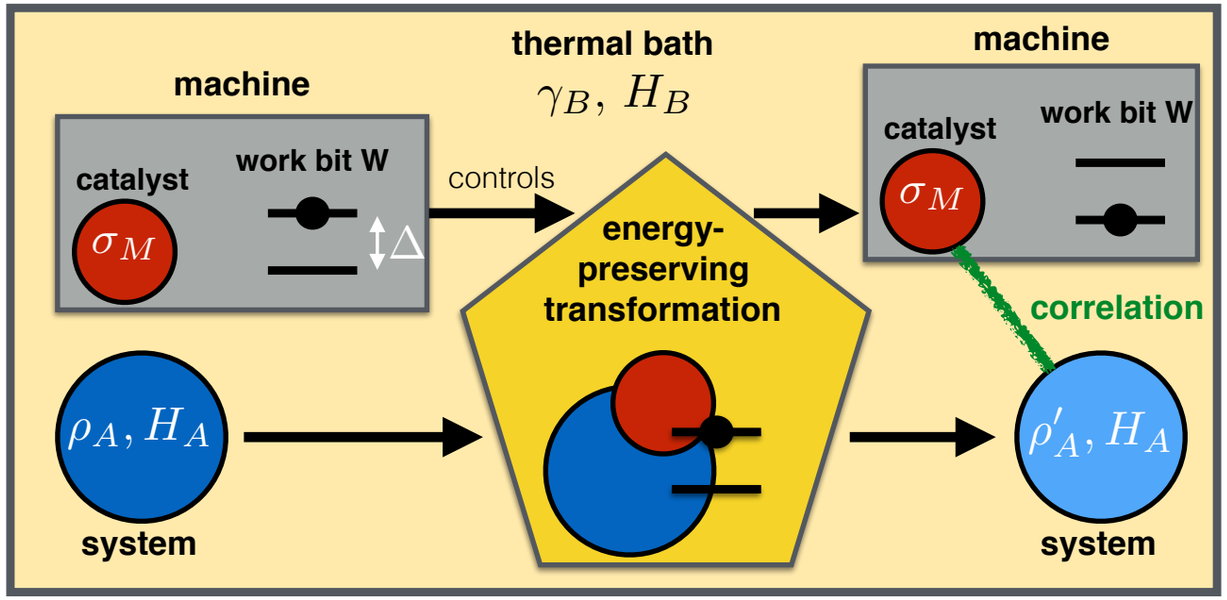


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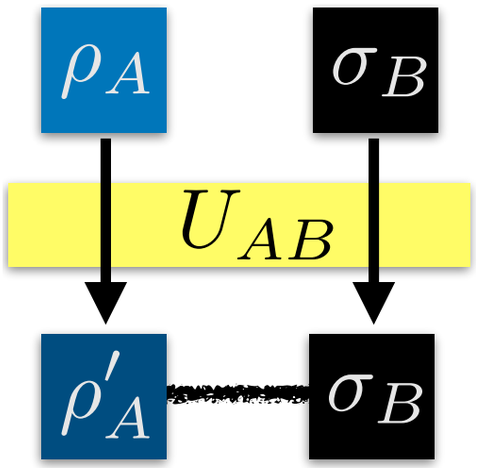


**Theorem**. Let $\rho_A$ and $\rho'_A$ be two quantum states with non-identical spectra on a finite-dimensional Hilbert space *A*. Then the following are equivalent:

- There exists another finite-dimensional system *B*, a unitary $U_{AB}$ and a state $\sigma_B$ such that

$$U_{AB}(\rho_A \otimes \sigma_B)U_{AB}^\dagger = \rho'_A \sigma_B.$$

- $\mathrm{rank}(\rho_A) \leq \mathrm{rank}(\rho'_A)$ and $S(\rho_A) < S(\rho'_A)$, where $S(\rho) = -\mathrm{tr}(\rho \log \rho)$ is von Neumann entropy.

H. Wilming, *Entropy and Reversible Catalysis*, Phys. Rev. Lett. **127**, 260402 (2021).

# Consequences for quantum information theory

This is perhaps relevant in contexts like holographic duality, where entropy has a **dual spacetime interpretation**:

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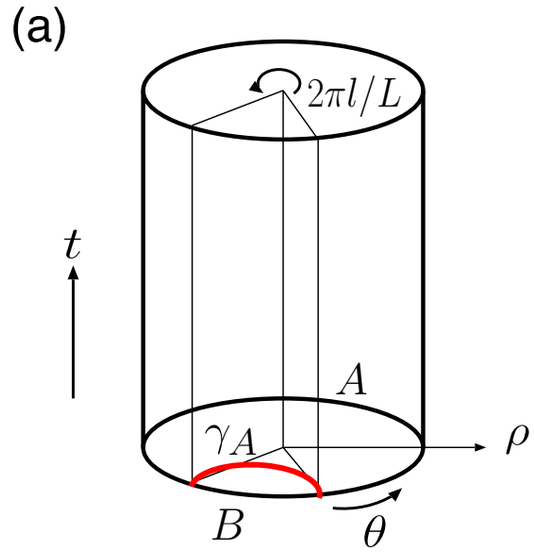
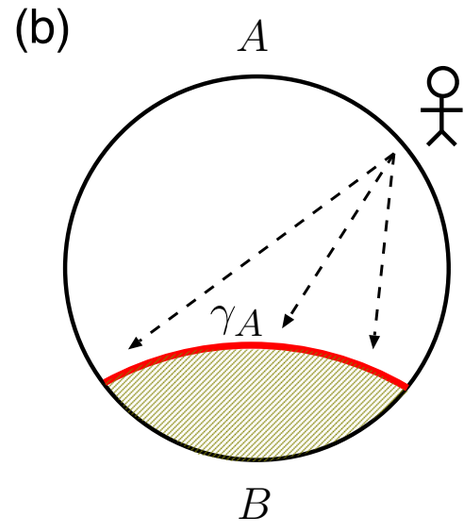
S. Ryu and T. Takayanagi, *Holographic Derivation of Entanglement Entropy from AdS/CFT*, Phys. Rev. Lett. **96**, 181602 (2006).

$$S_A = \frac{\text{Area of } \gamma_A}{4G_N^{(d+2)}}$$



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# Consequences for quantum information theory

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One interesting but random recent example:

**Quantum thermodynamics with coherence: Covariant Gibbs-preserving operation is characterized by the free energy**

Naoto Shiraishi*
*Department of Basic Science, The University of Tokyo,*
*3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan*

A map $\mathcal{E} : S \to S$ is called a covariant Gibbs-preserving operation (CGPO) if (i) $\mathcal{E}(\rho_{\rm Gibbs}) = \rho_{\rm Gibbs}$ and (ii) $\mathcal{E}(e^{-iHt}\rho e^{iHt}) = e^{-iHt}\mathcal{E}(\rho)e^{iHt}$ for any $t$ are satisfied. Here, $\rho_{\rm Gibbs} := e^{-\beta H}/Z$ is a Gibbs state with a given inverse temperature $\beta$ We define the free energy $F(\rho) := S(\rho||\rho_{\rm Gibbs})$ with the relative entropy $S$. The CGPO is also called enhanced thermal operation in Ref. [7].

We investigate the correlated-catalytic conversion with CGPO in this Letter. We say that $\rho$ is convertible to $\rho'$ through CGPO with a correlated-catalyst if for any $\varepsilon > 0$ there exist an auxiliary system $C$ called a catalyst, its state $c$, and a CGPO $\mathcal{E} : S \otimes C \to S \otimes C$ such that $\tau = \mathcal{E}(\rho \otimes c)$ with ${\rm Tr}_S[\tau] = c$ and $|{\rm Tr}_C[\tau] - \rho'|_1 < \varepsilon$. If the last condition is replaced by ${\rm Tr}_C[\tau] = \rho'$, we say this conversion *exact*.

**Theorem 1.** *Consider two states $\rho$ and $\rho'$ in $S$. We assume that the shortest period of $\rho$ is $2\pi/\Delta$ (i.e., all modes are coherent). Then, $\rho$ is convertible to $\rho'$ through CGPO with correlated-catalyst if and only if $F(\rho) \geq F(\rho')$. In addition, if $F(\rho) > F(\rho')$ and $\rho'$ is full-rank, then this conversion is exact.*

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- **Resource-theoretic** approach to thermodynamics: generalizes thermo. to small and strongly correlated systems. **Conceptually**, a different approach: restrictions for an agent who acts under reversibility and energy conservation.

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**Thank you!** Paper etc.: https://mpmueller.net