Title: Putting resource theories to work in chemistry

Speakers: Nicole Yunger Halpern

Series: Perimeter Institute Quantum Discussions

Date: March 30, 2022 - 11:00 AM

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Abstract: The past decade has seen an explosion of research into resource theories--simple, quantum-information-theoretic models for constrained agents. Resource theories have provided foundational insights about thermodynamics, entanglement, and more. Yet whether resource theories can inform science outside our neighborhood of quantum information theory has been an outstanding question. I will present what is, to my knowledge, the first application of a resource theory to answer a pre-existing question in another field. Molecular switches, or photoisomers, surface across nature and technologies, from our eyes to solar-fuel cells. What probability does a switch have of switching? A general answer defies standard chemistry tools, as photoisomers are small, quantum and far from equilibrium. I will bound the switching probability by modeling a photoisomer within a thermodynamic resource theory. This work has helped pave the path for resource theories to impact science broadly.

References

o NYH and Limmer, Phys. Rev. A 101, 042116 (2020). https://journals.aps.org/pra/abstract/10.1103/PhysRevA.101.042116

o NYH, in Eddington, Wheeler, and the Limits of Knowledge, Eds. Durham and Rickles, Springer (2017) arXiv:1509.03873.

Zoom Link: https://pitp.zoom.us/j/99315796008?pwd=dDJBMjR2ckRmdlhtdWJZeHJuNUI1QT09

PUTTING RESOURCE THEORIES TO WORK IN CHEMISTRY

NICOLE YUNGER HALPERN

NYH and Limmer, Phys. Rev. A 101, 042116 (2020).

NYH, Springer, Eds. Durham and Rickles (2015/2017), arXiv:1509.03873.

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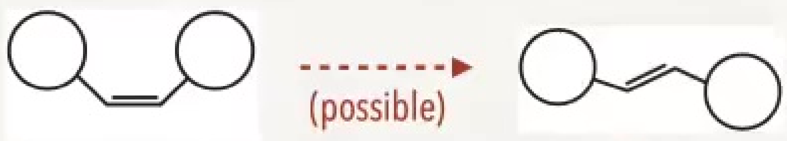
physics University of Maryland
NSF
Institute for Robust Quantum Simulation

Photoisomer



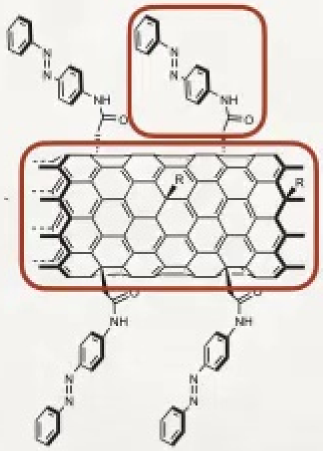
Cis
0°

Trans
180°

Photoisomers surface across nature and technologies.

- **Retinal**

- **Solar-fuel storage**



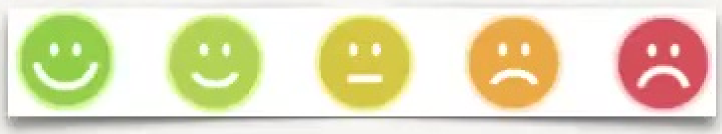
- Kucharski *et al.*, Nat. Chem. **6**, 441 (2014).

Photoisomers surface across nature and technologies.

⇓

Worth asking,

"How effectively can these molecular switches switch?"



But photoisomers are quantum, far from equilibrium and nonadiabatic.

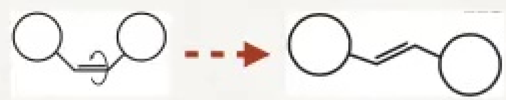
⇓

Headway seems to require assumptions,
some of which can be unpalatable.

Wanted

General, simple bounds
on photoisomers' switching probability

Photoisomerization
yield



Resource theories for thermodynamics

-Resource theories: simple models developed in quantum information theory for situations that involve constraints

-Being used to extend the laws of thermodynamics…

- to small scales
- to coherent quantum states
- far from equilibrium

-Assumptions

- Energy conservation
- Environmental temperature
- Quantum theory

Resource theories for thermodynamics

⋮

Theorem

Theorem

Corollary

-Style, until recently: *Theorem*

Theorem

Lemma

Lemma

Resource theories for thermodynamics

⋮

Theorem

Theorem

Corollary

-Style, until recently: *Theorem*

Theorem

Lemma

Lemma

-Needed: for resource theories to (1) connect to the physical world

(2) do good for the broader scientific community

-NYH, "Toward physical realizations of thermodynamic resource theories," Springer Eds. Durham and Rickles (2015/2017).

-Model a photoisomer within a thermodynamic resource theory. →  +

⋮

-Evaluate resource-theory theorems on the photoisomer. →

Theorem
Corollary
Theorem
Lemma

-Bound the switching probability, and characterize coherence's role in the switching.

-Use a thermodynamic resource theory to answer a pre-existing question in chemistry.

Editors' Suggestion

Fundamental limitations on photoisomerization from thermodynamic resource theories

Nicole Yunger Halpern and David T. Limmer
Phys. Rev. A **101**, 042116 – Published 17 April 2020

Game plan

- **Background: photoisomer**
- **Background: thermodynamic resource theories**
- **Main results**
  - Model photoisomer in resource theory
  - Bound photoisomerization probability

Editors' Suggestion

Fundamental limitations on photoisomerization from thermodynamic resource theories

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Game plan

- **Background: photoisomer**
- **Background: thermodynamic resource theories**
- **Main results**
  - Model photoisomer in resource theory
  - Bound photoisomerization probability
  - Electronic energy coherences can't increase the probability.
- **Bonus results**
- **Opportunities**

Editors' Suggestion

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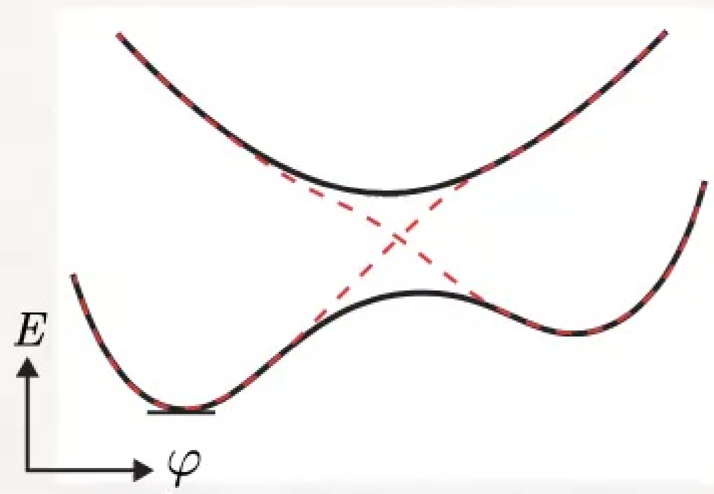
Phys. Rev. A **101**, 042116 – Published 17 April 2020

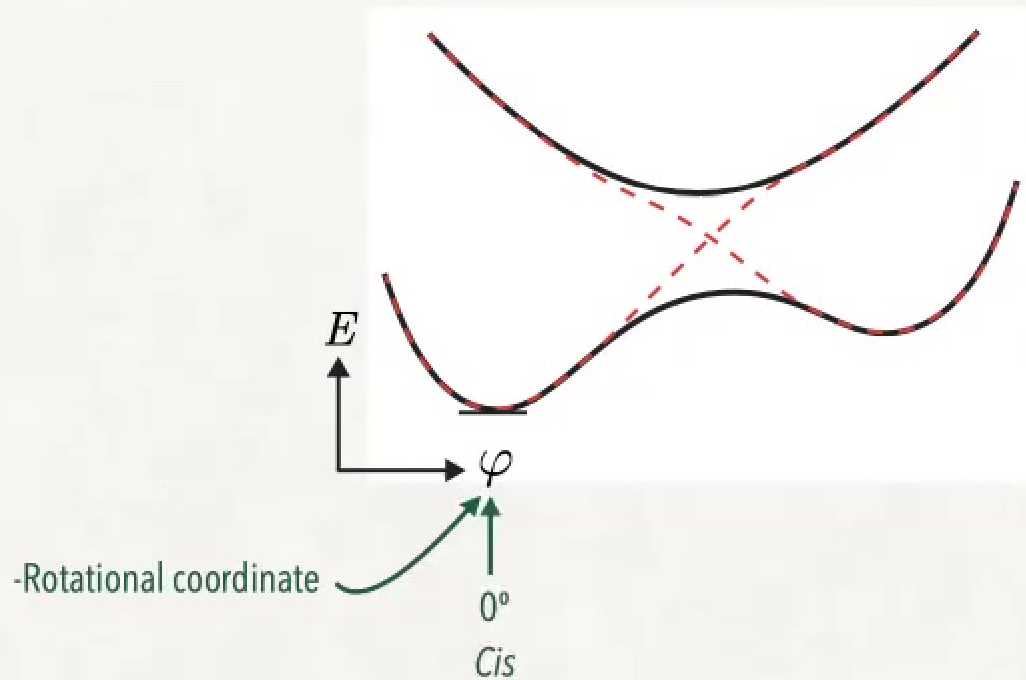
Energy landscape



-Rotational coordinate

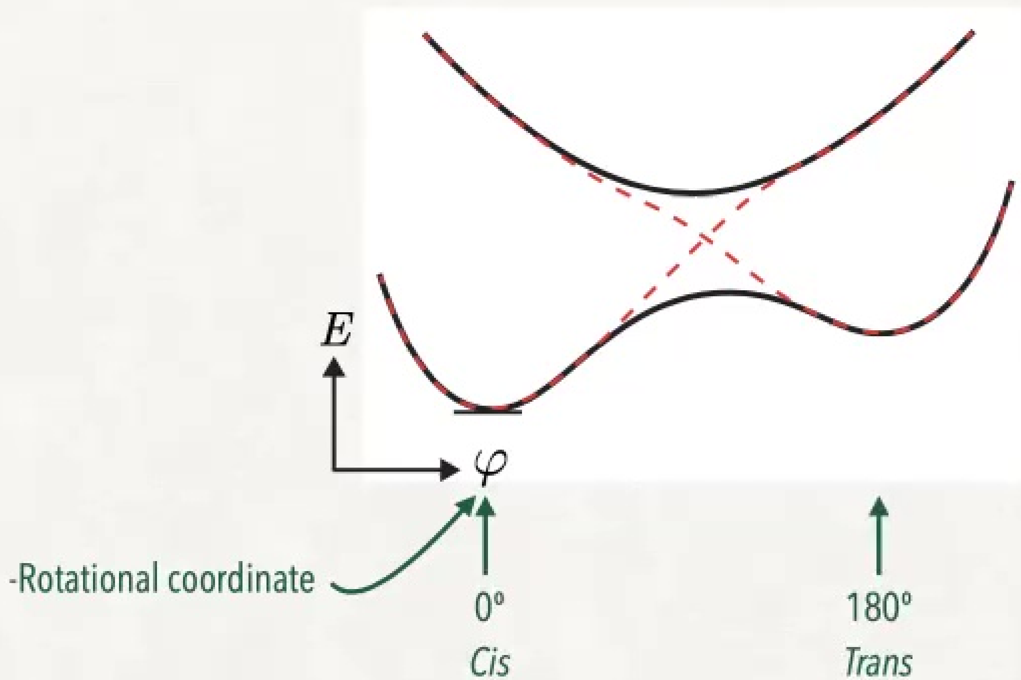
Hahn and Stock, J. Phys. Chem. (2000 and 2002).

Energy landscape



Hahn and Stock, J. Phys. Chem. (2000 and 2002).

Energy landscape



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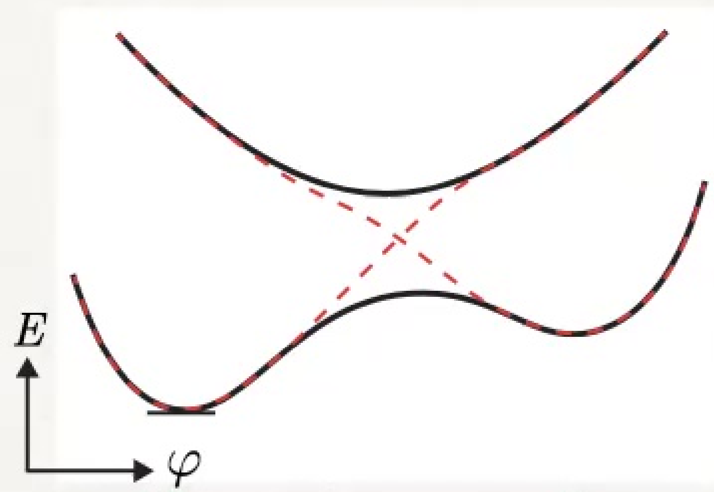
Energy landscape



-Rotational coordinate
-Nuclear degree of freedom

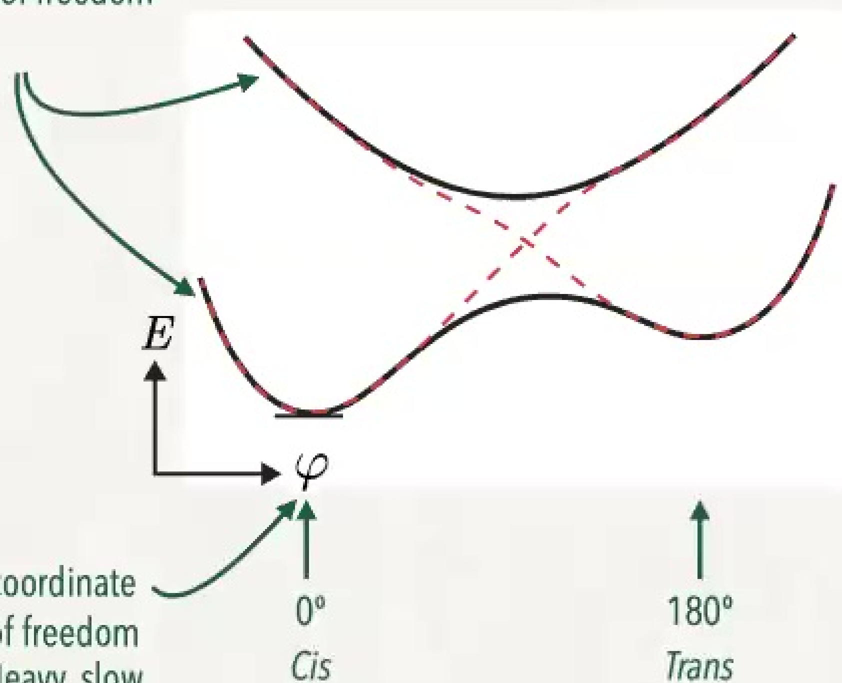
0°
Cis

180°
Trans

Hahn and Stock, J. Phys. Chem. (2000 and 2002).

Energy landscape

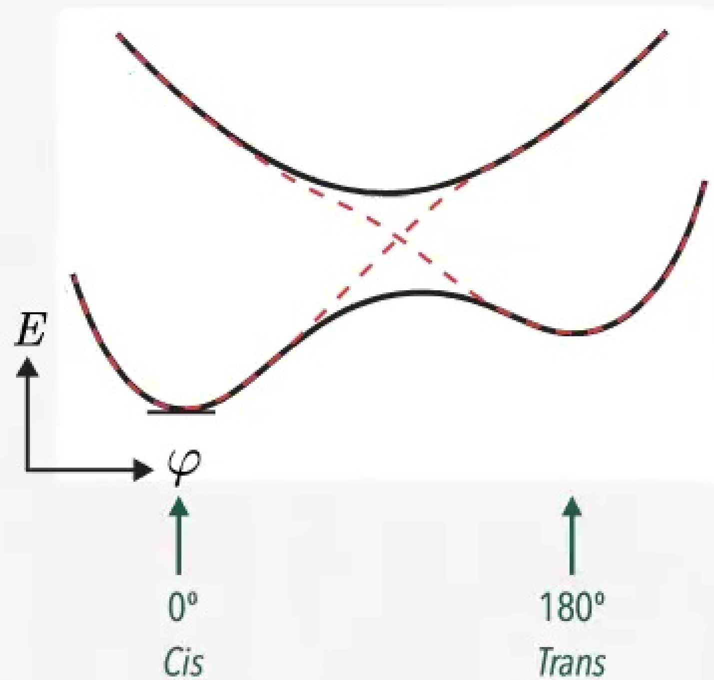
-Electronic degree of freedom



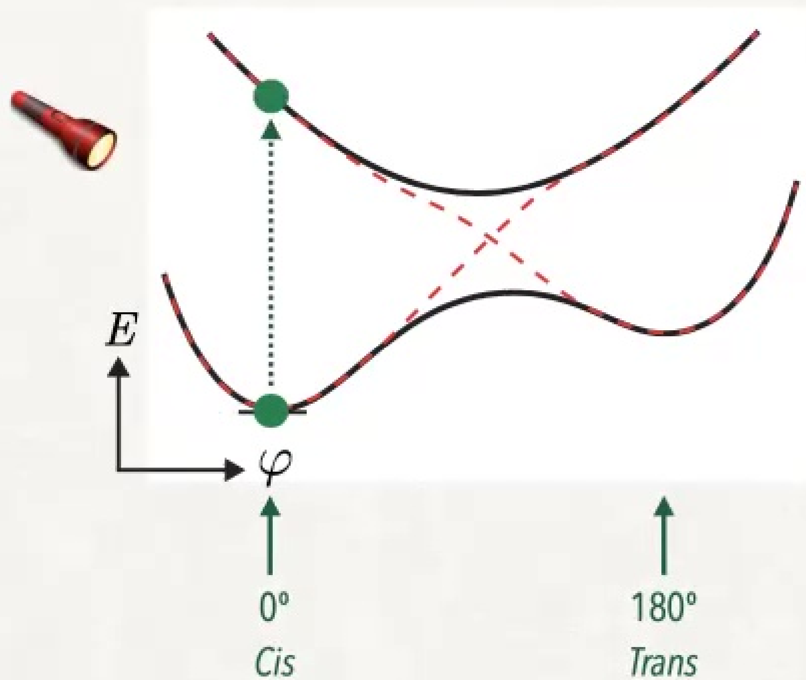
-Rotational coordinate
-Nuclear degree of freedom
-Heavy, slow

Hahn and Stock, J. Phys. Chem. (2000 and 2002).

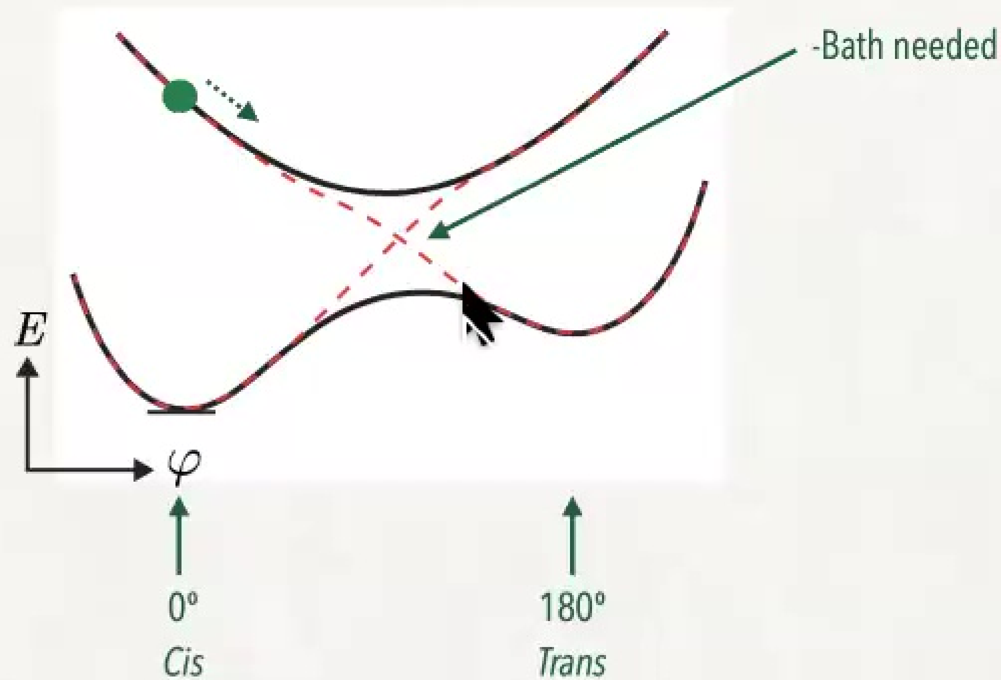
Photoisomerization



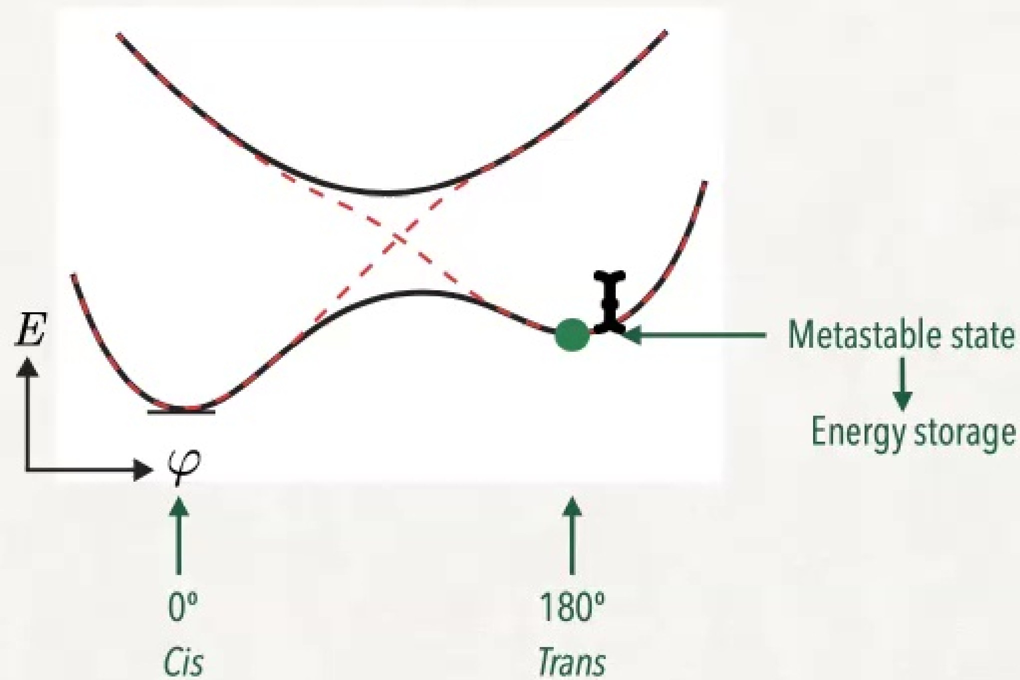
Photoisomerization



Photoisomerization



Photoisomerization



Resource-theory background

What are resources?

Things that are valuable, useful, and scarce

Memory

Time

Solve computational problems

What are resources?

Things that are valuable, useful, and scarce

Memory

Time

Money

Memory, Time → Solve computational problems

Money → Buying lab equipment

What are resources?

Things that are valuable, useful, and scarce

Memory

Time

Money

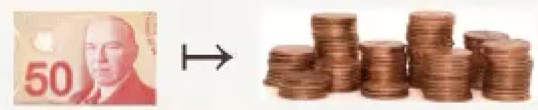
Sleep

Memory, Time → Solve computational problems

Money → Buying lab equipment/coffee

Sleep → Nearly everything

Resource goals

- Quantify resources → 
- Compare resources → 
- Identify which resources can transform into others, 

  which can't, 

  and how much you'd have to pay to effect a forbidden transformation

  
- Distinguish what's possible and what's impossible

Solution: resource theories

- Simple, information-theoretic models
  for any situation in which only certain systems are accessible
  and only certain operations can be performed

free operations

- Example: conserve energy (obey the first law)

free systems

- Example (thermodynamics in a temperature-T atmosphere):

$$e^{-H/(k_B T)}/Z$$

How to model your favorite system in a thermodynamic resource theory

How to model your favorite system in a thermodynamic resource theory

- A few early references: Lieb and Yngvason, Amer. Math. Soc. **45**, 5 (1998).
  Janzing *et al.*, Int. J. Theor. Phys. **39**, 12 (2000).
  Brandão *et al.*, Phys. Rev. Lett. **111**, 250404 (2013).

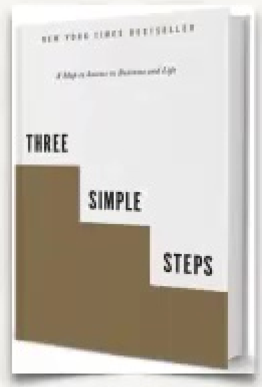
- How to specify a system: $\mathscr{H}, \ (\rho, H)$

- Agent given access to bath at $\beta = \dfrac{1}{k_{\mathrm{B}} T}$

- Free states: 

thermal relative to $\beta \longrightarrow \left(\dfrac{e^{-\beta H_{\mathrm{B}}}}{Z}, H_{\mathrm{B}} \right)$

Free operations

- **Thermal operations**
- Tend to thermalize states
- Each free operation consists of 

.

1) Draw any free state from the bath.
2) Perform any unitary that conserves the total energy. → $U = e^{-iH_{\text{int}}t}$
3) Discard a subsystem.

Free operations

- $$(\rho, H) \mapsto \left(\mathrm{Tr}_{\mathrm{a}}\left(U \left[\rho \otimes \frac{e^{-\beta H_{\mathrm{B}}}}{Z} \right] U^{\dagger} \right),\ H + H_{\mathrm{B}} - H_{\mathrm{a}} \right)$$

- $[U, H_{\mathrm{tot}}] = 0$

  $$H_{\mathrm{tot}} = H + H_{\mathrm{B}} \equiv (H \otimes 1) + (1 \otimes H_{\mathrm{B}})$$

~First law of thermodynamics

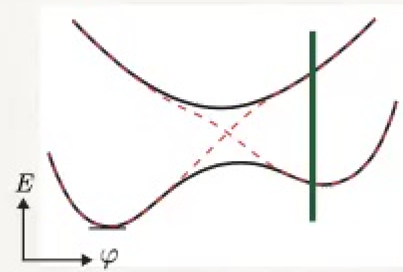
Modeling the photoisomer in the resource theory

 +

NYH and Limmer, Phys. Rev. A **101** 042116 (2020).

Modeling the photoisomer in the resource theory

- Hilbert space: $\mathscr{H}_{\text{mol}} = \mathscr{H}_{\text{elec}} \otimes \mathscr{H}_{\text{nuc}}$

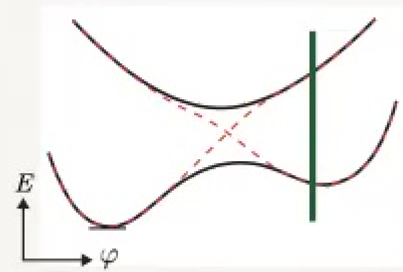


- Hamiltonian: $H_{\text{mol}} = \int_0^\pi d\varphi \left[H_{\text{elec}}(\varphi) \otimes |\varphi\rangle\langle\varphi| + 1_{\text{elec}} \otimes \frac{\ell_\varphi^2}{2I} \right]$

⟶ (Imperfect/realizable) quantum clock

Modeling the photoisomer in the resource theory

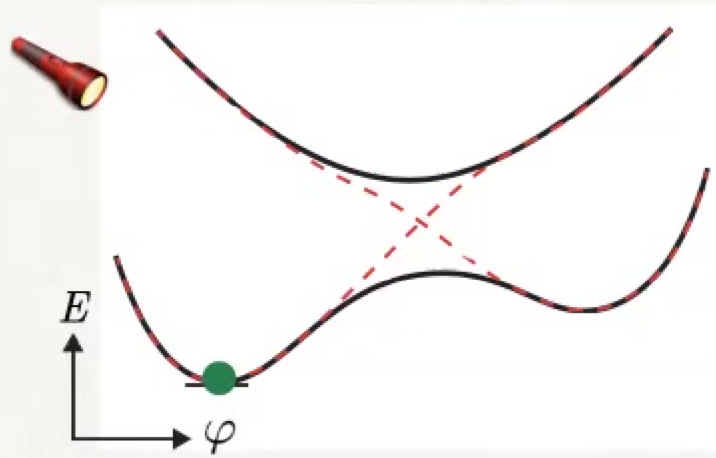
- Hilbert space: $\mathscr{H}_{\text{mol}} = \mathscr{H}_{\text{elec}} \otimes \mathscr{H}_{\text{nuc}}$



- Hamiltonian: $H_{\text{mol}} = \int_0^{\pi} d\varphi \left[H_{\text{elec}}(\varphi) \otimes |\varphi\rangle\langle\varphi| + 1_{\text{elec}} \otimes \frac{L_\varphi^2}{2I} \right]$

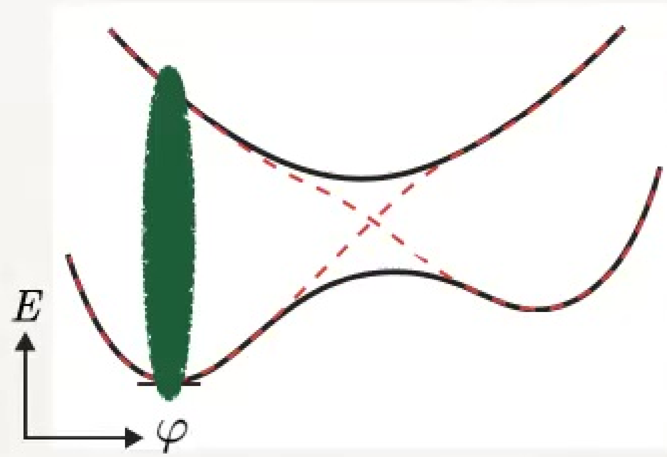
→ (Imperfect/realizable) quantum clock

Modeling photoisomerization's steps with thermal operations



Initial molecule-and-laser state: $e^{-\beta H_{\rm mol}}/Z_{\rm mol} \otimes \rho_{\rm laser}$

Modeling photoisomerization's steps with thermal operations



Initial molecule-and-laser state: $e^{-\beta H_{\text{mol}}}/Z_{\text{mol}} \otimes \rho_{\text{laser}} \mapsto$ (photoexcitation)

$$\rho_{\text{elec}} \otimes |\varphi = 0\rangle\langle\varphi = 0|$$

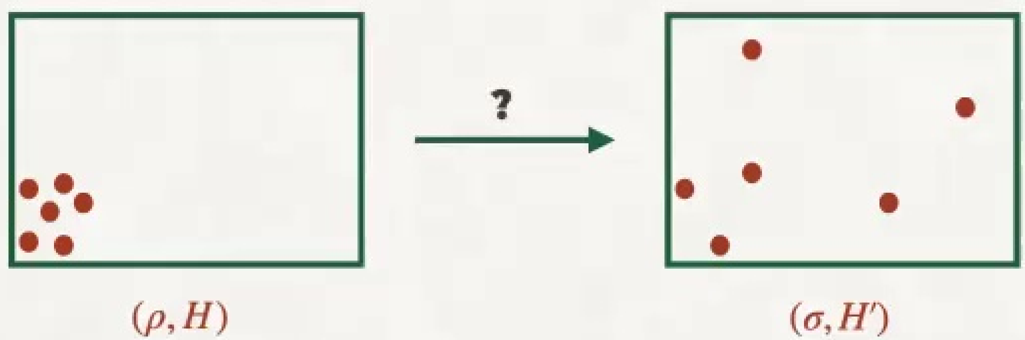
Second law in conventional thermodynamics

Second law in conventional thermodynamics

- Can a system transition from one state to another spontaneously?
  - Compare free energies. ⟶ $F = E - TS$
- Do they satisfy (the appropriate manifestation of) the second law? ⟶ $\Delta F \leq 0$
  - Setting: equilibrium, large-system limit, implicit averaging

In thermodynamic resource theory

- Does any free operation map (ρ, H) to (σ, H')?



Second laws of thermodynamics

- One subfamily of inequalities governs the state's energy diagonal.

$$(\rho, H) \mapsto (\sigma, H')?$$

Second laws of thermodynamics

- One subfamily of inequalities governs the state's energy diagonal.

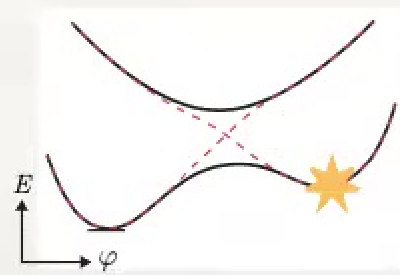
$$(\rho, H) \mapsto (\sigma, H')?$$

$$\downarrow H$$

$$\begin{bmatrix} p_1 & \boxed{a} & \boxed{c} & \\ \boxed{a^*} & p_2 & \boxed{b} & \\ \boxed{c^*} & \boxed{b^*} & \ddots & \\ & & & p_d \end{bmatrix}$$

- Another subfamily governs the coherences.

- We want to bound a diagonal element.

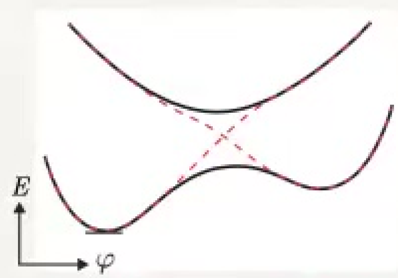


Applying the second laws of thermodynamics to the photoisomer

$$(\rho, H) \mapsto (\sigma, H')?$$

$\rho_{\text{elec}} \otimes |\varphi = 0\rangle\langle\varphi = 0|$ $\qquad \sigma$

$$H_{\text{mol}} = \int_0^{\pi} d\varphi \left[H_{\text{elec}}(\varphi) \otimes |\varphi\rangle\langle\varphi| + 1_{\text{elec}} \otimes \frac{\ell_\varphi^2}{2I} \right]$$



$\varphi = 0 \qquad \varphi = \pi$

Applying the second laws of thermodynamics to the photoisomer

Coherence theorem

A density operator can be broken into modes, each defined by a gap.

- $\rho = \sum_{j,k} r_{jk} |j\rangle\langle k|$

Marvian and Spekkens, Phys. Rev. A **90**, 062110 (2014).
Lostaglio *et al.*, Phys. Rev. X **5**, 021001 (2015).

Applying the second laws of thermodynamics to the photoisomer

Coherence theorem

A density operator can be broken into modes, each defined by a gap.

- $\rho = \sum_{j,k} r_{jk} |j\rangle\langle k|$
- $\rho^{(\omega)} := \sum_{\substack{j,k\ : \\ E_j - E_k = \omega}} r_{j,k}$

$$\begin{bmatrix} r_{11} & r_{12} & r_{13} & \\ r_{12}^* & r_{22} & r_{23} & \\ r_{13}^* & r_{23}^* & \ddots & \\ & & & r_{dd} \end{bmatrix}$$

Marvian and Spekkens, Phys. Rev. A **90**, 062110 (2014).

Lostaglio *et al.*, Phys. Rev. X **5**, 021001 (2015).

Applying the second laws of thermodynamics to the photoisomer

Coherence theorem

A density operator can be broken into modes, each defined by a gap.
The modes transform independently under thermal operations.
Basic physical reason: Markovianity

- $\rho = \sum_{j,k} r_{jk} |j\rangle\langle k|$
- $\rho^{(\omega)} := \sum_{\substack{j,k\ : \\ E_j - E_k = \omega}} r_{j,k}$

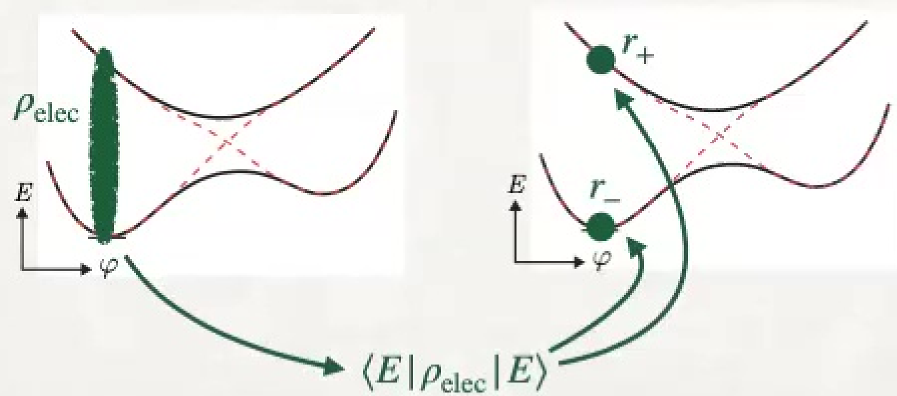
$$\begin{bmatrix} r_{11} & r_{12} & r_{13} & \\ r_{12}^* & r_{22} & r_{23} & \\ r_{13}^* & r_{23}^* & \ddots & \\ & & & r_{dd} \end{bmatrix}$$

Marvian and Spekkens, Phys. Rev. A **90**, 062110 (2014).
Lostaglio *et al.*, Phys. Rev. X **5**, 021001 (2015).

Applying the second laws of thermodynamics to the photoisomer

Implication for photoisomer

- We want to bound a diagonal element.
- Coherences can't affect it, in the absence of external resources.
- So our bound will depend on just the states' diagonal elements.
- So, in our calculations, we can replace the states with decohered states.



Second laws of thermodynamics for the energy diagonal

- Janzing *et al.*, Int. J. Theor. Phys. **39**, 12 (2000).
Horodecki and Oppenheim, Nat. Comm. **4**, 2059 (2013).

- Mathematical toolkit: *d*-majorization

How to check whether $(\rho, H) \mapsto (\sigma, H)$ for free

- Rescale each probability with an inverse Boltzmann factor.

$$r_\mu \mapsto r_\mu e^{\beta E_\mu}$$

Informational resource (r_μ) Energetic resource ($e^{\beta E_\mu}$)

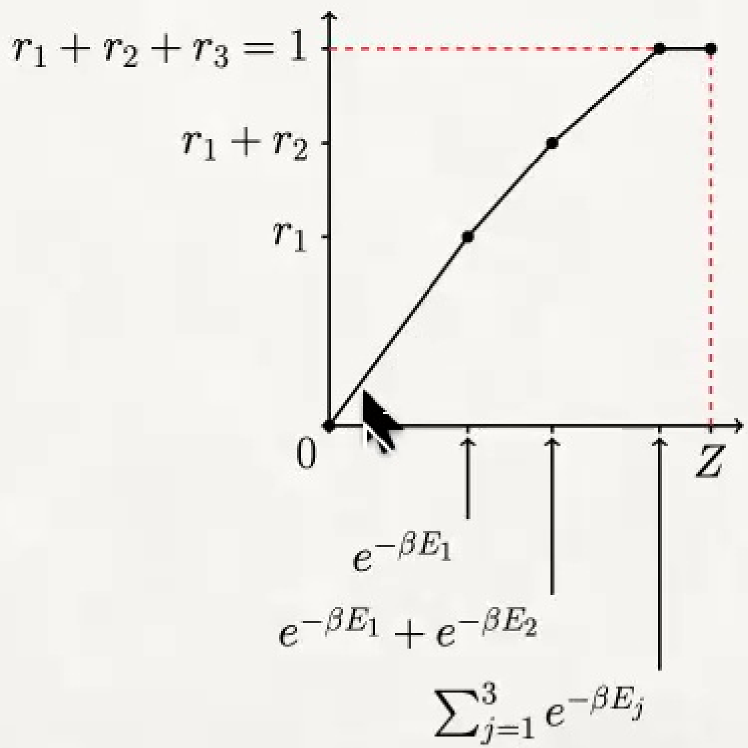
- Order the rescaled probabilities from greatest to least.

$$r_1 e^{\beta E_1} \geq r_2 e^{\beta E_2} \geq \ldots \geq r_d e^{\beta E_d}$$

- Plot partial sums.

Second laws of thermodynamics

How to check whether $(\rho, H) \mapsto (\sigma, H)$ for free

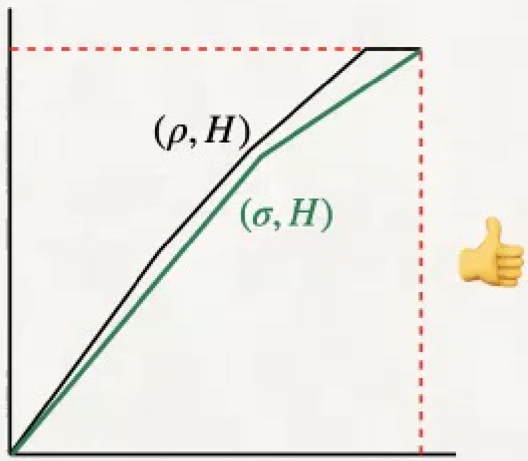


Second laws of thermodynamics

How to check whether $(\rho, H) \mapsto (\sigma, H)$ for free

- Plot the (ρ, H) and (σ, H) curves on the same plot.
- Theorem: $(\rho, H) \mapsto (\sigma, H)$ if and only if the (ρ, H) curve lies, everywhere, above or on the (σ, H) curve.

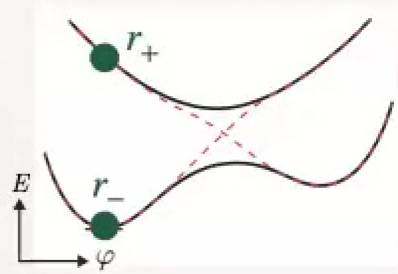
Encodes a bunch of inequalities



Applying the second laws to the photoisomer

Strategy

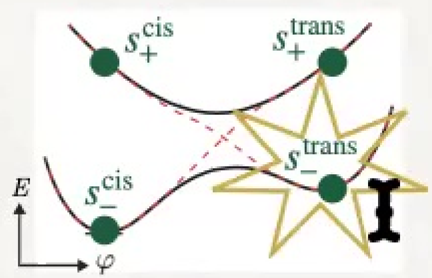
- For any state ρ to which the laser can excite the molecule,



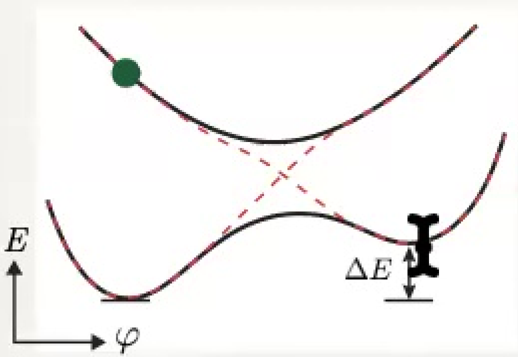
Applying the second laws to the photoisomer

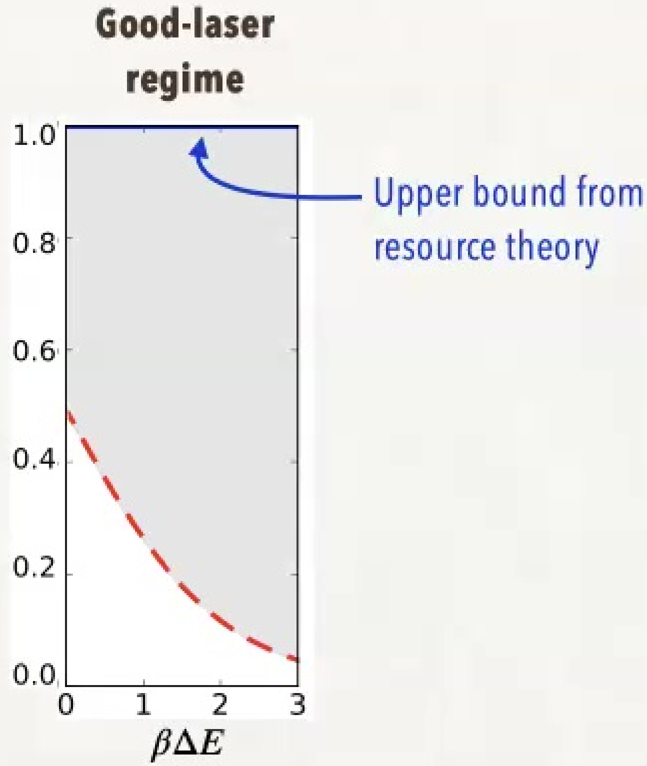
Strategy

- For any state ρ to which the laser can excite the molecule, four parameters specify the final state.
- Plug into the second laws for the energy diagonal.
- Solve for the greatest s_-^{trans} for which the ρ curve lies above/on the σ curve.

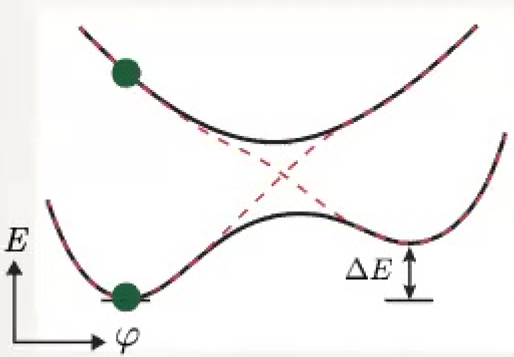


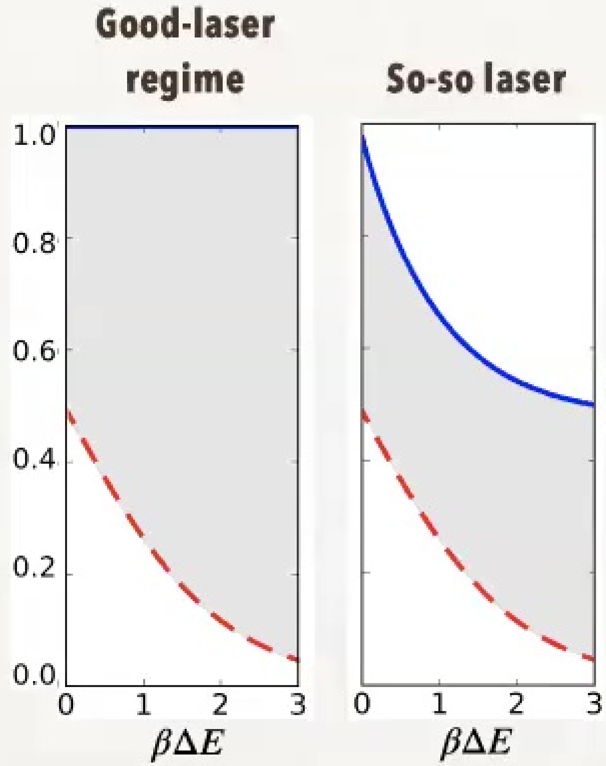
Bounds on photoisomerization yield



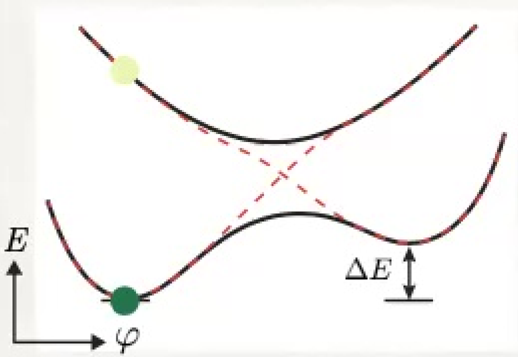


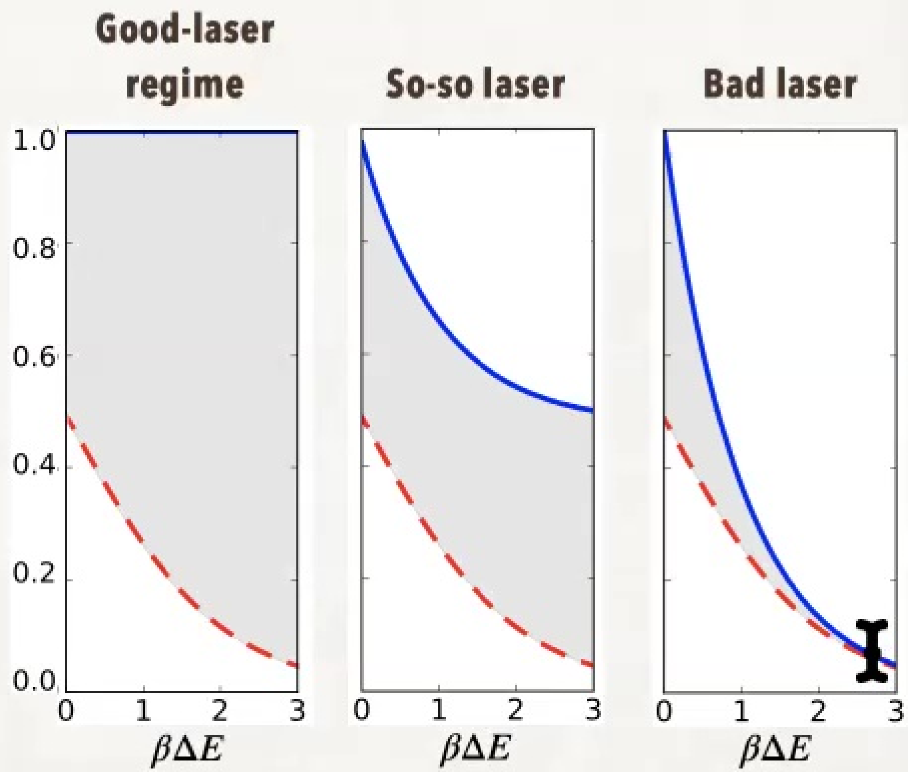
Bounds on photoisomerization yield





Bounds on photoisomerization yield





Compare resource-theory bound with Lindblad hopping

- Toy: particle hopping amongst 4 energy levels, in contact with bath

- Lindblad master equation: $\dot{\rho}(t) = -\frac{i}{\hbar}[H, \rho(t)] + \mathscr{L}\big(\rho(t)\big)$

  ~Closed-system | Bath's action

- Lindbladian's action: $\mathscr{L}(\rho) = \sum_i \Gamma_i \left(B_i \rho B_i^\dagger - \frac{1}{2}\left\{ B_i^\dagger B_i, \rho(t) \right\} \right)$

  Mixes | Preserves state's norm

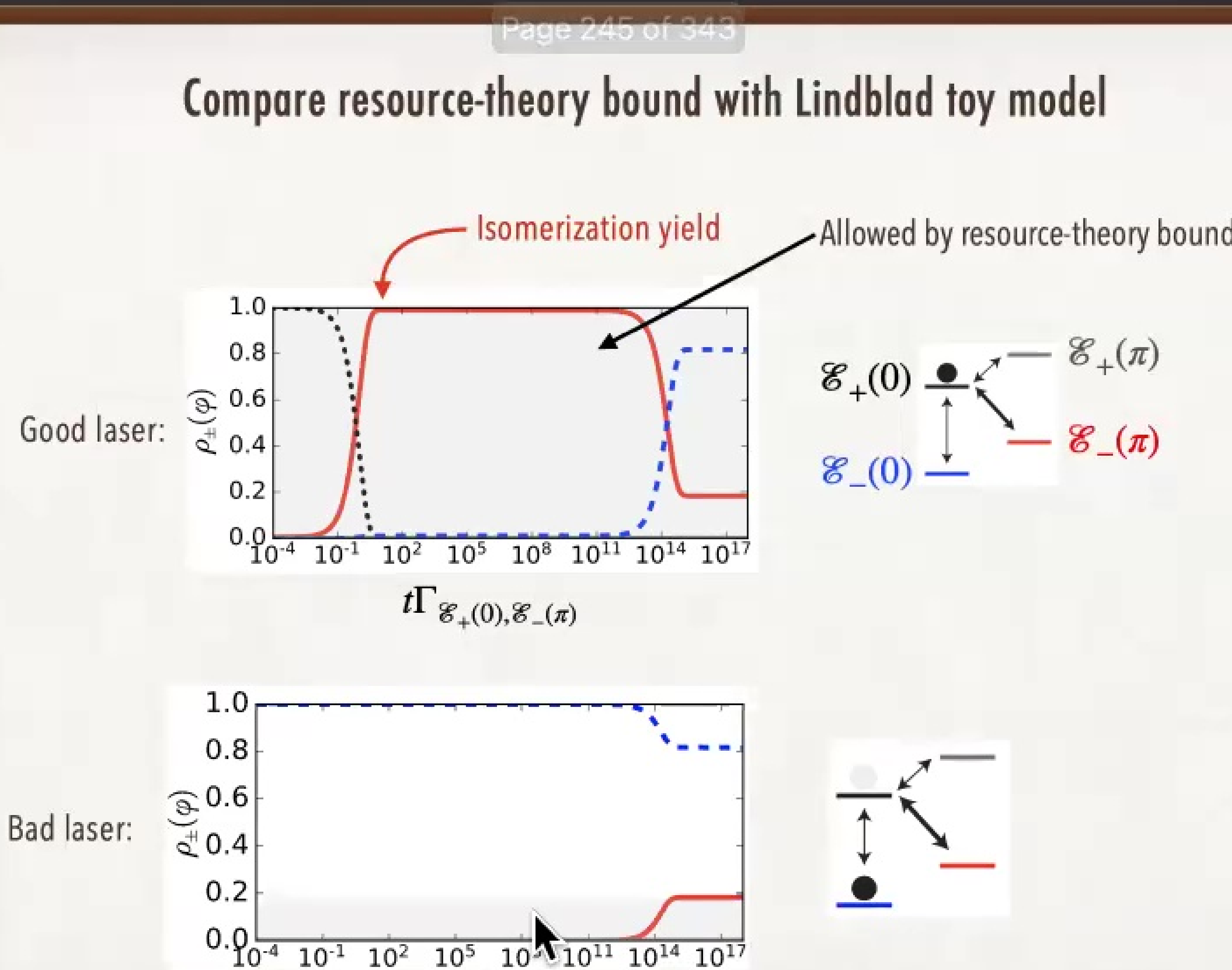
Dissipation rate
Satisfies detailed balance:

$$\frac{\Gamma_{E_1,E_2}}{\Gamma_{E_2,E_1}} = e^{-\beta(E_1 - E_2)}$$

Lindblad operators:

$$B_i \equiv B_{E_1,E_2} = |E_1\rangle\langle E_2|$$

Compare resource-theory bound with Lindblad toy model



Takeaways

- We've derived fundamental thermodynamic limitations on the molecule's switching probability

What more can we learn about photoisomers from thermodynamic resource theories?

What more can we learn about photoisomers from thermodynamic resource theories?

(1) The molecular switch serves as a quantum clock.

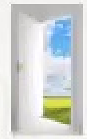
(2) Minimal work required to photoexcite the molecule in a single shot

(3) Work can be extracted from coherences.

(4) Quantification of the post-photoisomerization energy coherences

Capacity of non-Markovianity to boost the efficiency of molecular switches

Giovanni Spaventa, Susana F. Huelga, and Martin B. Plenio
Phys. Rev. A **105**, 012420 – Published 24 January 2022

Opportunity 

- <u>Proposals of experiments designed to realize resource-theory results</u>
  - Lörch, Bruder, Brunner, and Hofer, Q. Sci. and Tech. **3**, 035014 (2018).
  - Holmes, Weidt, Jennings, Anders, and Mintert, Quantum **3**, 124 (2019).

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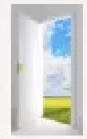
Opportunity 

- Proposals of experiments designed to realize resource-theory results
  - Lörch, Bruder, Brunner, and Hofer, Q. Sci. and Tech. **3**, 035014 (2018).
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- See also
  - Alhambra, Lostaglio, and Perry, Quantum **3**, 188 (2019).
  - Pusuluk, Farrow, Deliduman, Burnett, and Vedral, Proc. R. Soc. A **474**, 20180037 (2018).
  - Chin and Huh, arXiv:1807.11187 (2018). ⟵ BosonSampling
  - Song, Huang, Ling, and Yung, arXiv:1806.00715 (2018). ⟵ Neutrino oscillations
  - Cipolla and Landi, arXiv:1808.01224 (2018). ⟵ Spin-boson model
  - NYH, Beverland, and Kalev, Phys. Rev. E **101**, 042117 (2020).
  - Tan, arXiv:2003.04527 (2020). ⟵ Quantum phase transitions

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Recap

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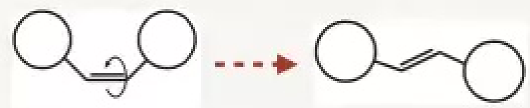
- **Photoisomer**

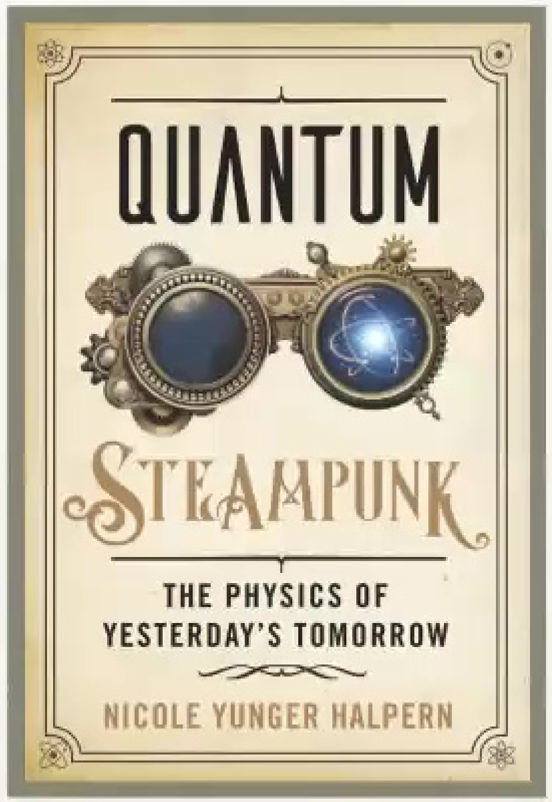


- **Thermodynamic resource theories**
  - How to model your favorite system
  - "Second laws" of thermodynamics
- **Results**
  - Modeled the photoisomer in a resource theory

Recap

NYH and Limmer, Phys. Rev. A **101** 042116 (2020).

NYH, Springer (2017) arXiv:1509.03873.



Thanks for your time!

Editors' Suggestion

Fundamental limitations on photoisomerization from thermodynamic resource theories

Nicole Yunger Halpern and David T. Limmer
Phys. Rev. A **101**, 042116 – Published 17 April 2020

NYH, Springer, Eds. Durham and Rickles (2015/2017), arXiv:1509.03873.