SIMPLE BOUNDS ON FAR-FROM-EQUILIBRIUM MACHINES, FROM QUANTUM INFORMATION THEORY

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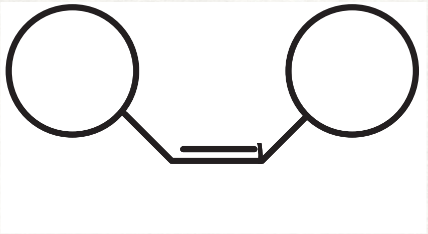
Harvard University Department of Physics

NYH and Limmer, arXiv:1811.06551 (2018).

"Exploring Open Quantum Systems in Quantum Simulators" conference, KITP, 4/19

The photoisomer

The photoisomer



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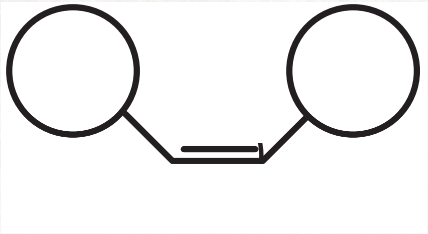
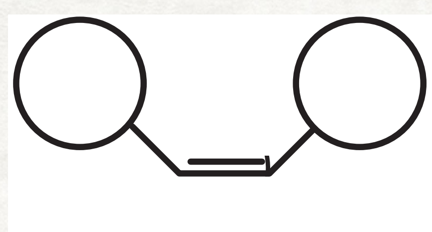


Cis

0º

The photoisomer



Cis

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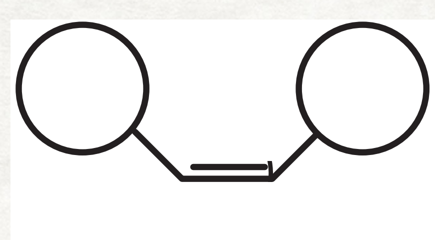

(possible)

Cis

0°

The photoisomer

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0°

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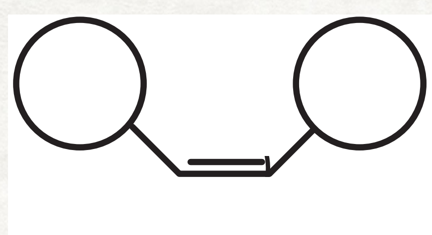

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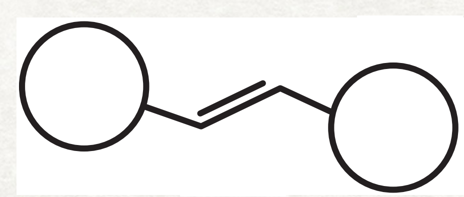

Cis

0º

Trans

180º

Photoisomers surface across nature and technologies.

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- **Retinal**

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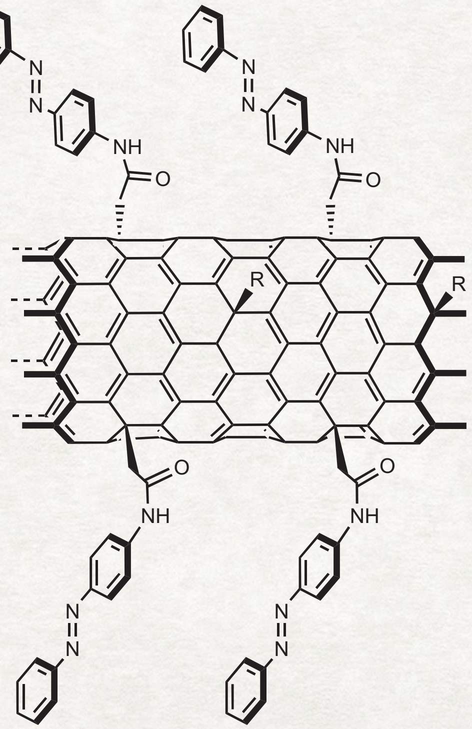
- **Retinal**

- **Solar-fuel storage**



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

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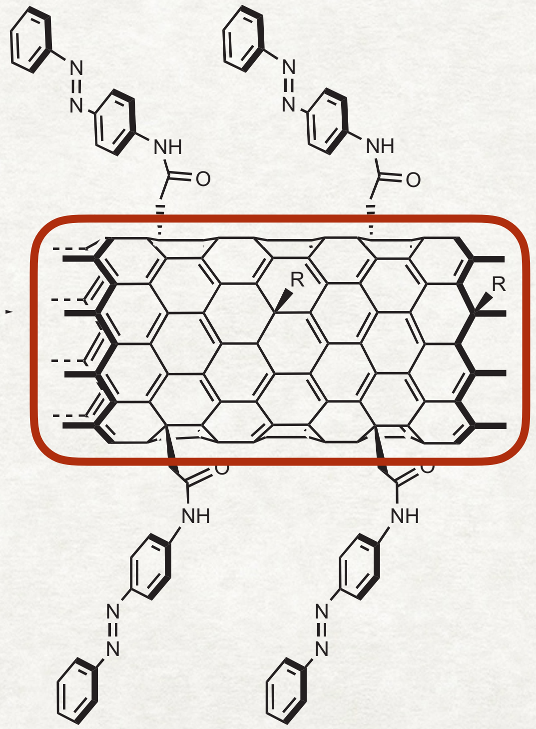

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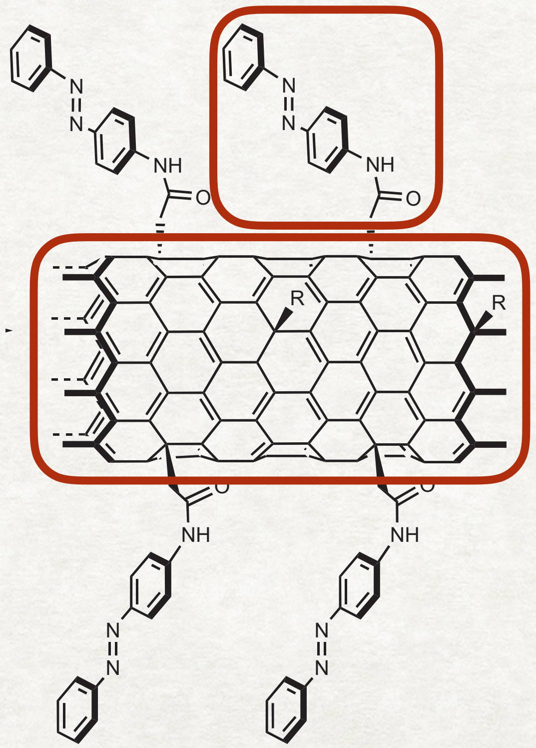

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$\Downarrow$

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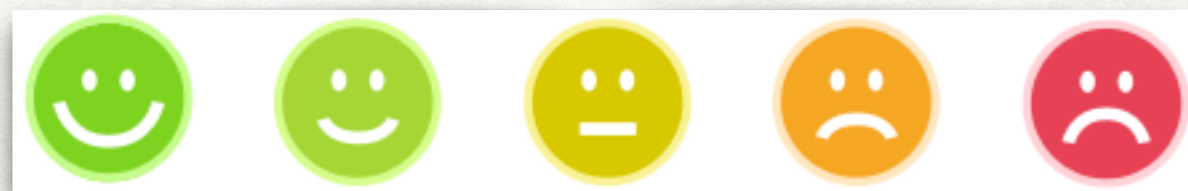
⇓

Worth asking,

"How effectively can these molecular switches switch?"



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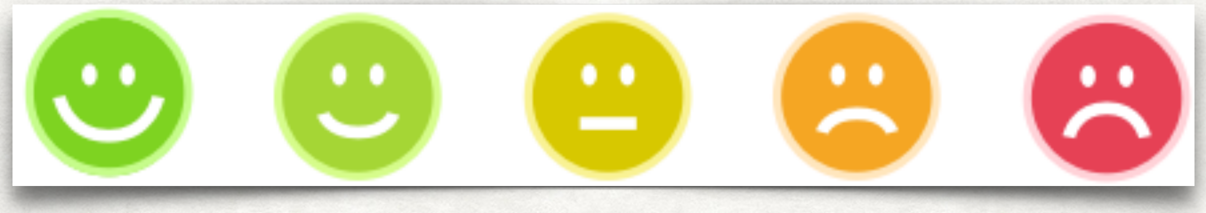

But photoisomers are small, quantum, and far from equilibrium.

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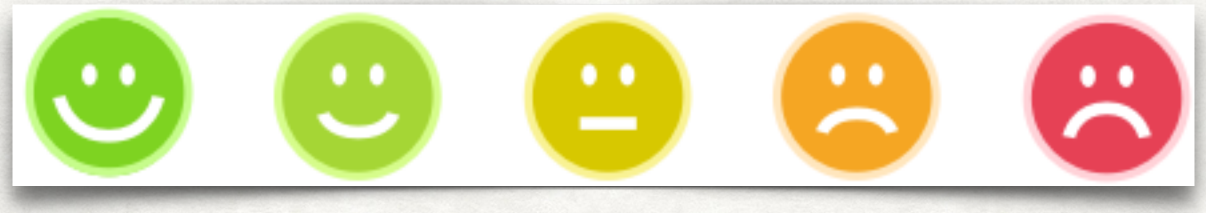

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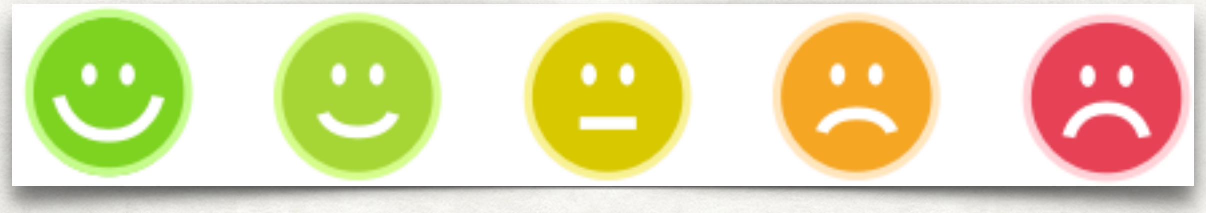

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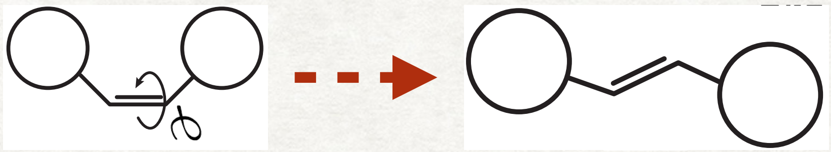
⇓

Headway seems to require assumptions,

but the usual ones can be violated.

Wanted

General, simple bounds
on photoisomers' switching probability



Wanted

General, simple bounds
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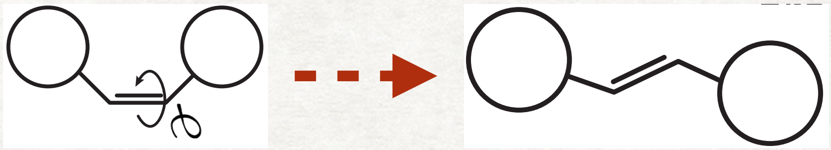
Photoisomerization
yield



Quantum information theory

Quantum information theory

Resource theories for thermodynamics

Quantum information theory

Resource theories for thermodynamics

-Simple models developed in quantum information theory

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-Being used to extend the laws of thermodynamics…

- to small scales

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- to coherent quantum states
- far from equilibrium

Resource theories for thermodynamics

-Assumptions

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- Energy conservation

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- Environmental temperature

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-<u>Assumptions</u>

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-Style: abstract quantum information theory

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⋮

Theorem

Theorem

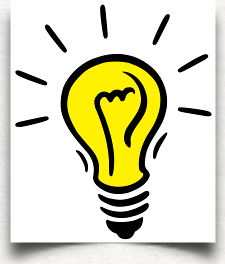
Corollary

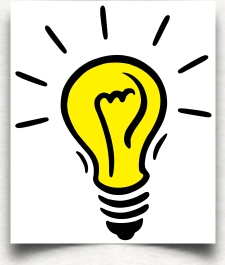
Theorem

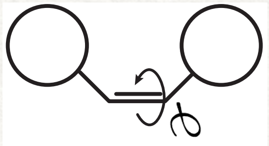
Theorem

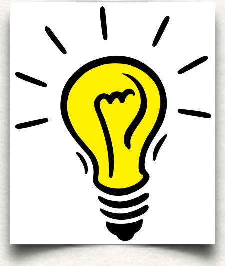
Lemma

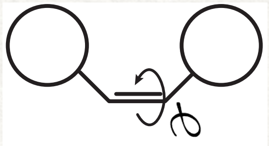
Lemma





Model a photoisomer within a thermodynamic resource theory. →  +



Model a photoisomer within a thermodynamic resource theory. →  +

⋮

Theorem

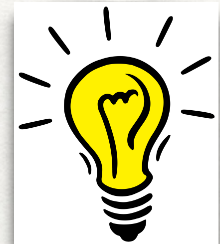
Corollary

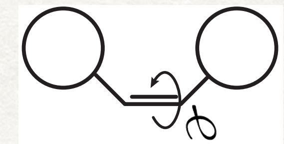
Theorem

Theorem

Lemma

Evaluate resource-theory theorems on the photoisomer. →



Model a photoisomer within a thermodynamic resource theory. →  +

⋮

Theorem

Corollary

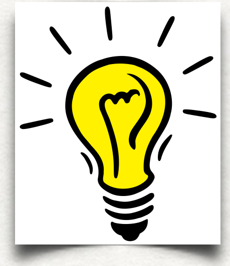
Theorem

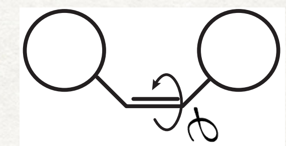
Theorem

Lemma

Evaluate resource-theory theorems on the photoisomer. →

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



Model a photoisomer within a thermodynamic resource theory. →  +

⋮

Evaluate resource-theory theorems on the photoisomer. → Theorem Corollary *Theorem* Theorem Lemma

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NYH and Limmer, arXiv:1811.06551 (2018).

Game plan

Game plan

- **Photoisomer background**

Game plan

- **Photoisomer background**
- **Resource-theory background**

Game plan

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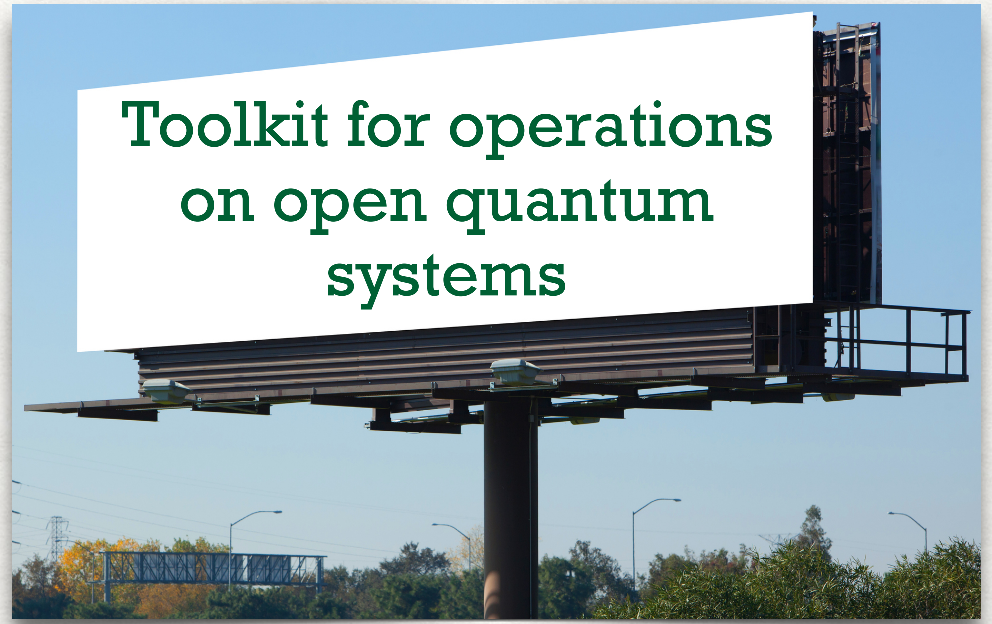
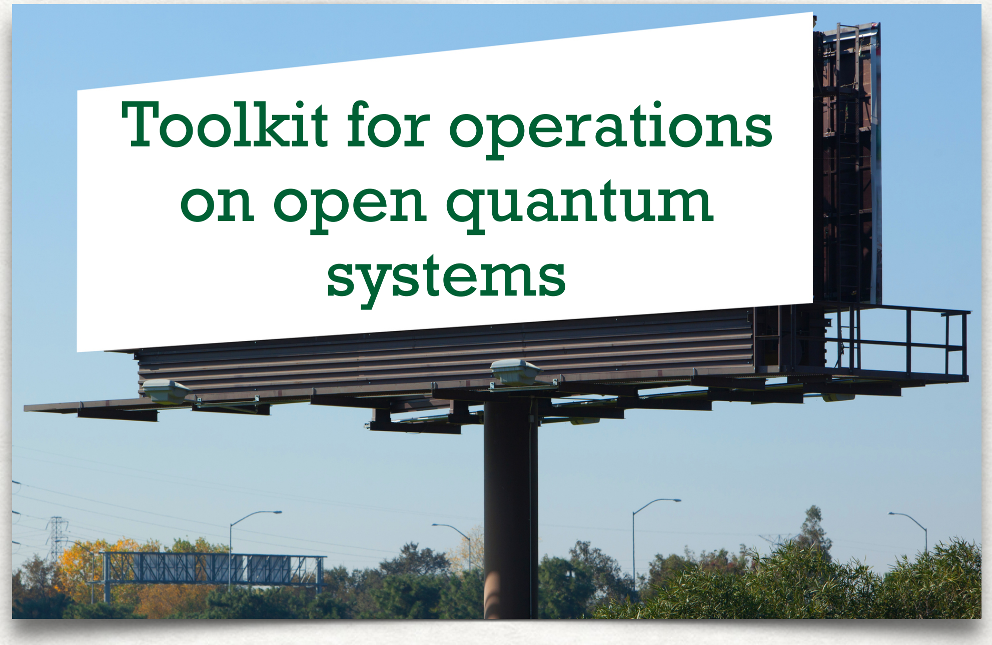


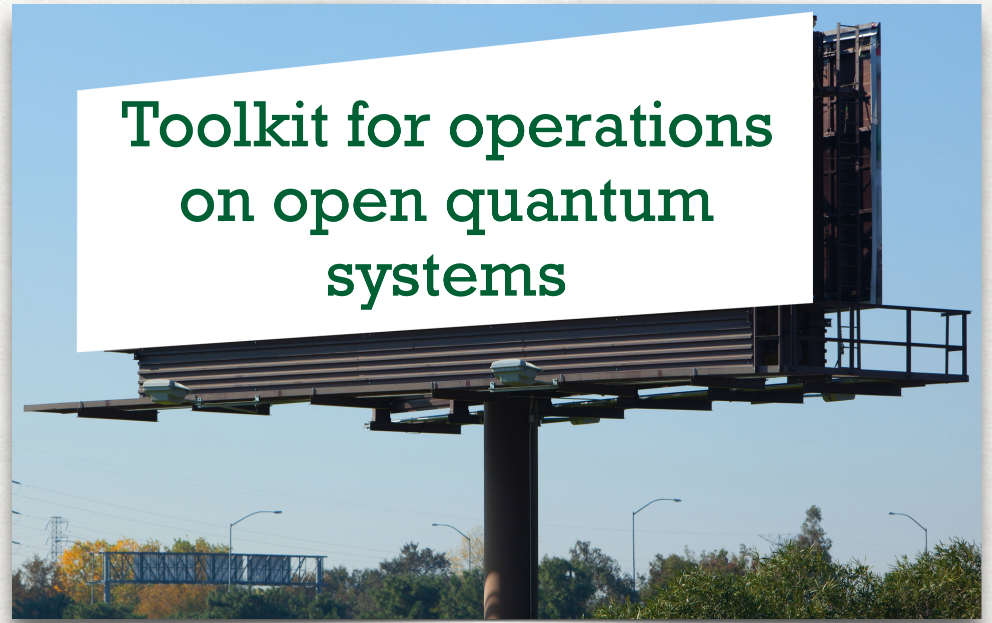
Game plan

- **Photoisomer background**
- **Resource-theory background**
- **Results**



Game plan

- **Photoisomer background**
- **Resource-theory background** →
- **Results**
  - Model photoisomer in resource theory



Game plan

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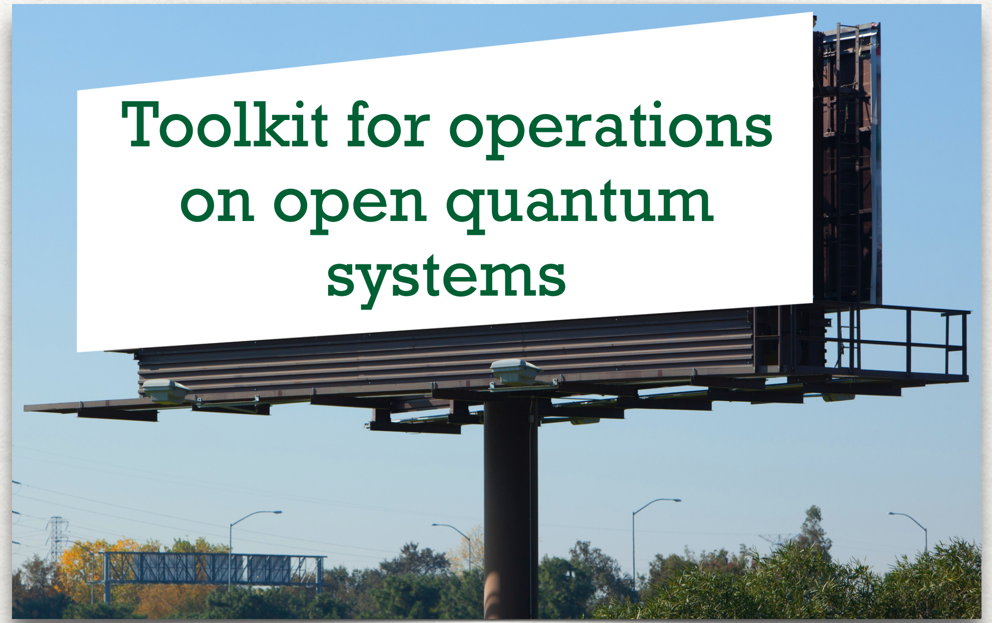
  - Bound photoisomerization probability



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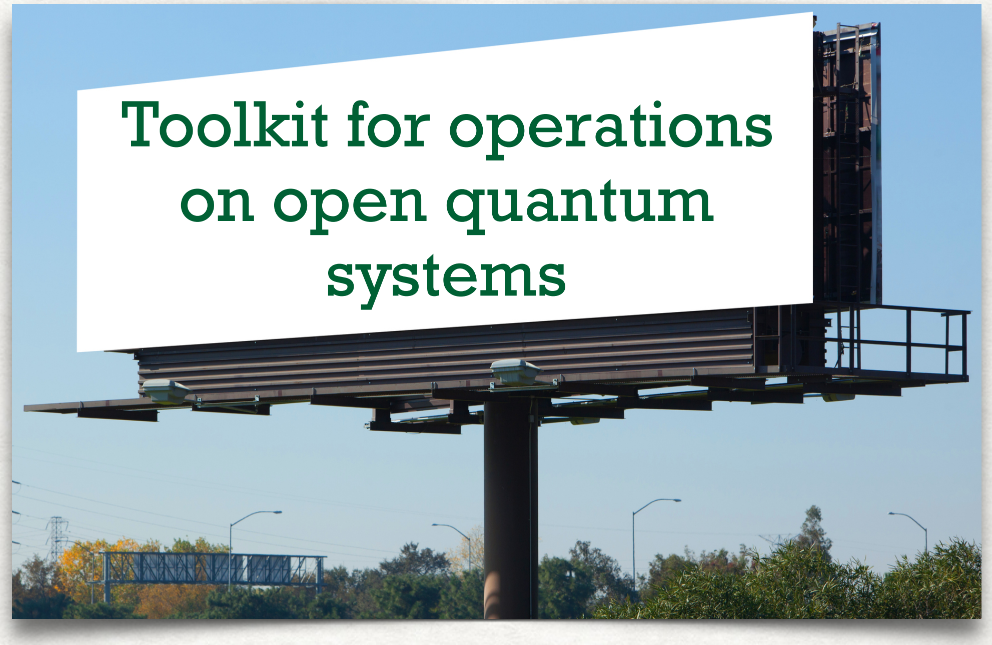

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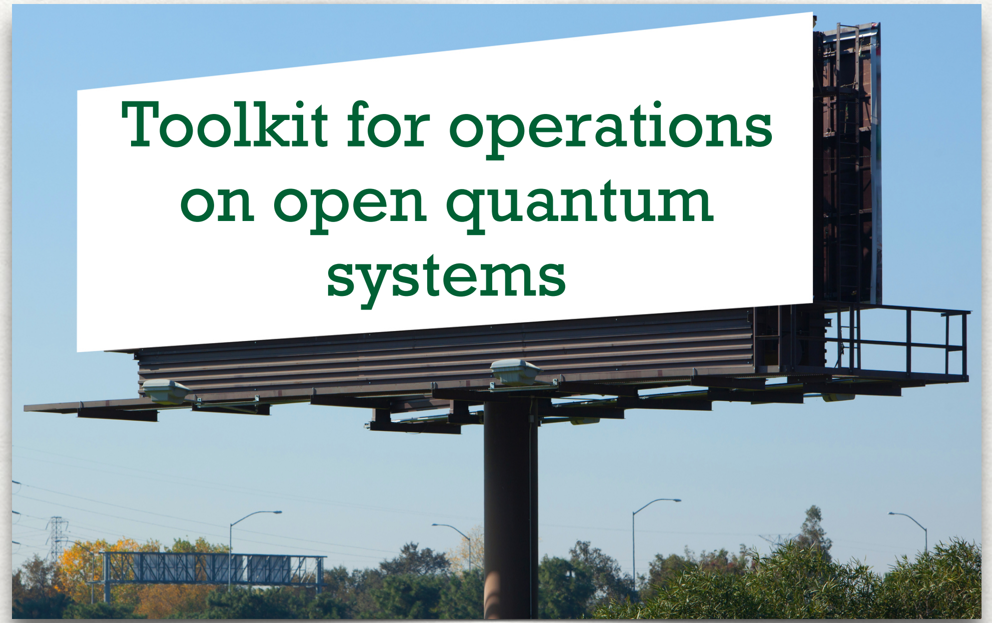

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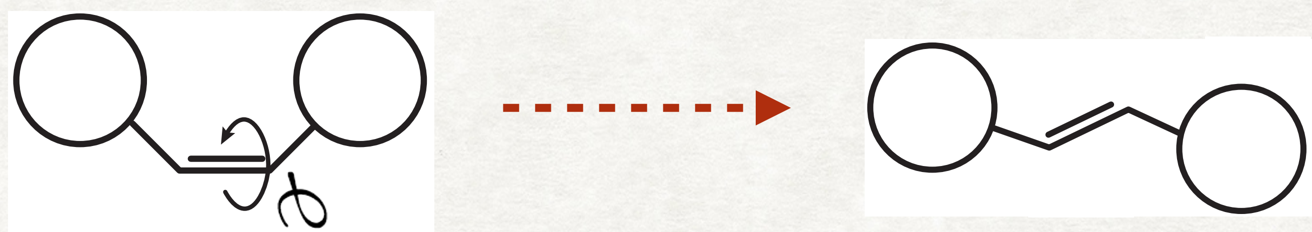
- 

What can thermodynamic resource theories do for you?

Photoisomer background

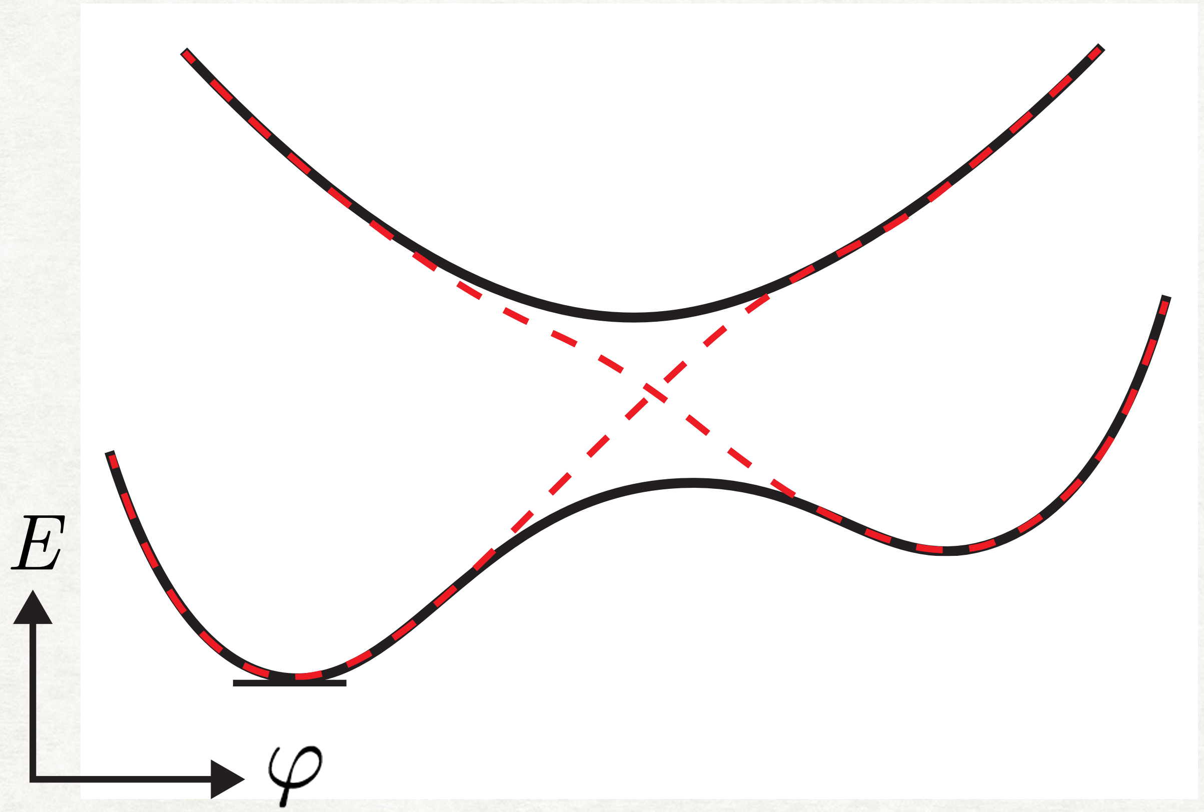


Cis *Trans*

Energy landscape

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

Energy landscape



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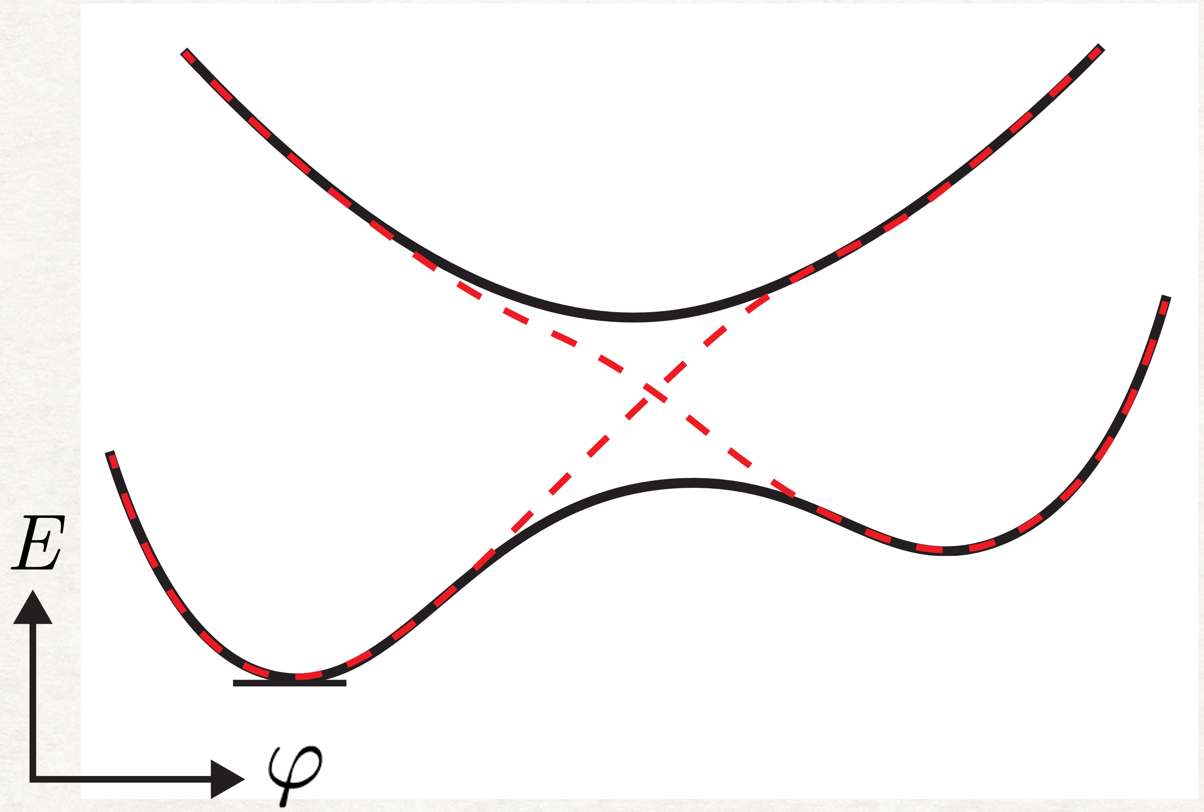

-Rotational coordinate

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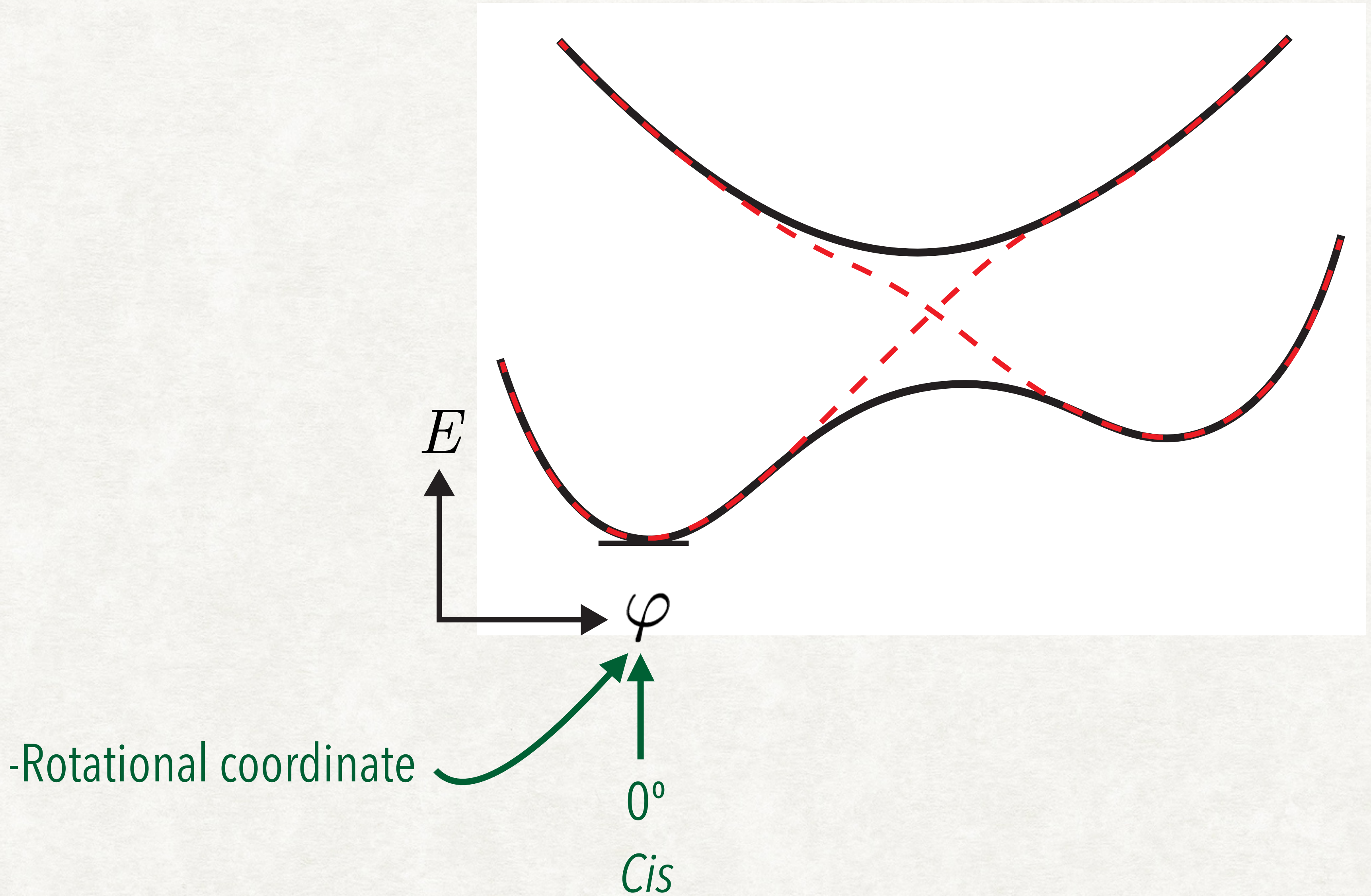

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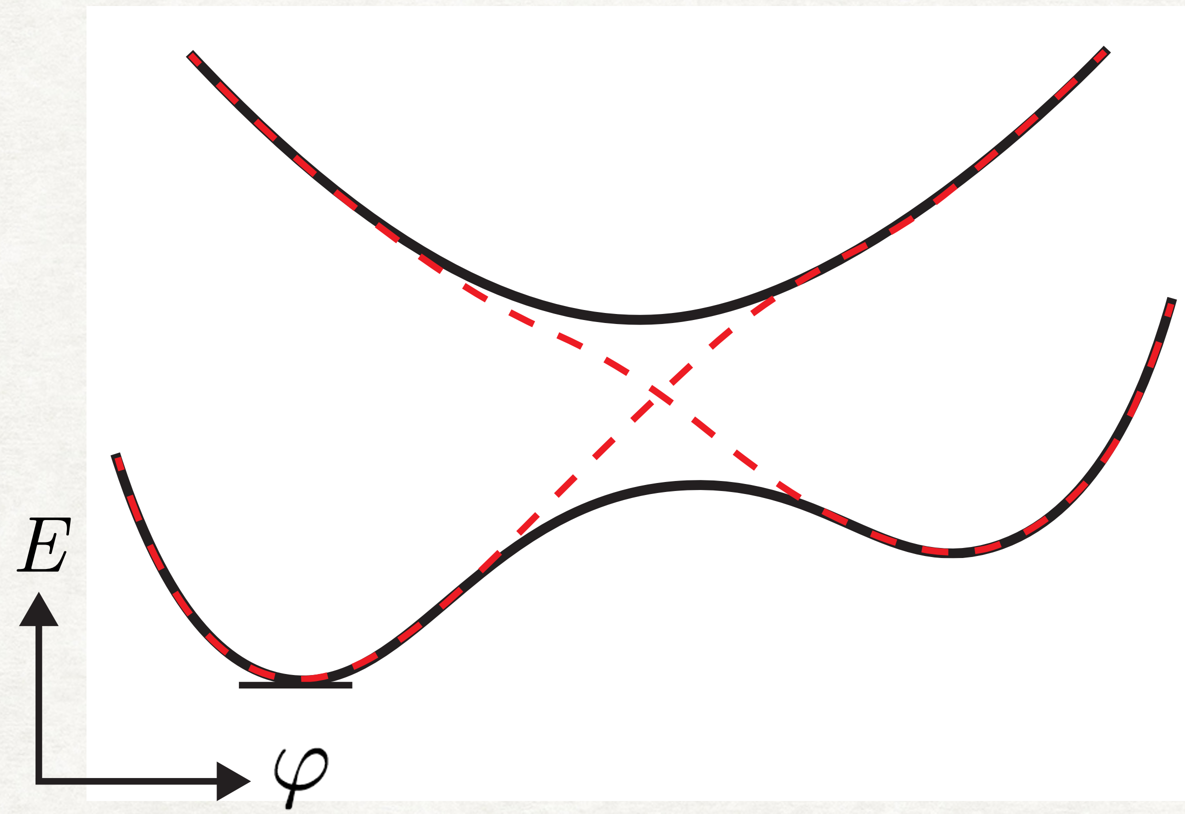

-Rotational coordinate

0º *Cis*

180º *Trans*

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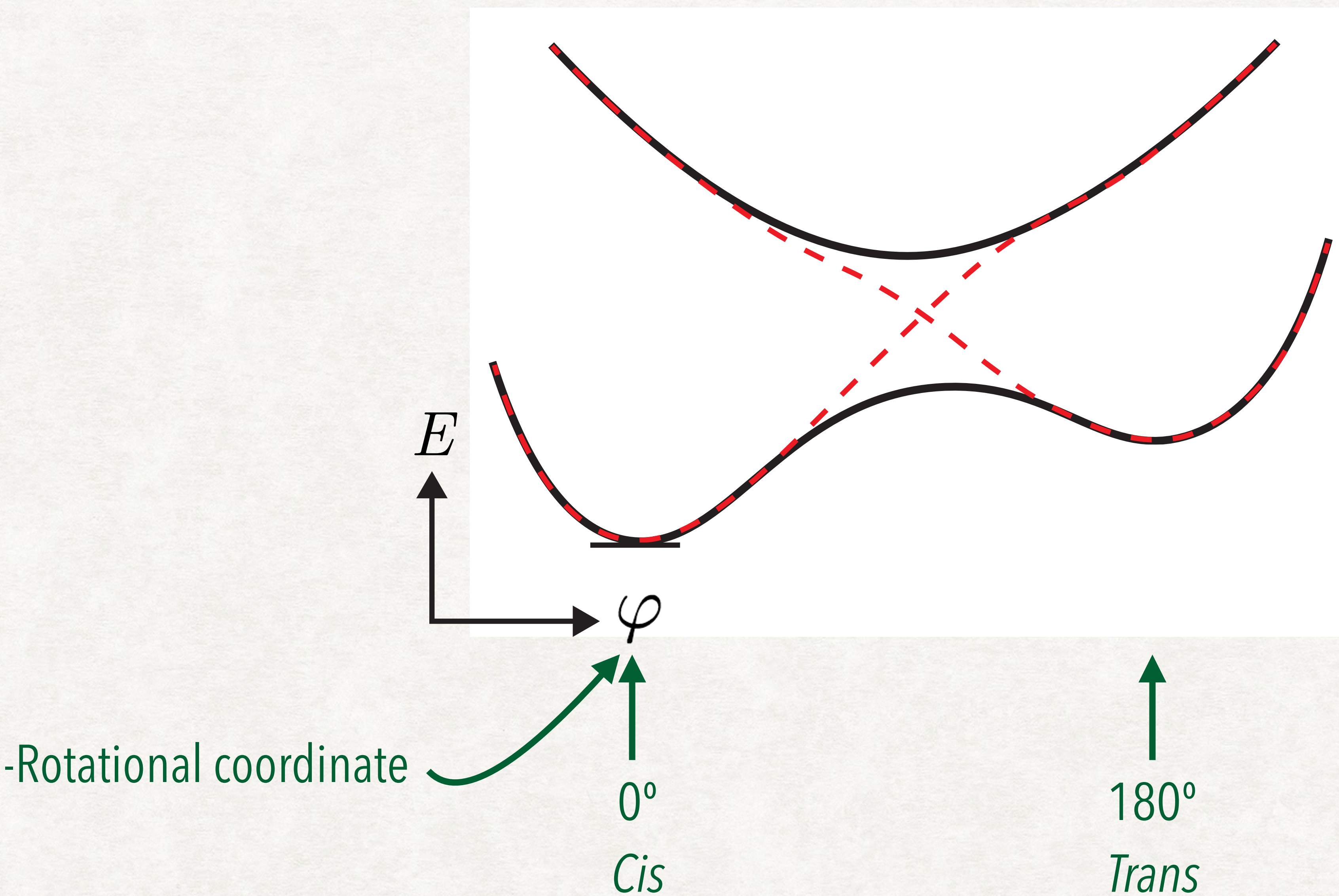
Energy landscape



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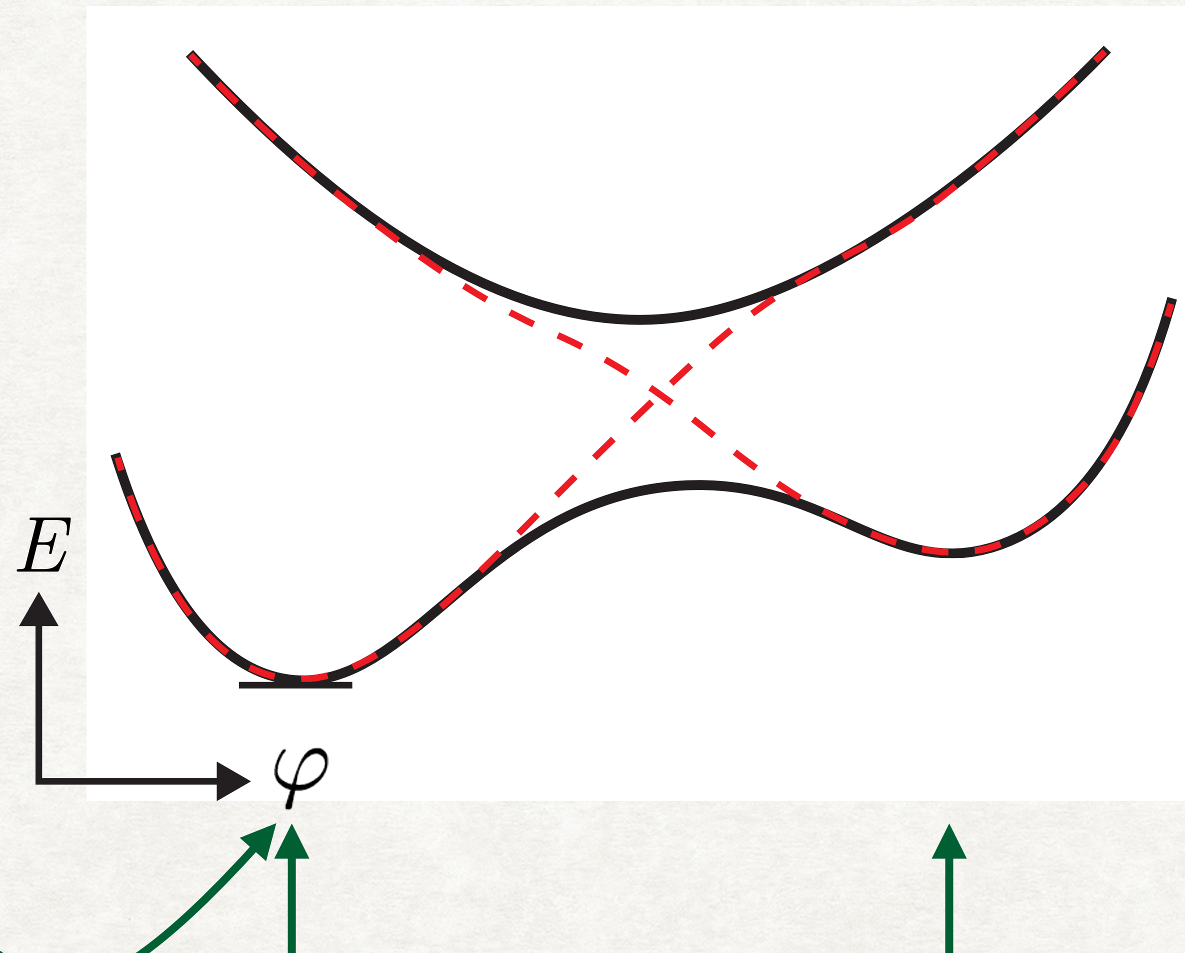

-Rotational coordinate
-Nuclear degree of freedom

0º
Cis

180º
Trans

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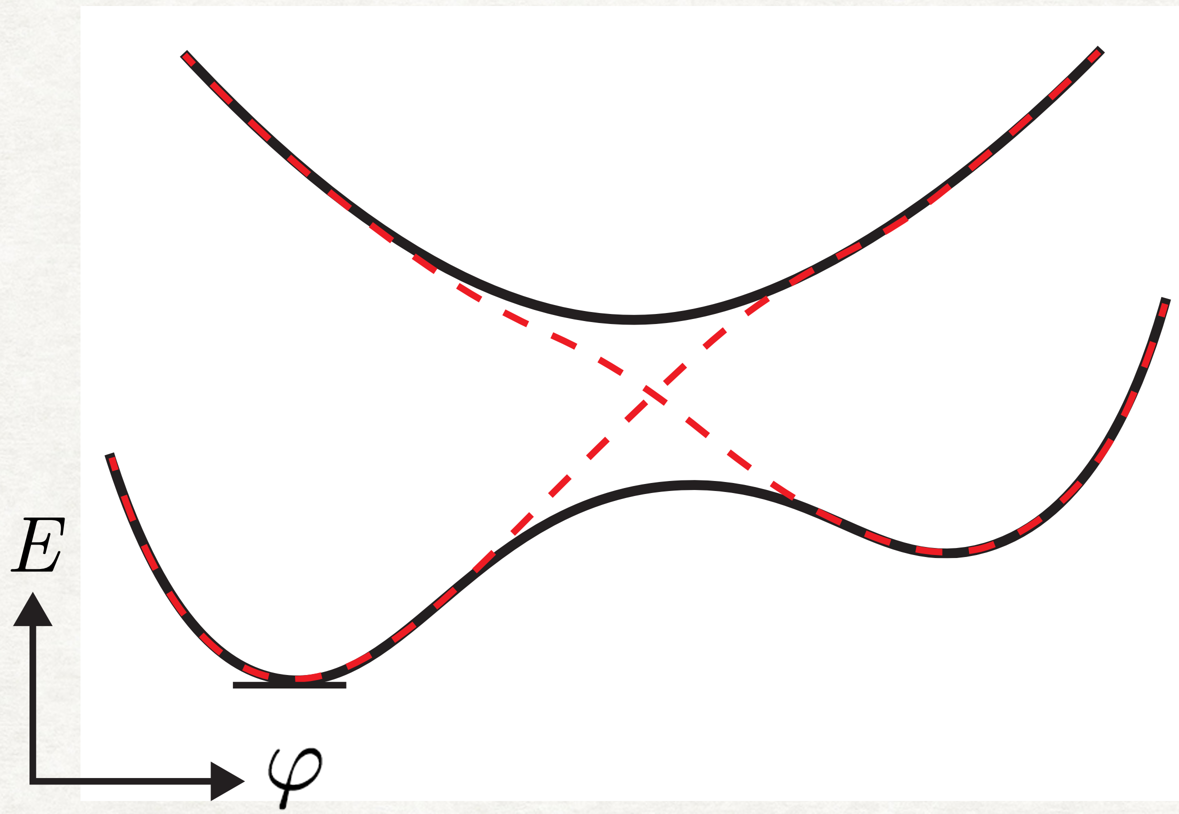
Energy landscape



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

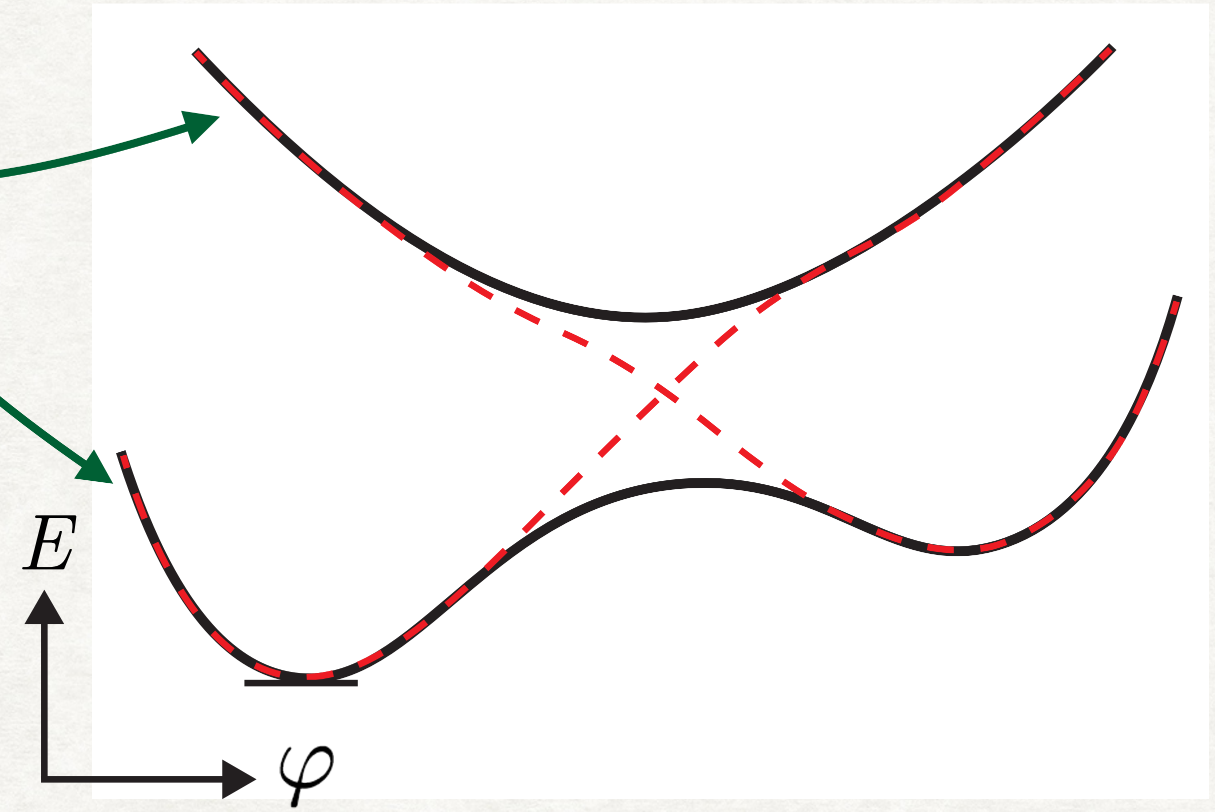
0º
Cis

180º
Trans

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

Energy landscape

-Electronic degree of freedom



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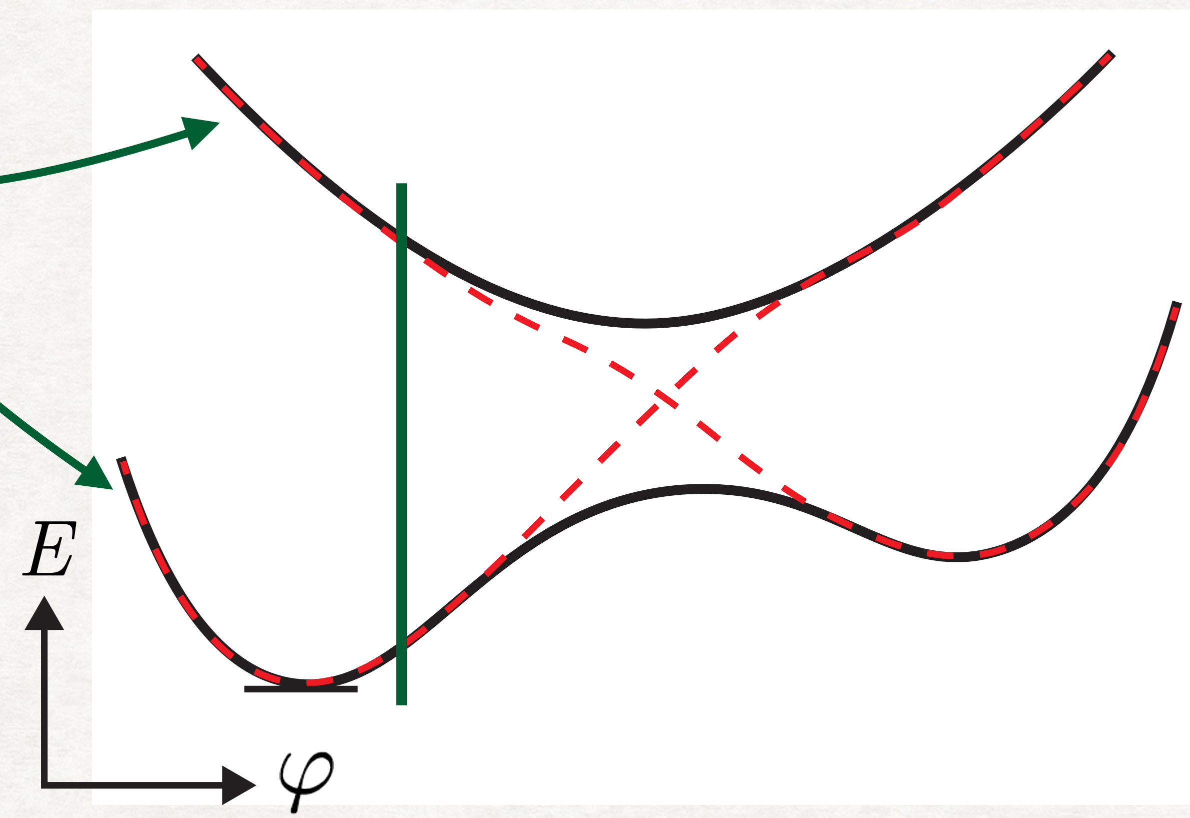

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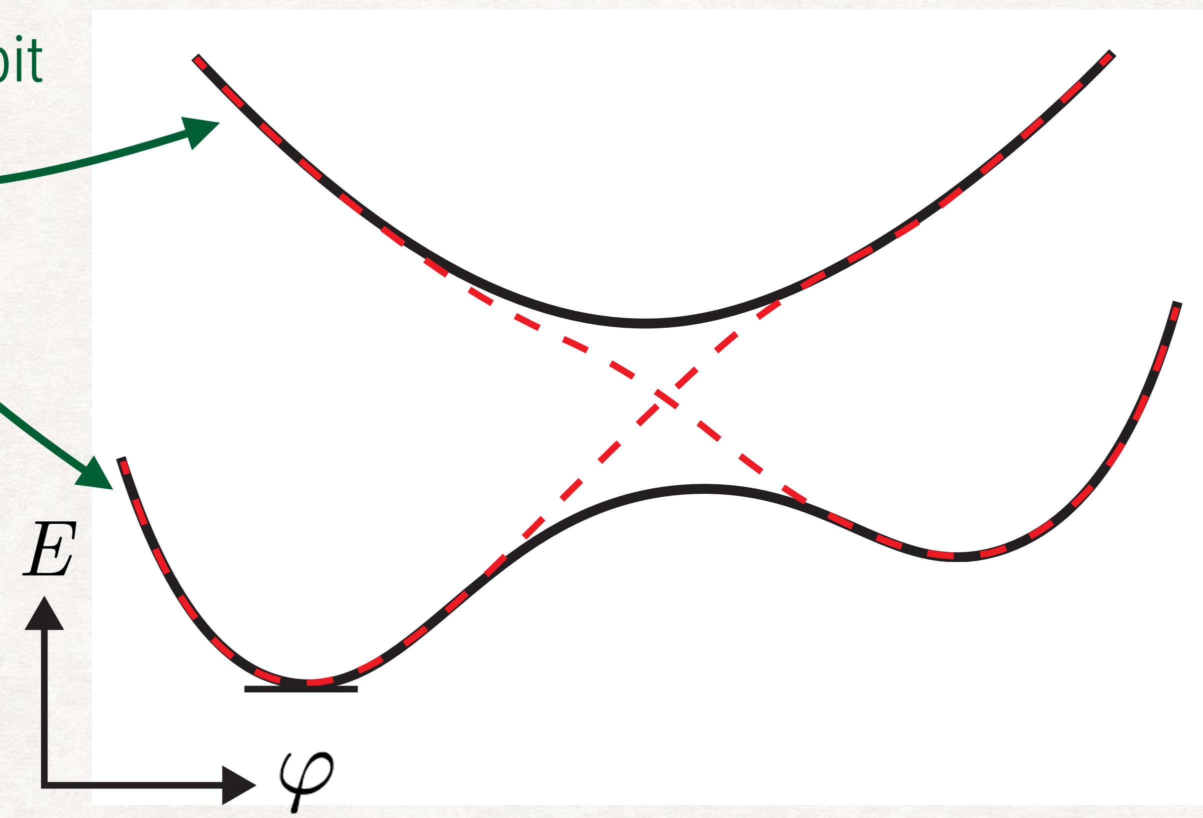
0º
Cis

180º
Trans

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

Energy landscape

-Electronic degree of freedom
-Effective qubit



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Cis

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Trans

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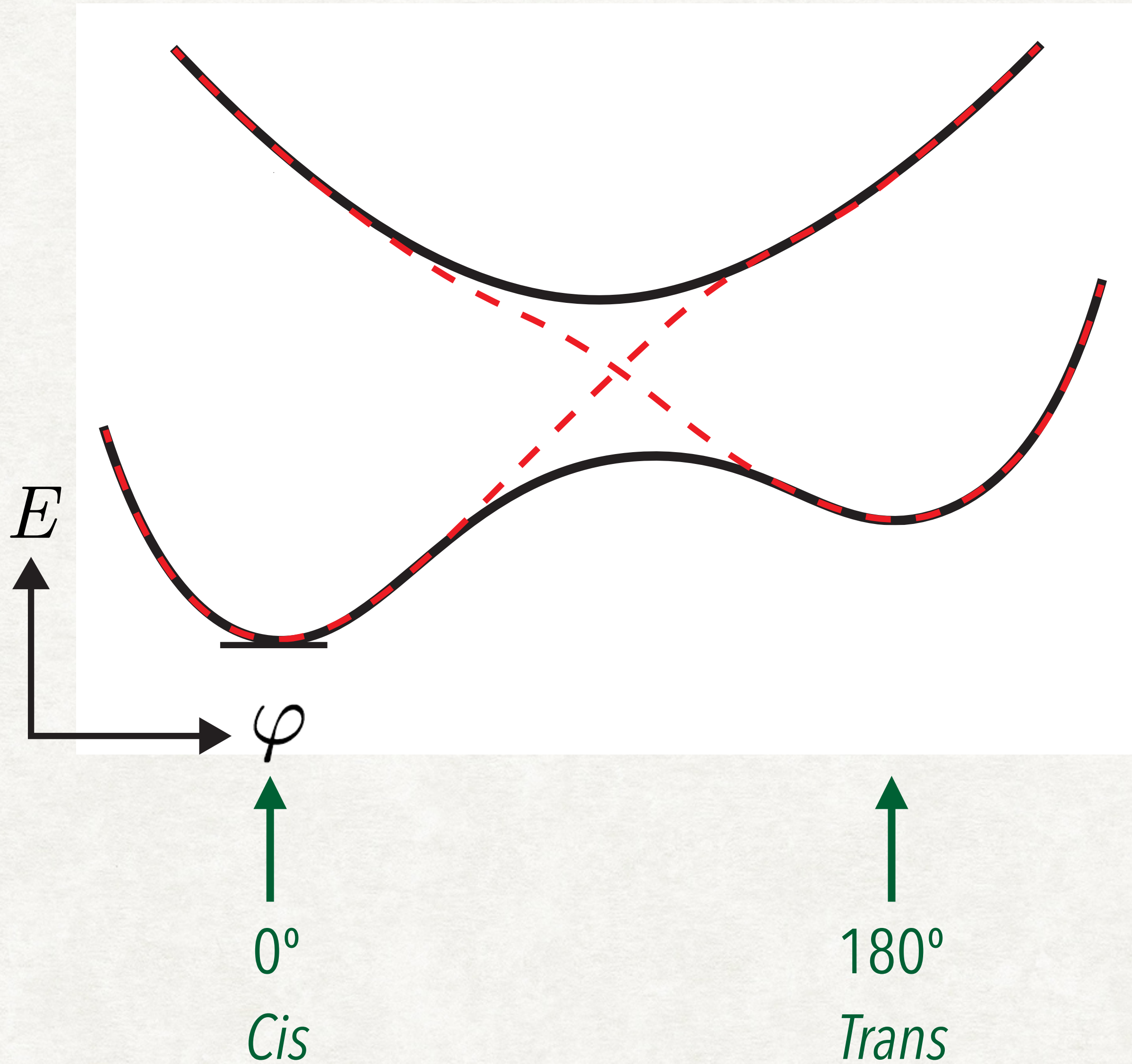

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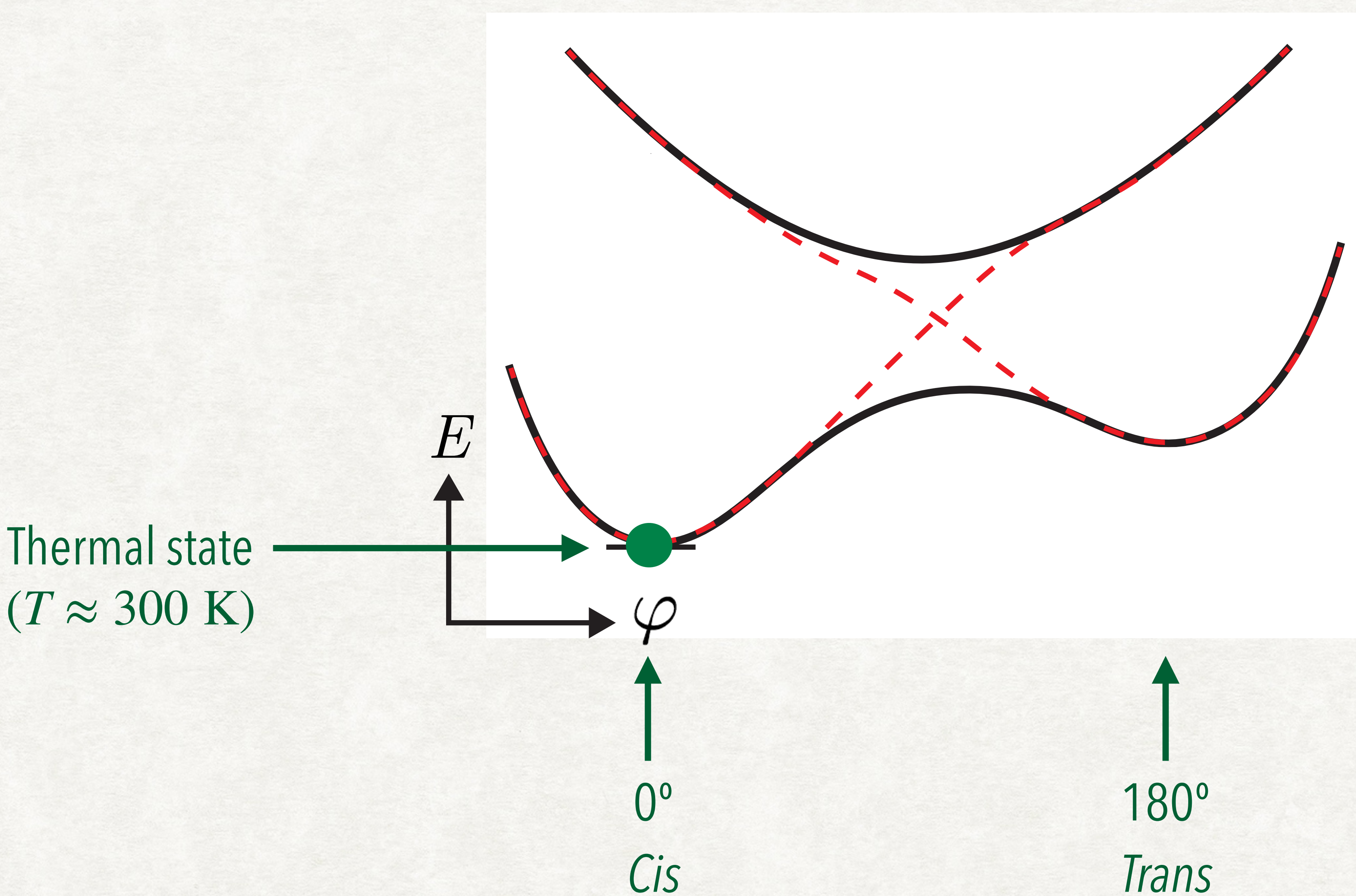

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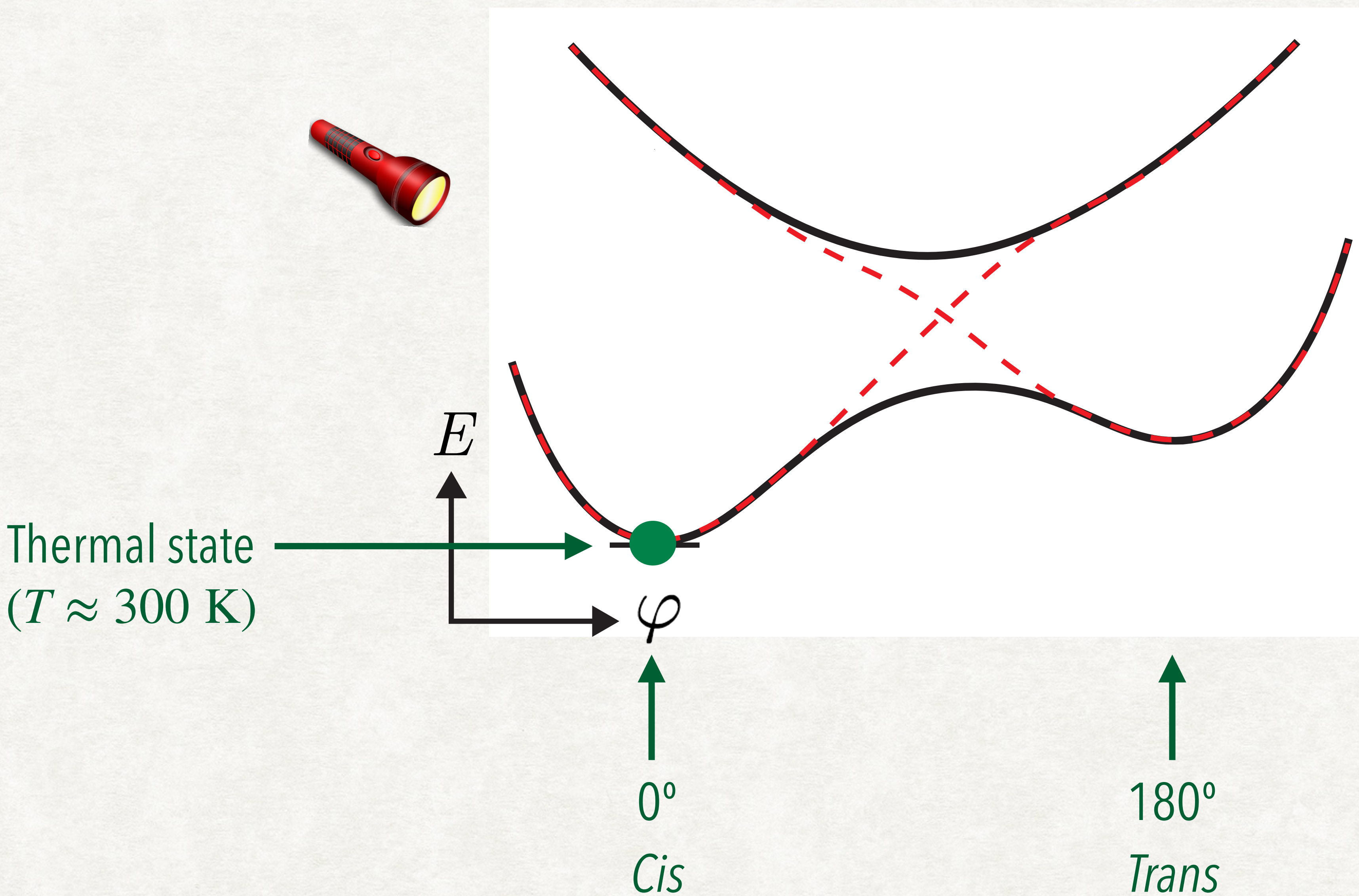

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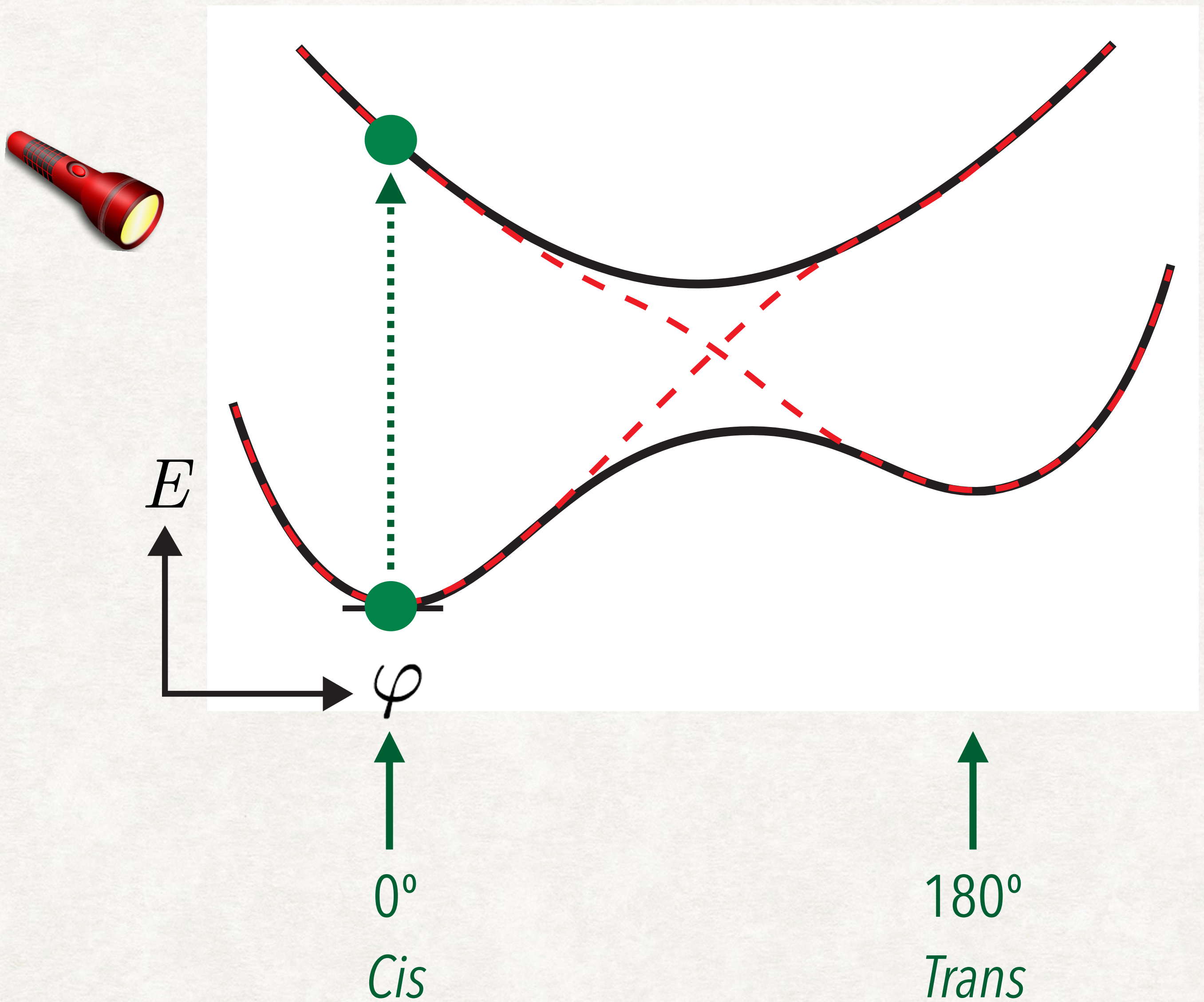

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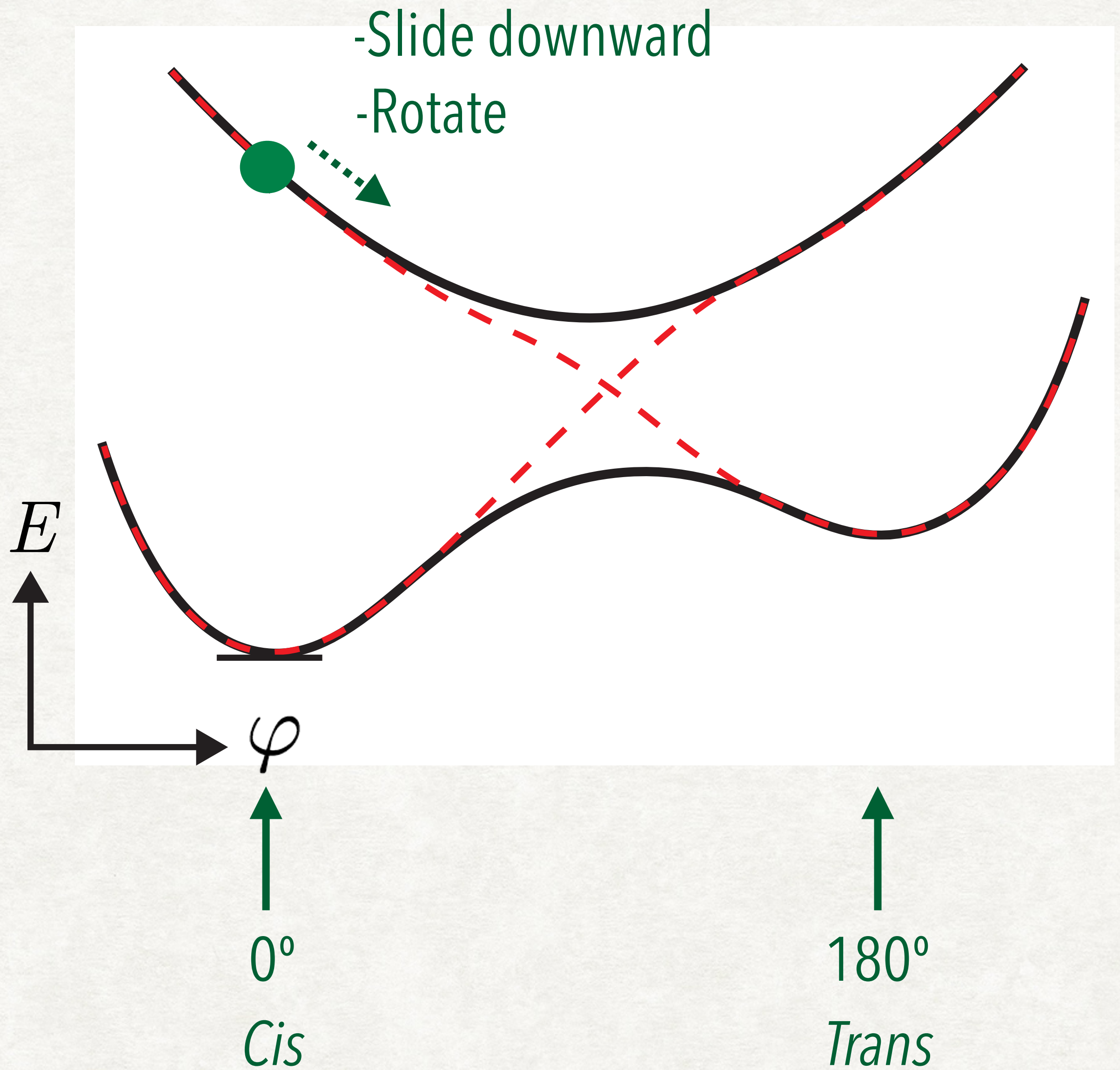

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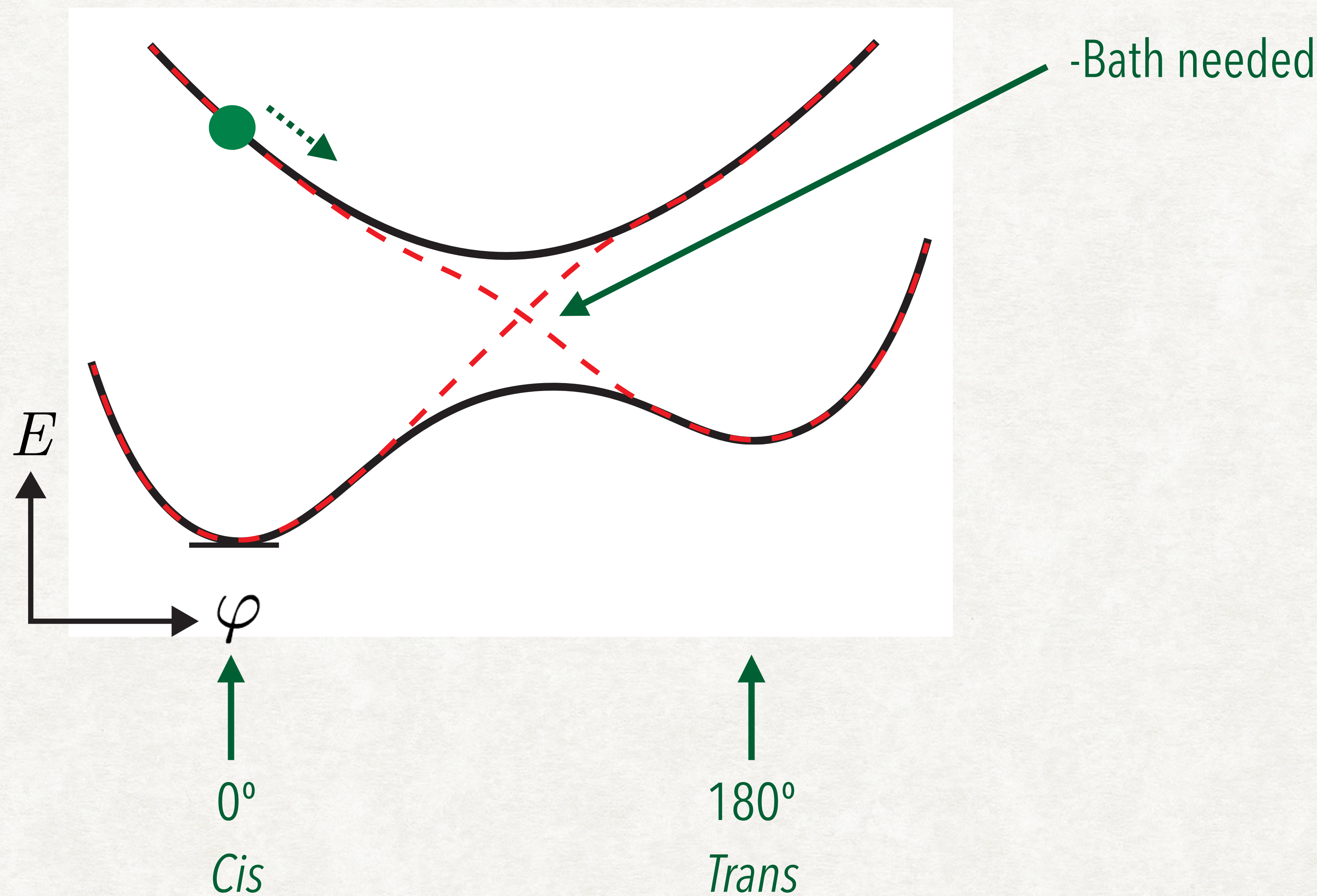

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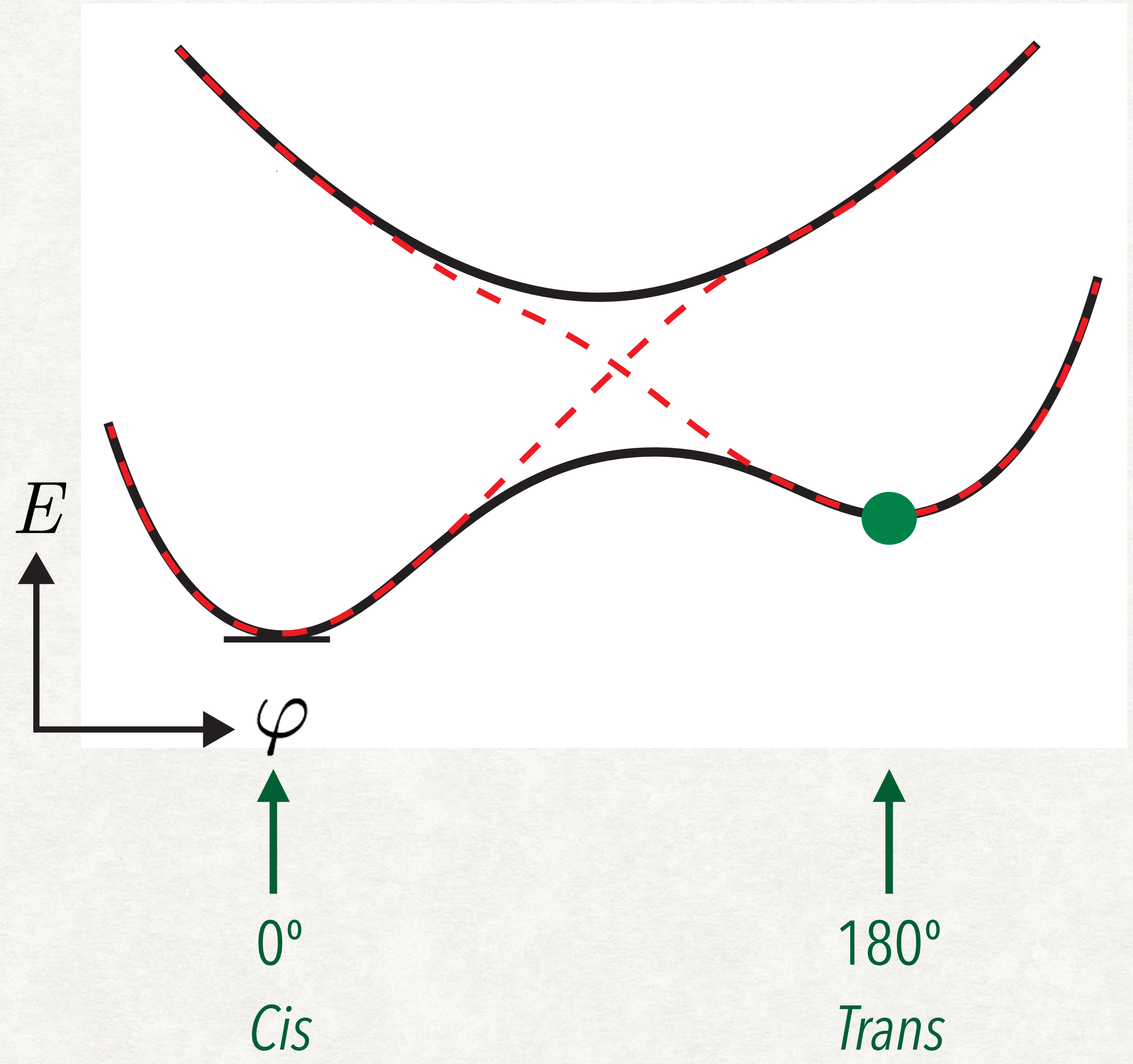

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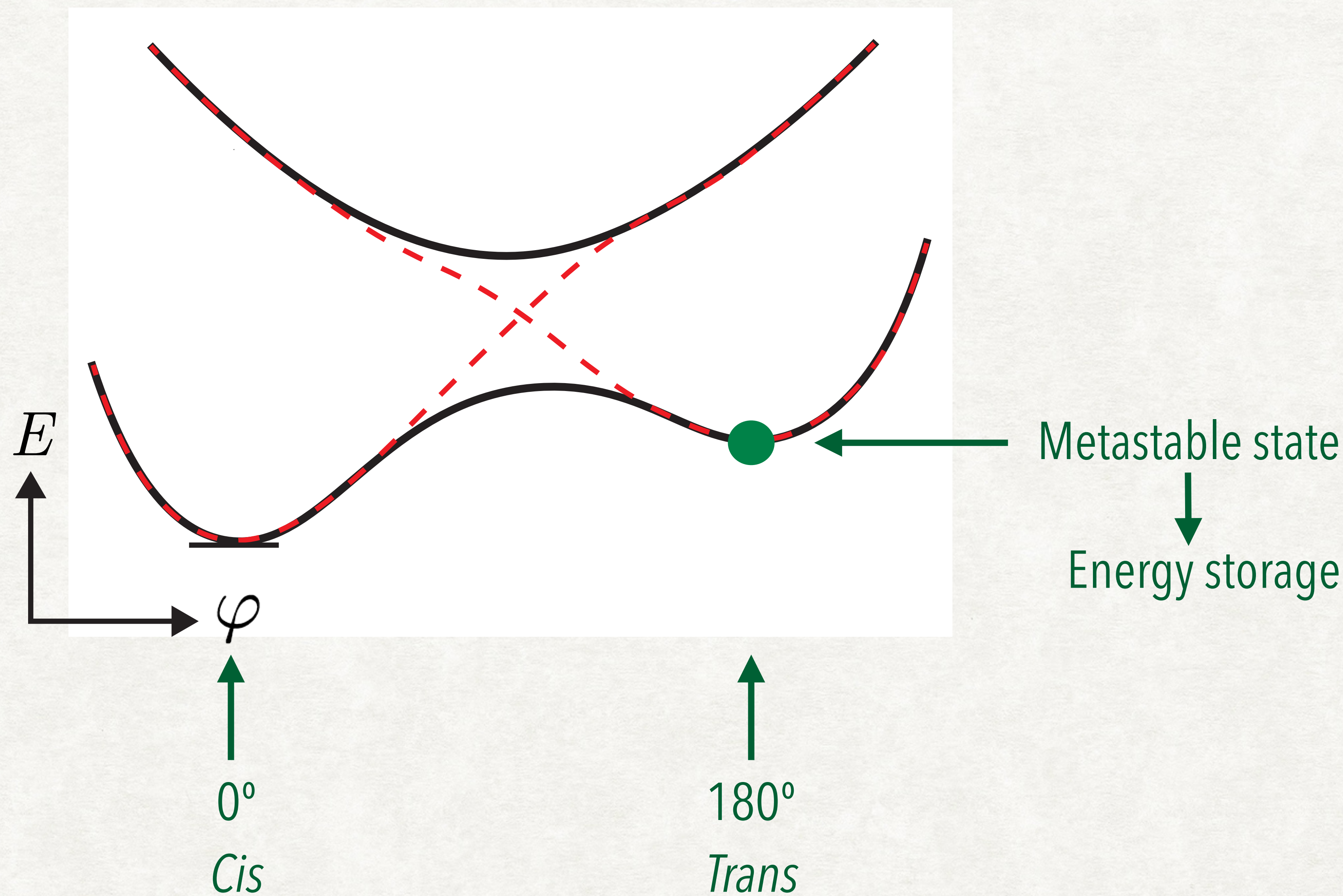

Resource-theory background

Resource theories in general

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- Simple, information-theoretic models

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  for any situation in which only certain systems are accessible
  and only certain operations can be performed

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- <u>Example</u> (thermodynamics in a temperature-T atmosphere):

$$e^{-H/(k_{\mathrm{B}}T)}/Z$$

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- Example: conserve energy (obey the first law)

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- Everything not free is a **resource**.

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free operations

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

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- Everything not free is a **resource**.
  - Example: athermal states ⟶ $\rho \neq e^{-H/(k_B T)}/Z$

How to model your favorite system in a thermodynamic resource theory

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  Janzing *et al.*, Int. J. Theor. Phys. **39**, 12 (2000).
  Brandão *et al.*, Phys. Rev. Lett. **111**, 250404 (2013).

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

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

How to model your favorite system in a thermodynamic resource theory

- Earliest literature: 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**

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- Tend to thermalize states

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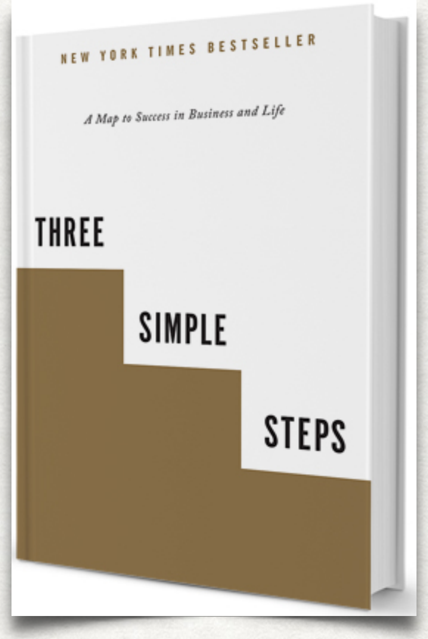
- Each free operation consists of  .

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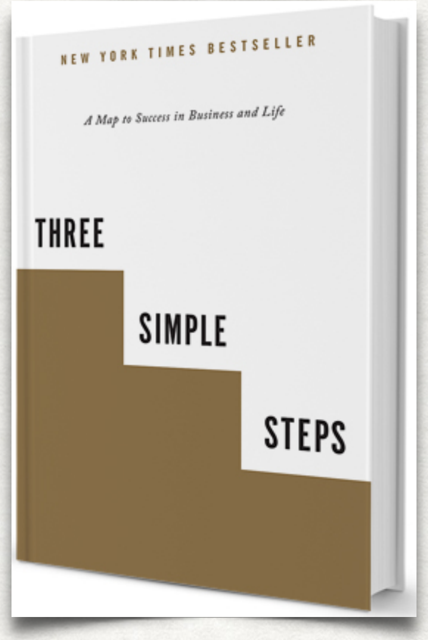
- Each free operation consists of  .

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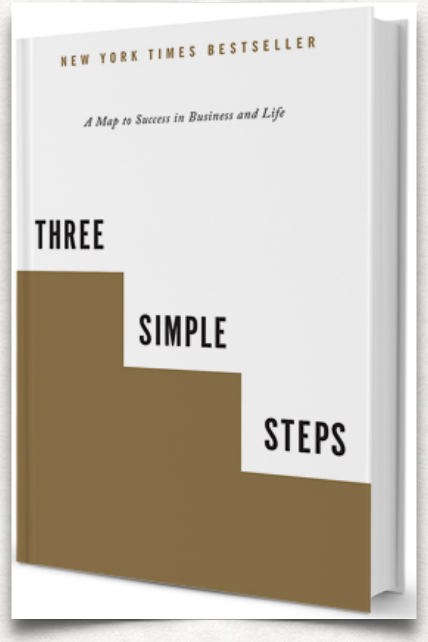
- Each free operation consists of  .

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$$U = e^{-iH_{\text{int}}t}$$

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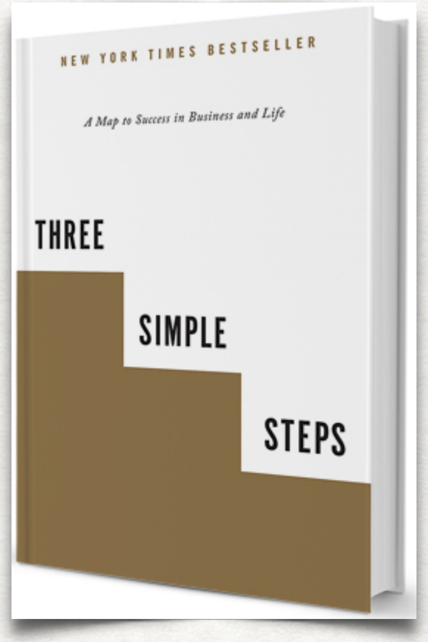
- Each free operation consists of  .

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

- $(\rho, H) \mapsto$

Free operations

- $(\rho, H) \mapsto \left(\qquad \rho \otimes \frac{e^{-\beta H_{\mathrm{B}}}}{Z} \qquad \right)$

Free operations

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$$\rotatebox{90}{=}$$

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

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

~First law of thermodynamics

Free operations

- $(\rho, H) \mapsto \left(\mathrm{Tr}_a\left(U \left[\rho \otimes \frac{e^{-\beta H_B}}{Z} \right] U^\dagger \right), \qquad \right)$

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    $\shortparallel$

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Free operations

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

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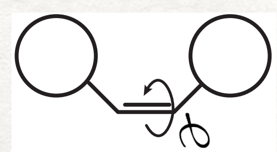
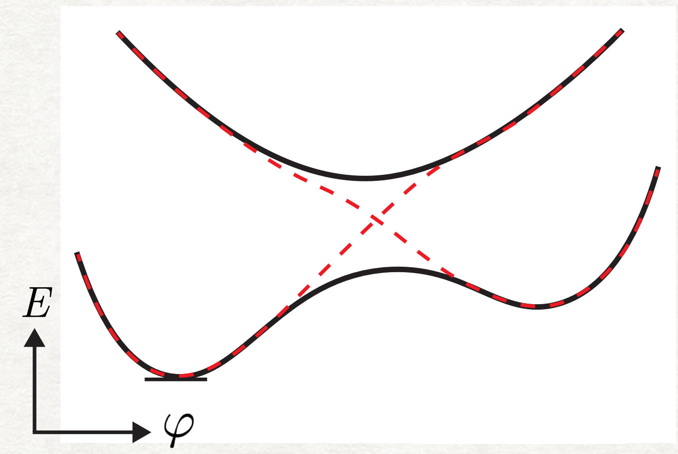
Modeling the photoisomer in the resource theory



NYH and Limmer, arXiv:1811.06551 (2018).

Modeling the photoisomer in the resource theory

- Hilbert space: $\mathscr{H}_{\text{mol}}$



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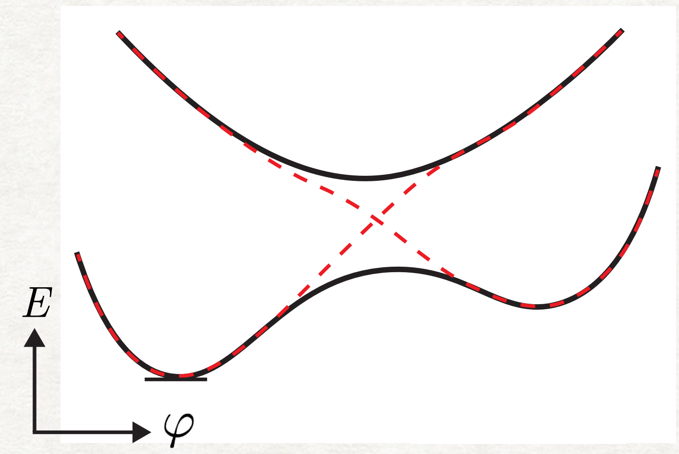
- Hilbert space: $\mathscr{H}_{\mathrm{mol}} = \mathscr{H}_{\mathrm{elec}} \otimes \mathscr{H}_{\mathrm{nuc}}$



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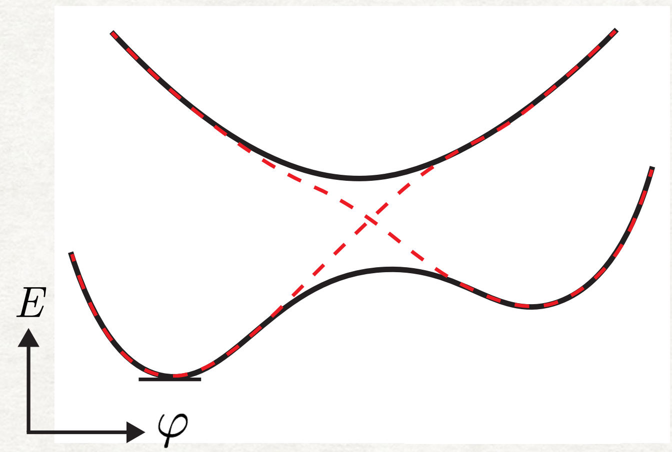

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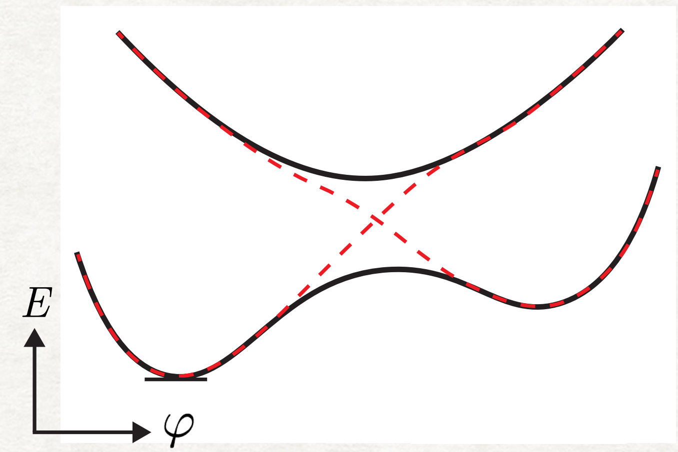

- Hamiltonian: $H_{\text{mol}} =$ $1_{\text{elec}} \otimes \frac{\ell_\varphi^2}{2m}$

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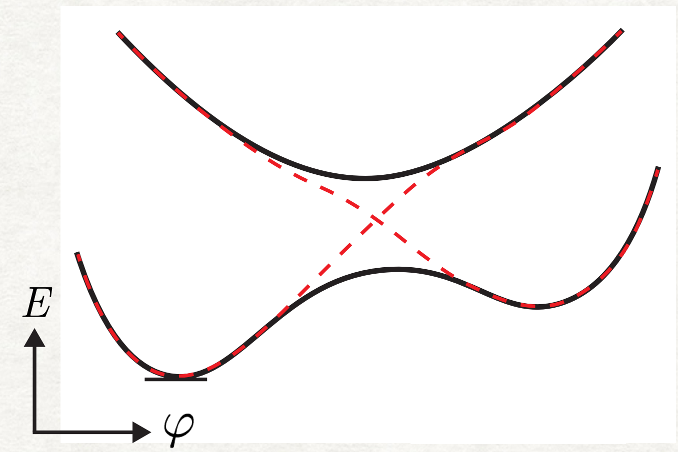

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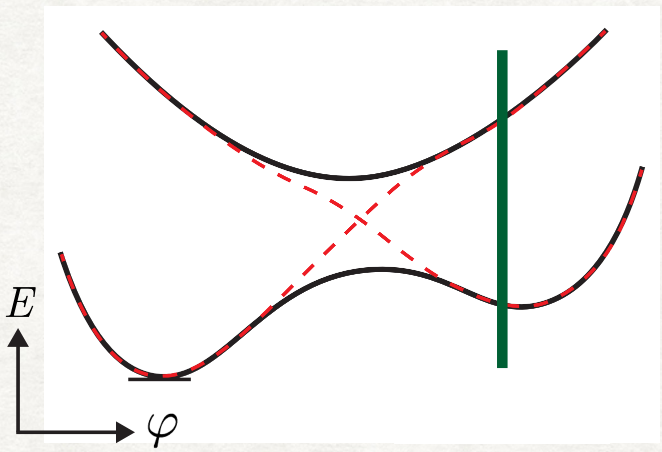

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Modeling photoisomerization’s steps with thermal operations

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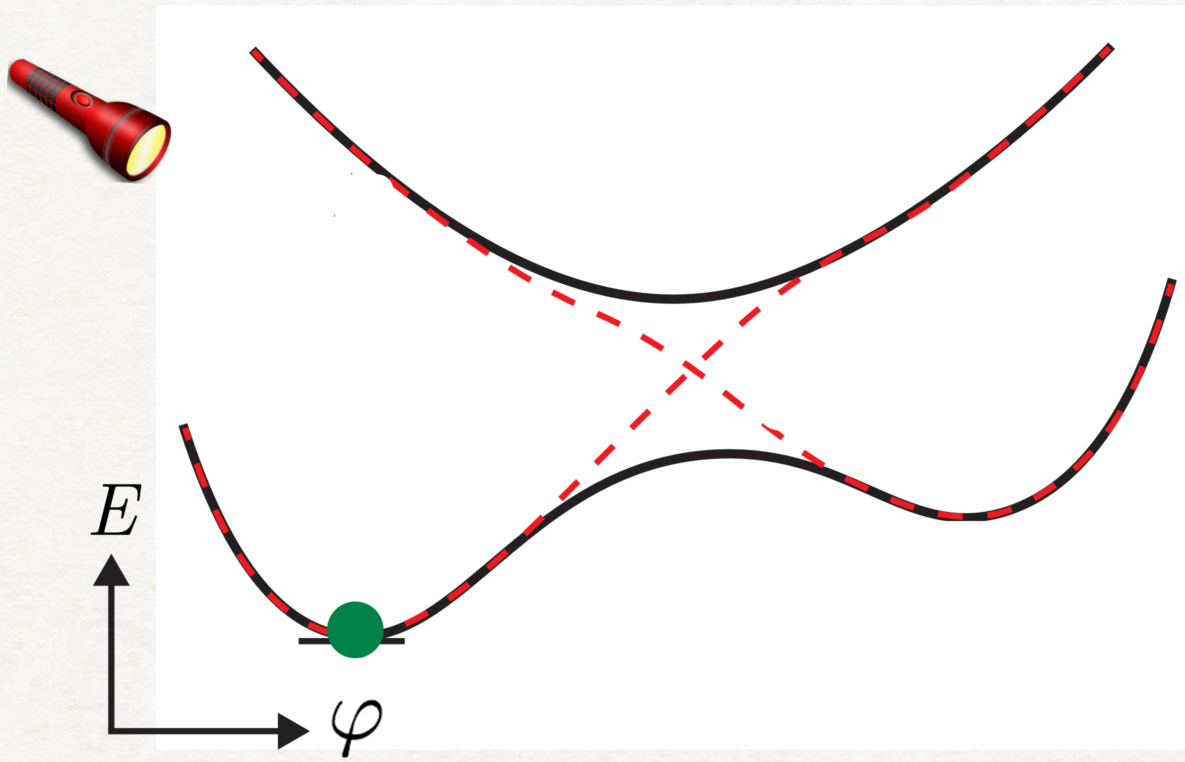

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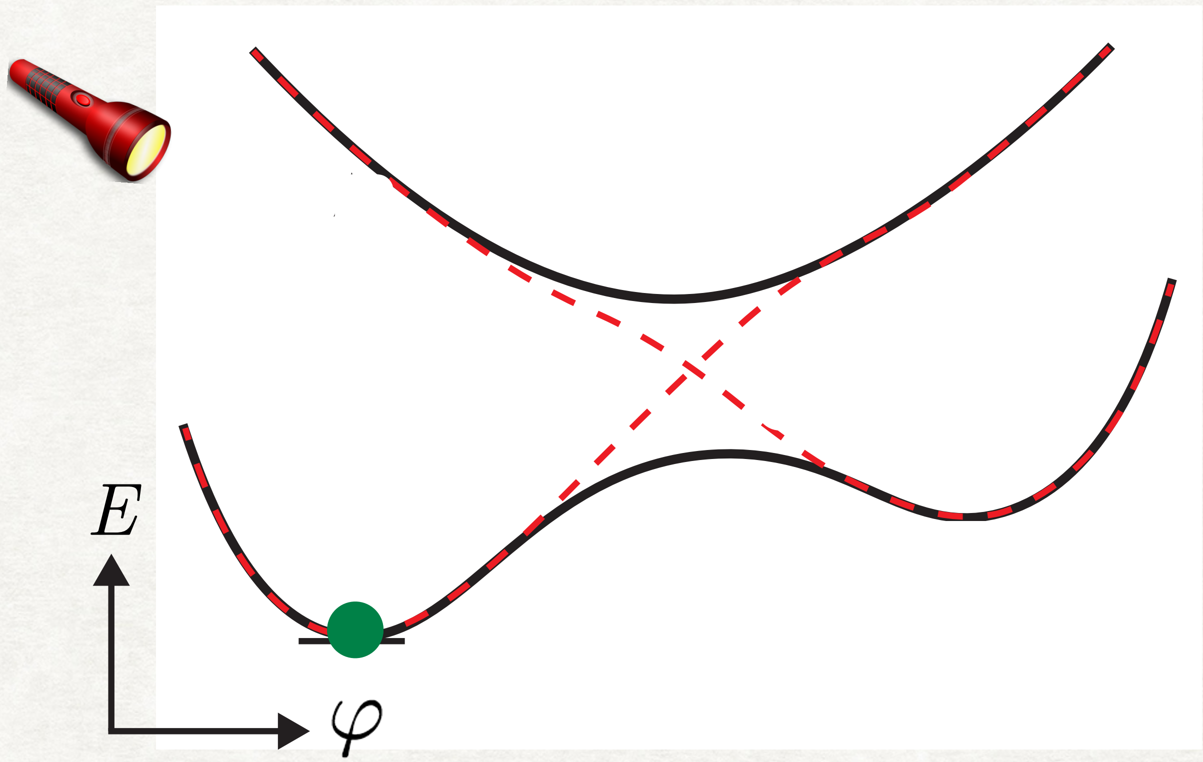

Initial molecule-and-laser state: $e^{-\beta H_{\rm elec}}/Z_{\rm elec} \otimes |\varphi = 0\rangle\langle\varphi = 0| \otimes \rho_{\rm laser}$

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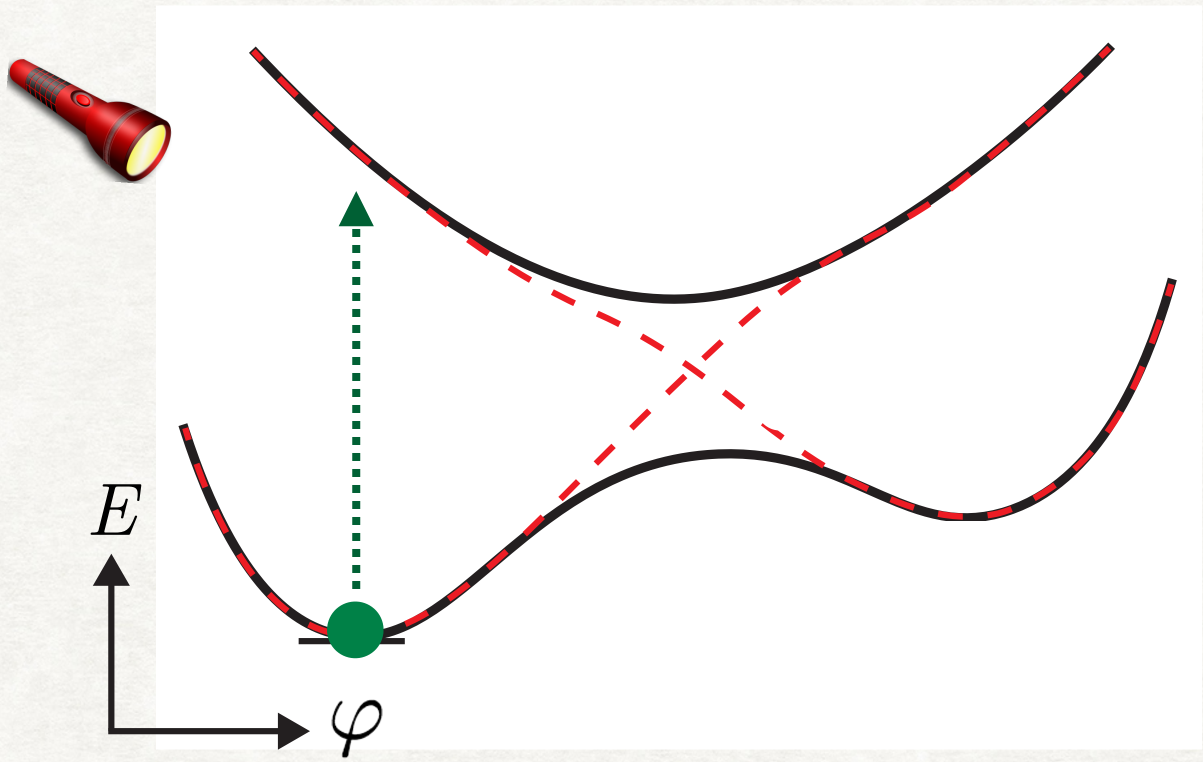

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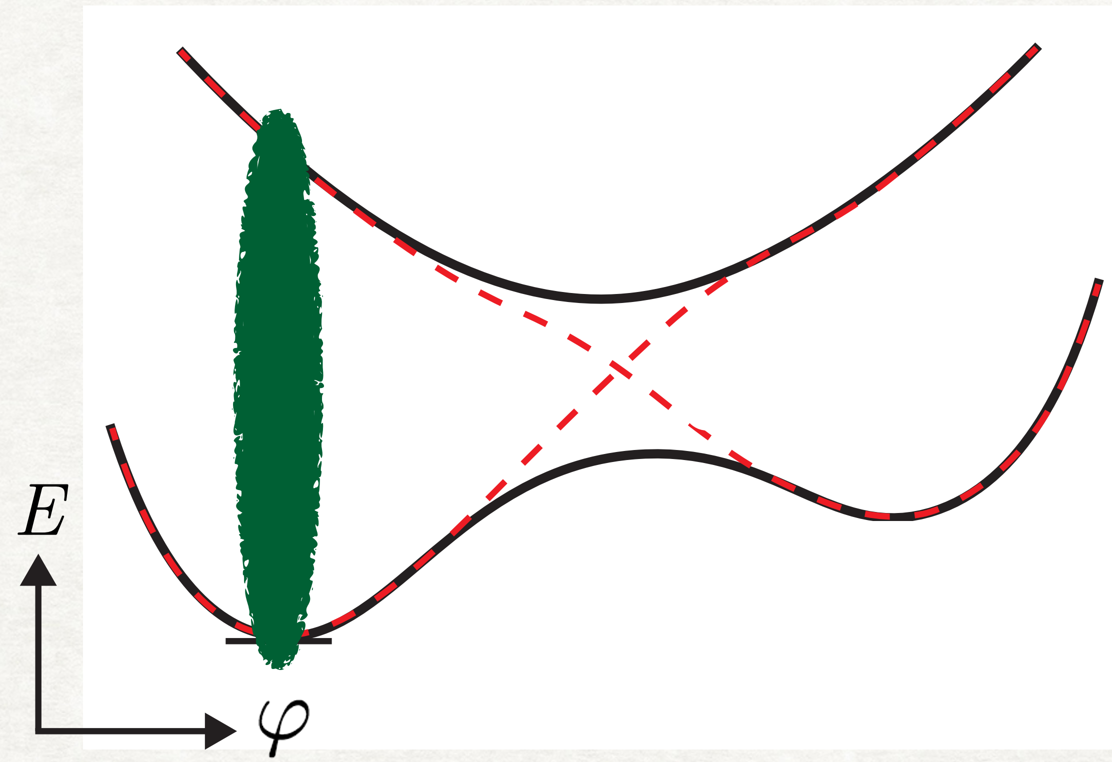

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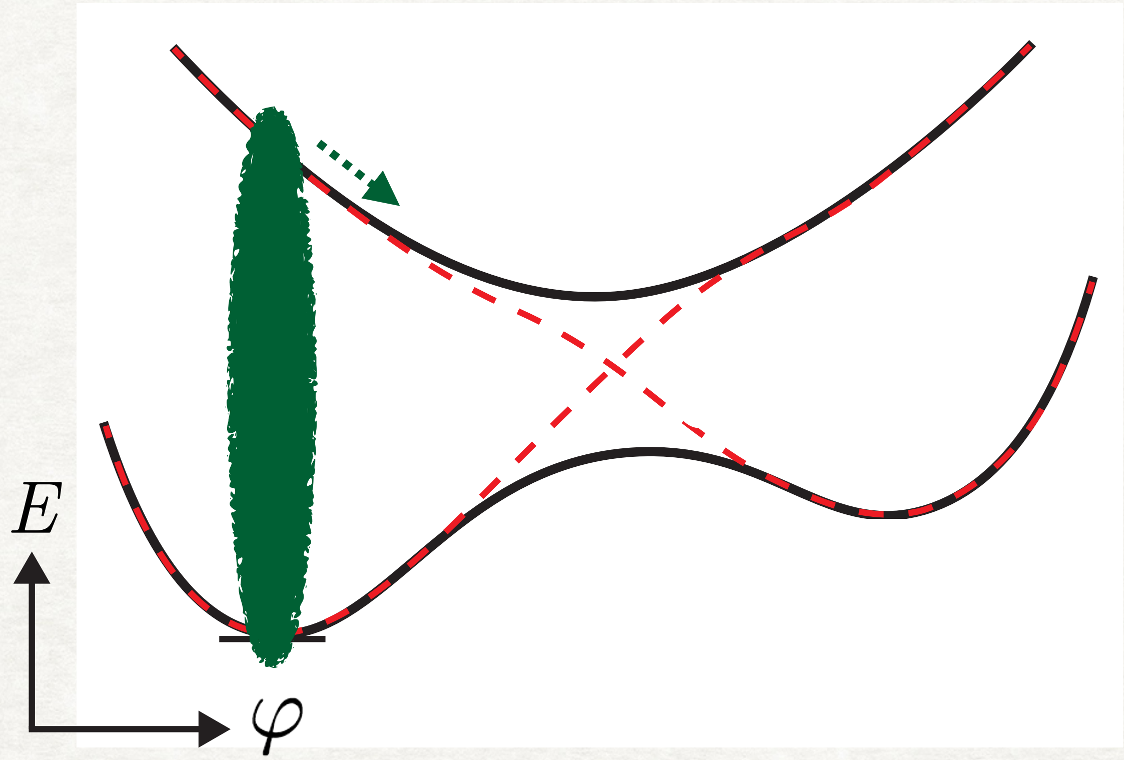

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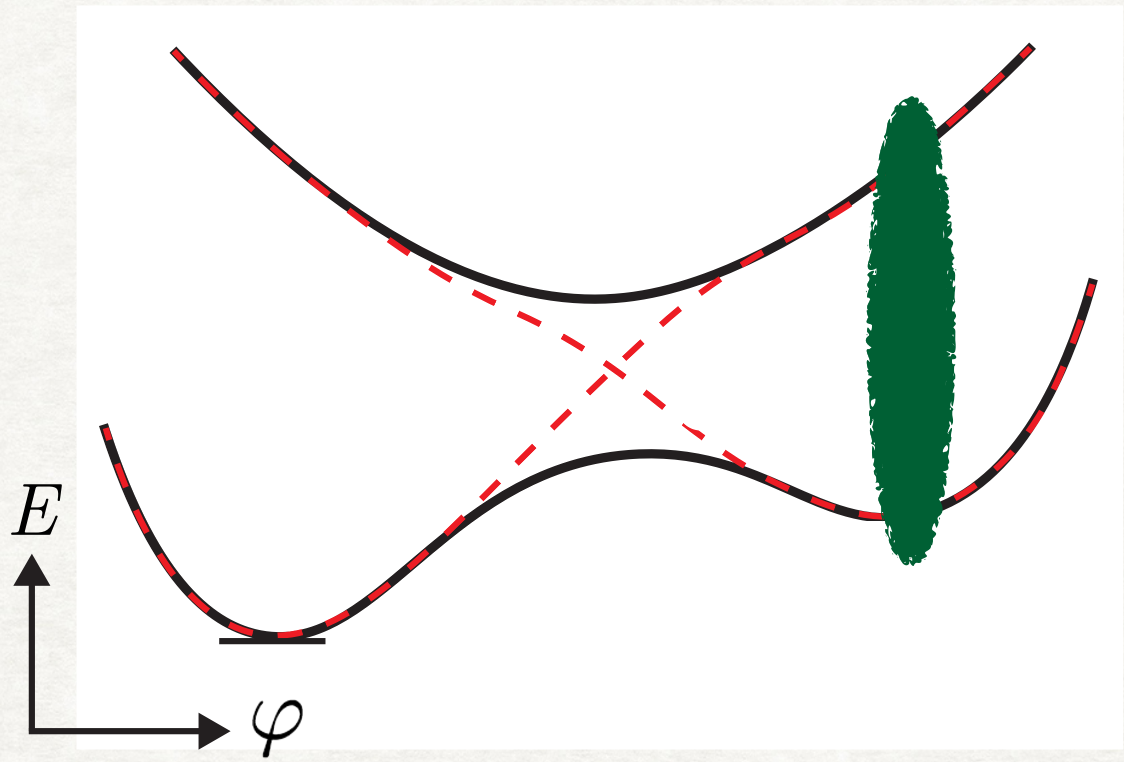

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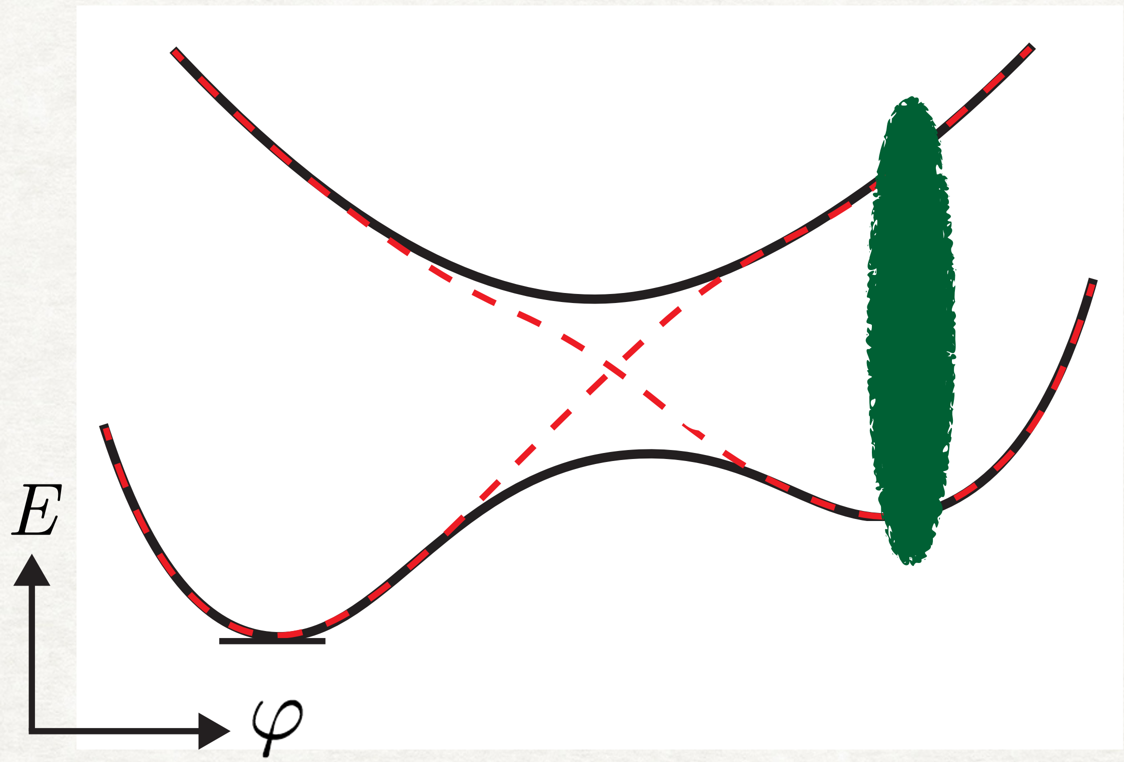
$\rho_{\text{elec}} \otimes |\varphi = 0\rangle\langle\varphi = 0|$ $\mapsto$ (rotation)

$\sigma_{\text{elec}} \otimes |\varphi = \pi\rangle\langle\varphi = \pi|$

Question



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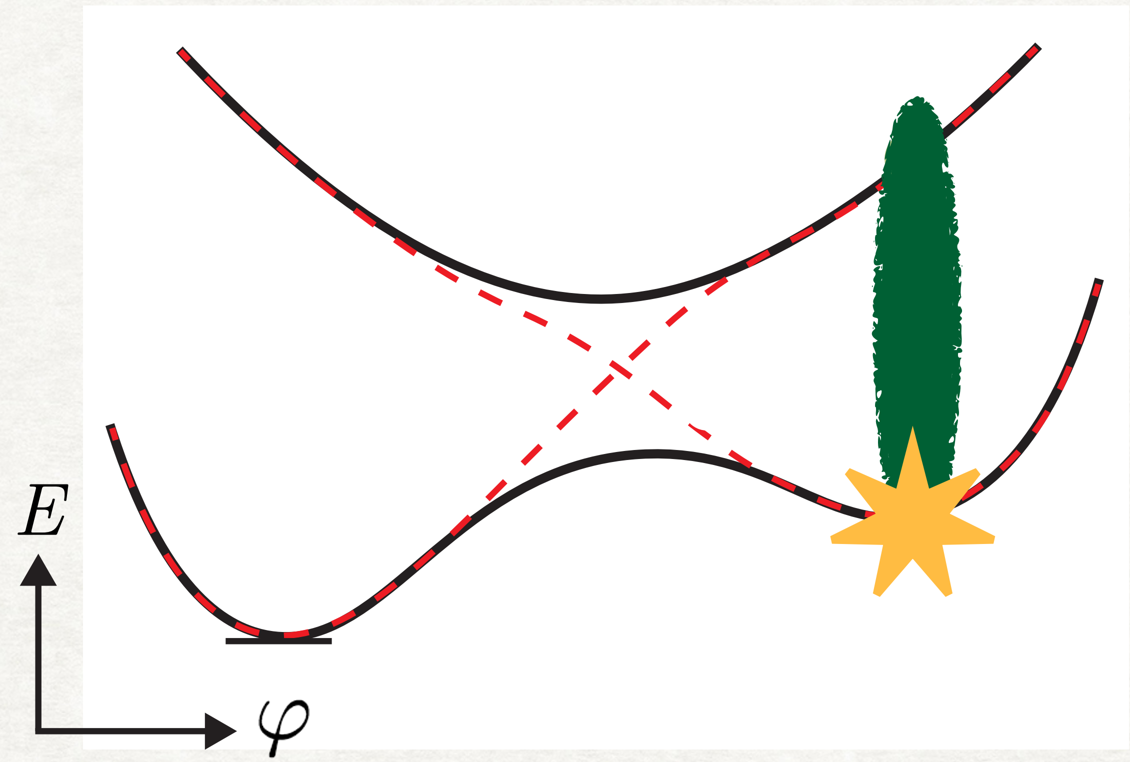

- How large a probability weight can the final state have on the lower level?

Tool:

Second laws of thermodynamics

Theorems proved with help from the resource theory

Second law in conventional thermodynamics

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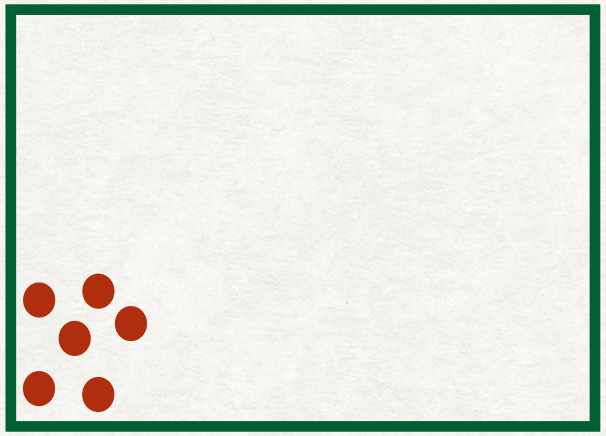

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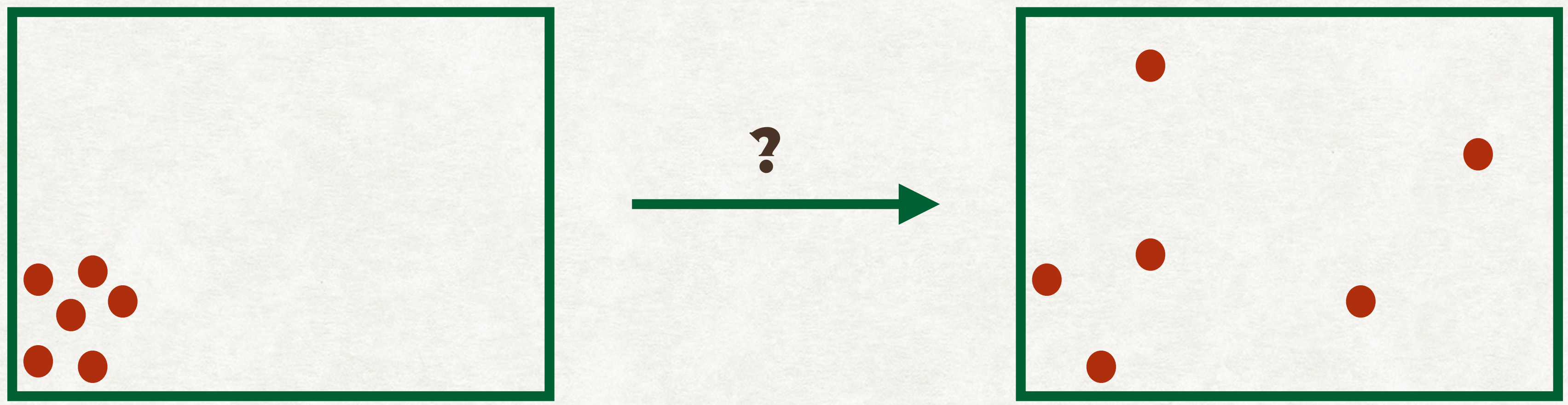

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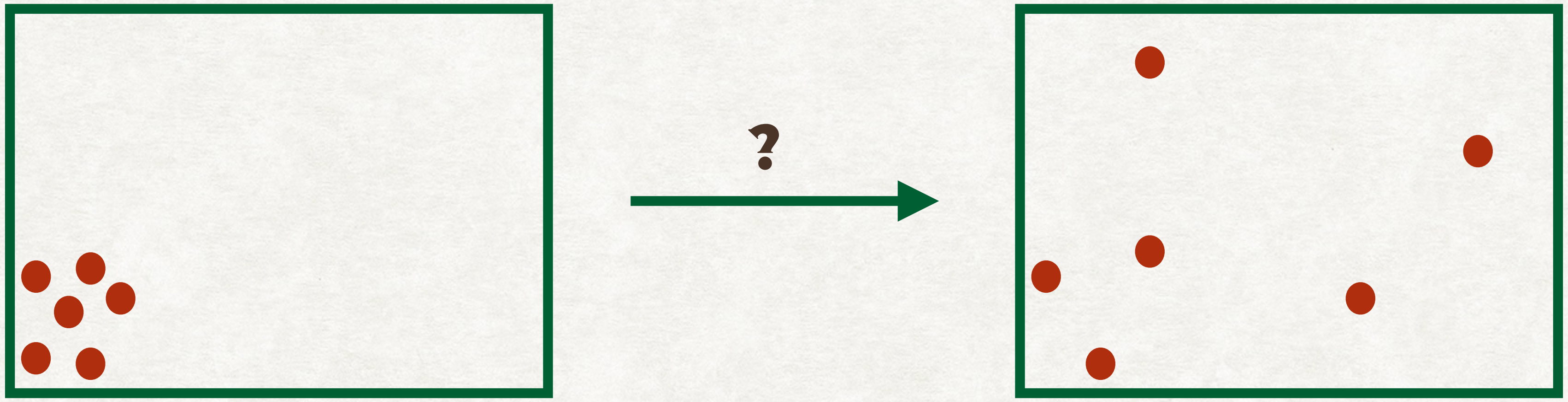

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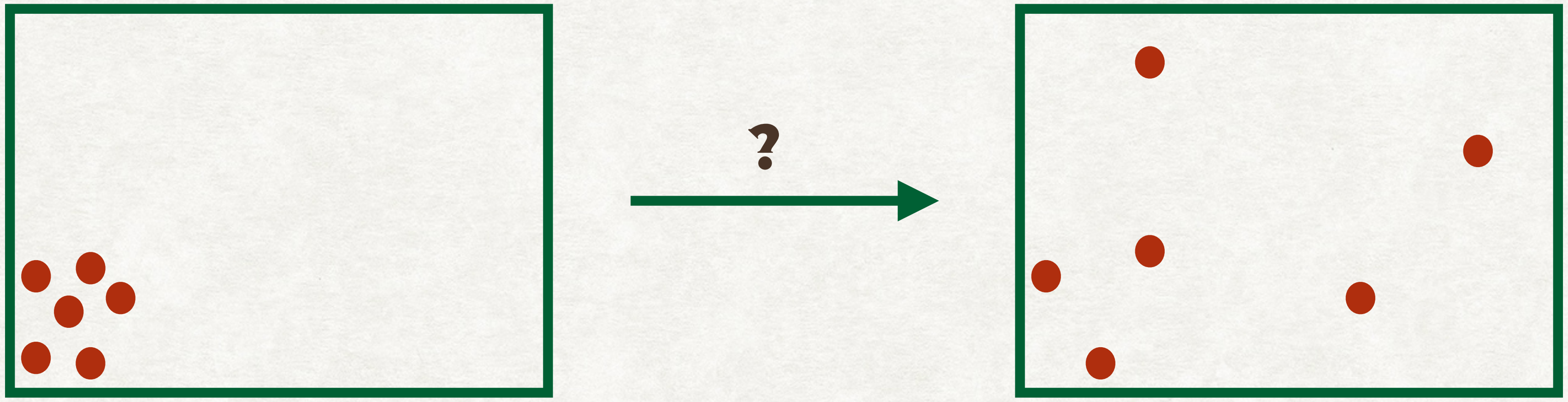

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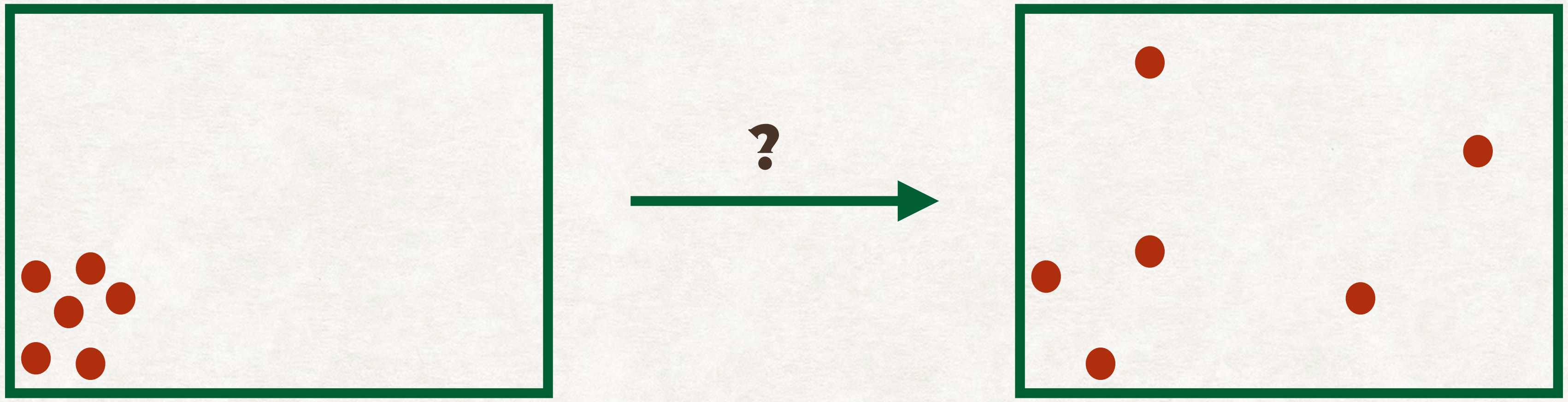
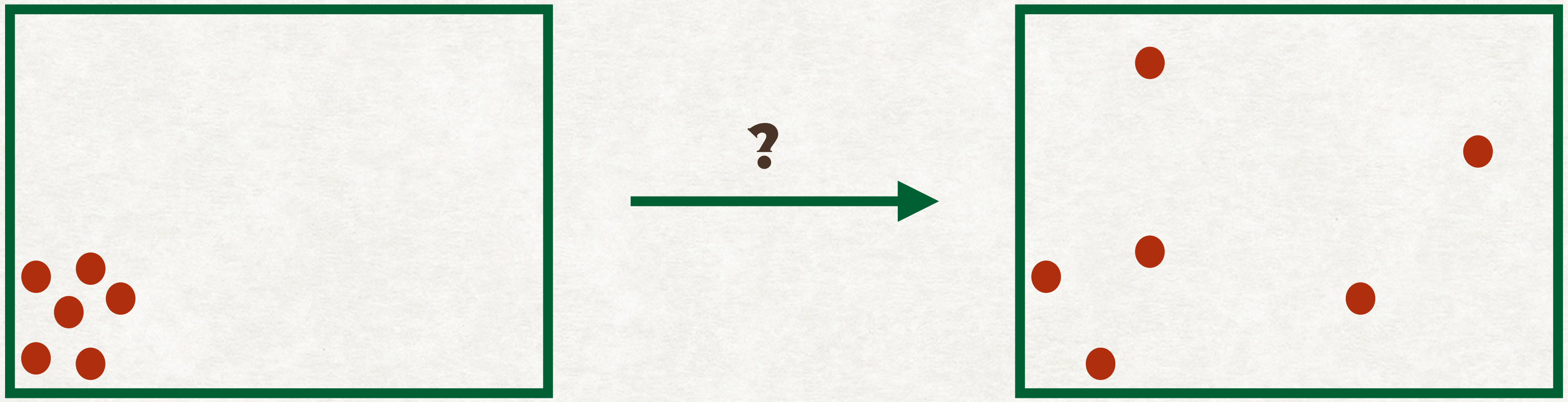
  - Setting: equilibrium, large-system limit, implicit averaging



In thermodynamic resource theory



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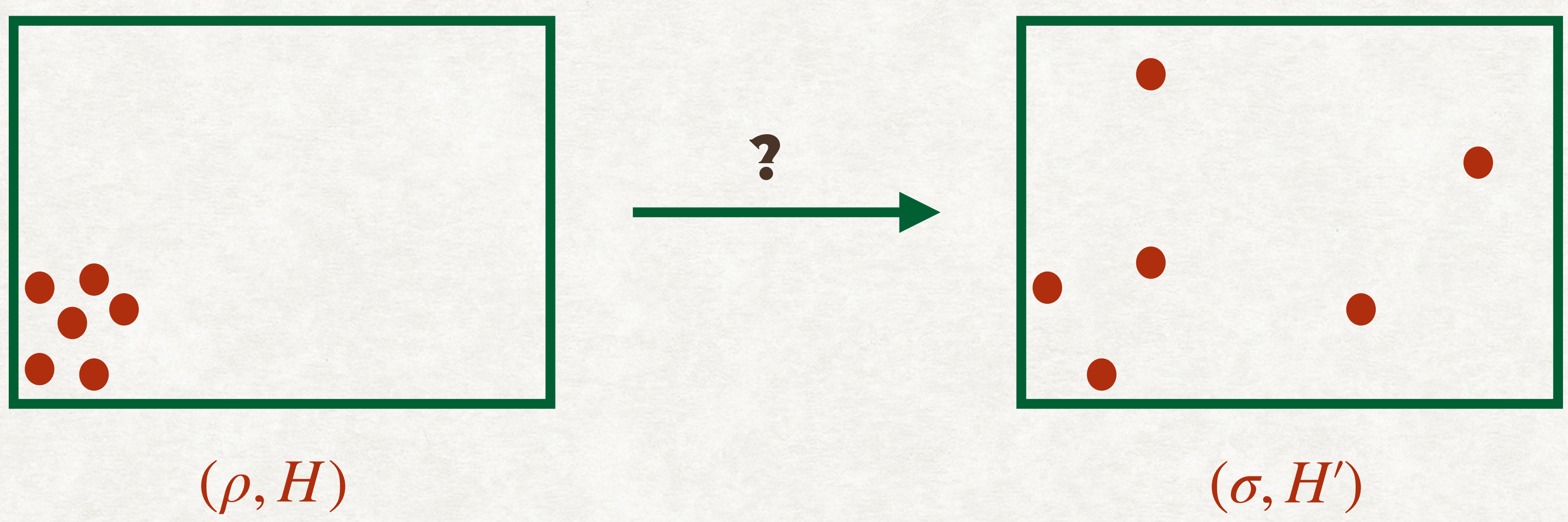
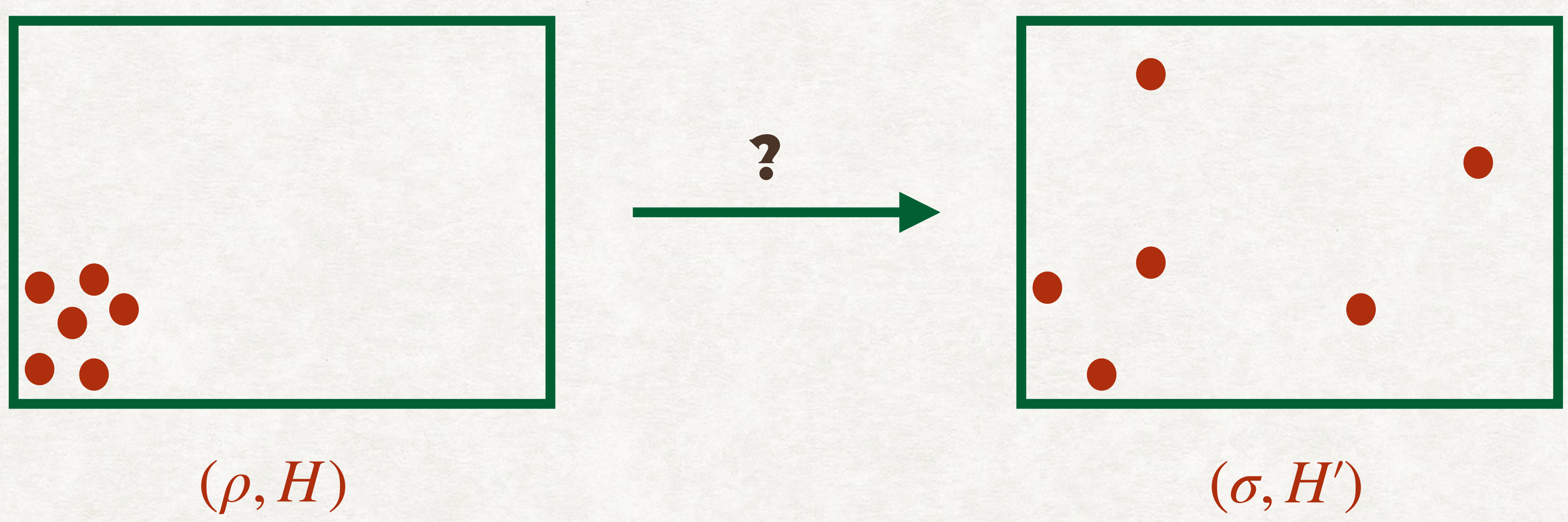


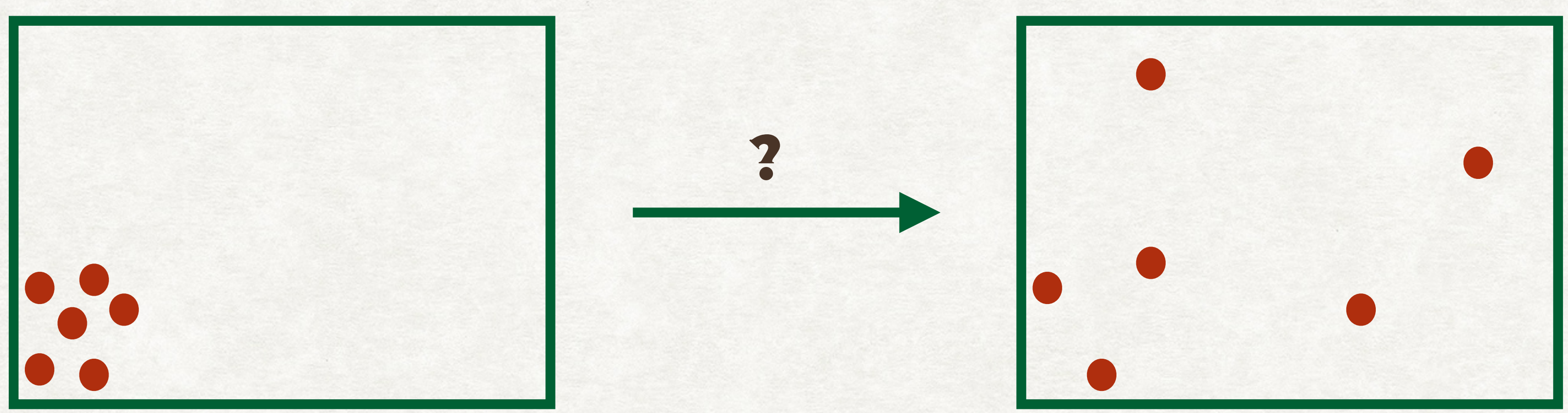
In thermodynamic resource theory

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



In thermodynamic resource theory

- Does any free operation map (ρ, H) to (σ, H')?
- Must check a family of inequalities ⟶ **"second laws"**



(ρ, H) (σ, H')

Second laws of thermodynamics

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$$\Big\downarrow H$$

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Second laws of thermodynamics

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

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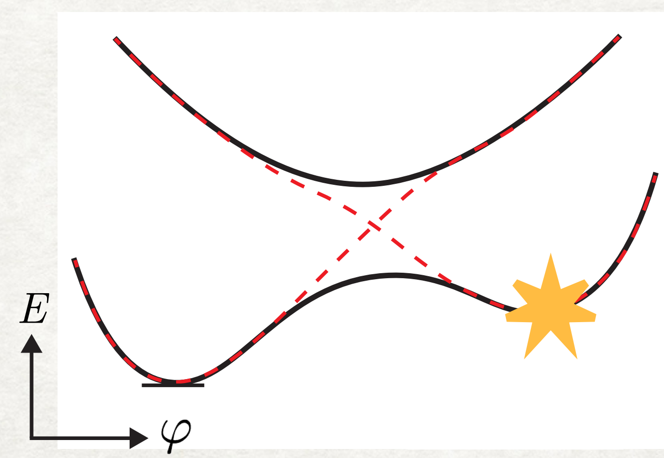
- Another subfamily governs the coherences.

- We want to bound a diagonal element.



Applying the second laws of thermodynamics to the photoisomer

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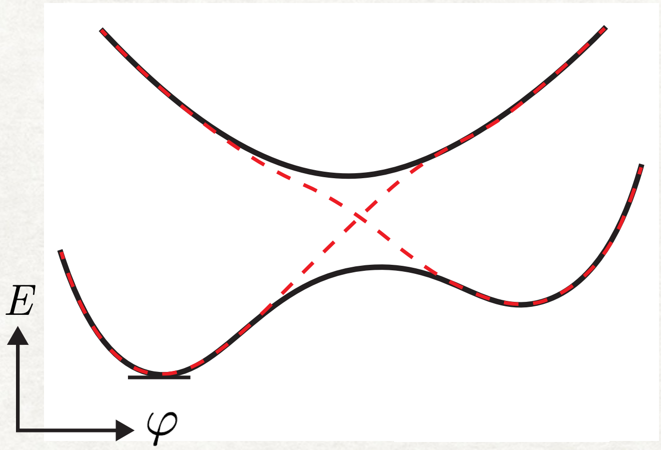

$\varphi = 0$ $\varphi = \pi$

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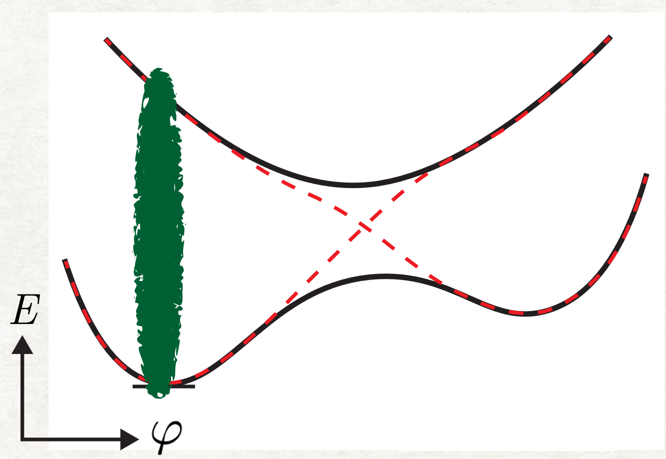
$\rho_{\text{elec}} \otimes |\varphi = 0\rangle\langle\varphi = 0|$



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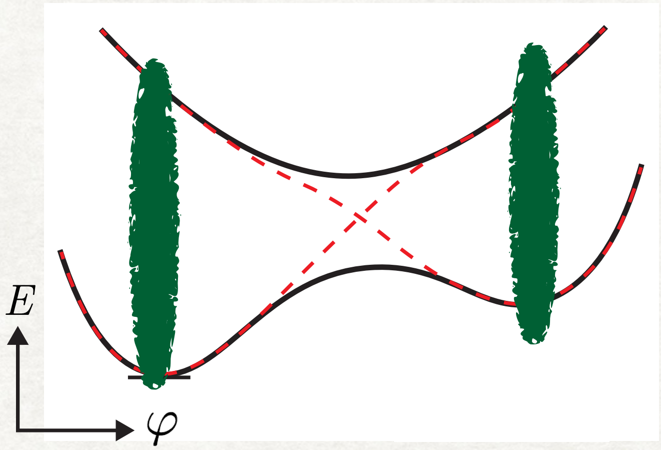

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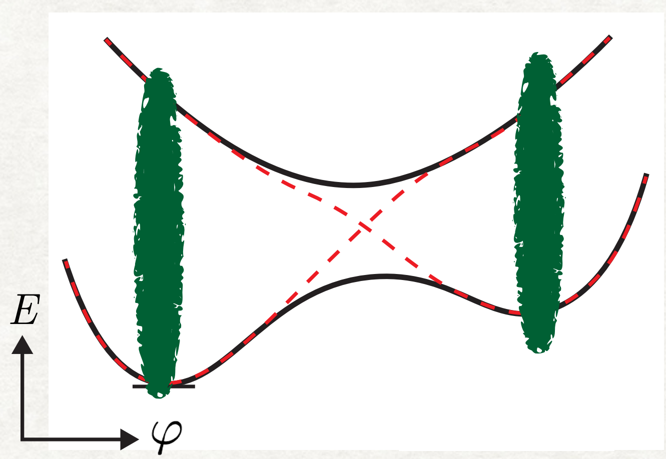

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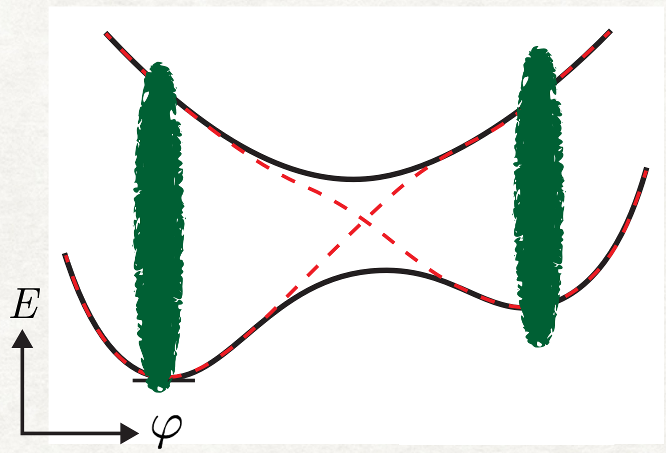
Effective 4-level system:



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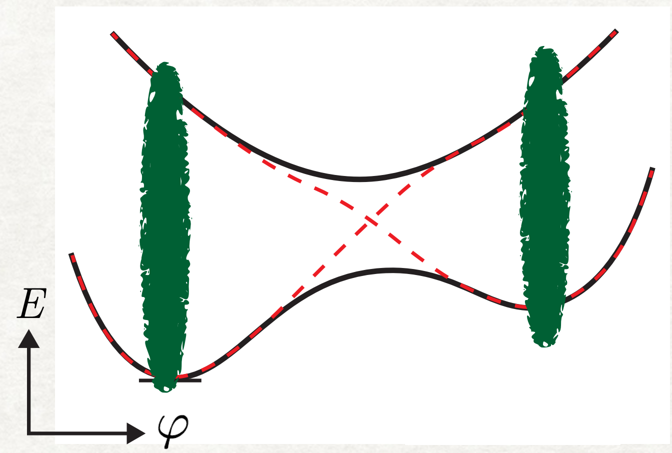
Effective 4-level system:

(2 nuclear states)

× (2 electronic states)



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Coherence theorem

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.

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

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<u>Coherence theorem</u>

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

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Implication for photoisomer

- We want to bound a diagonal element.
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- So our bound will depend on just the states' diagonal elements.

Applying the second laws of thermodynamics to the photoisomer

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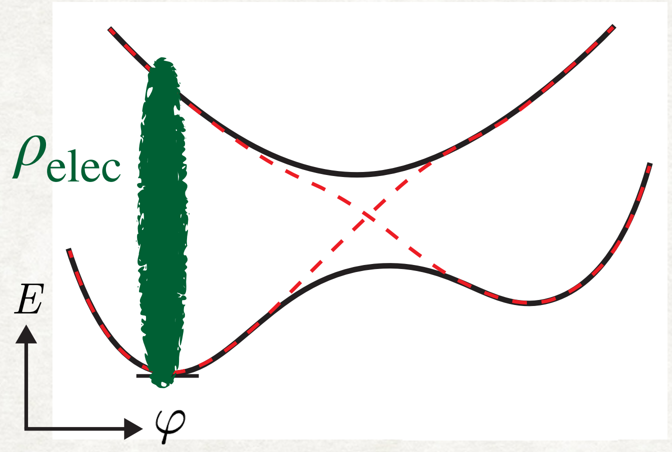

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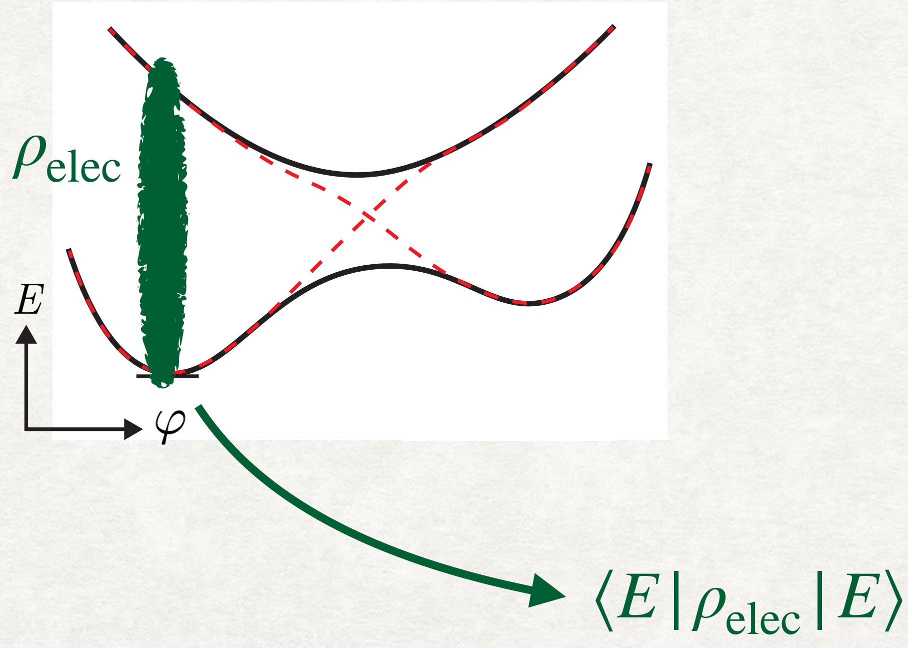

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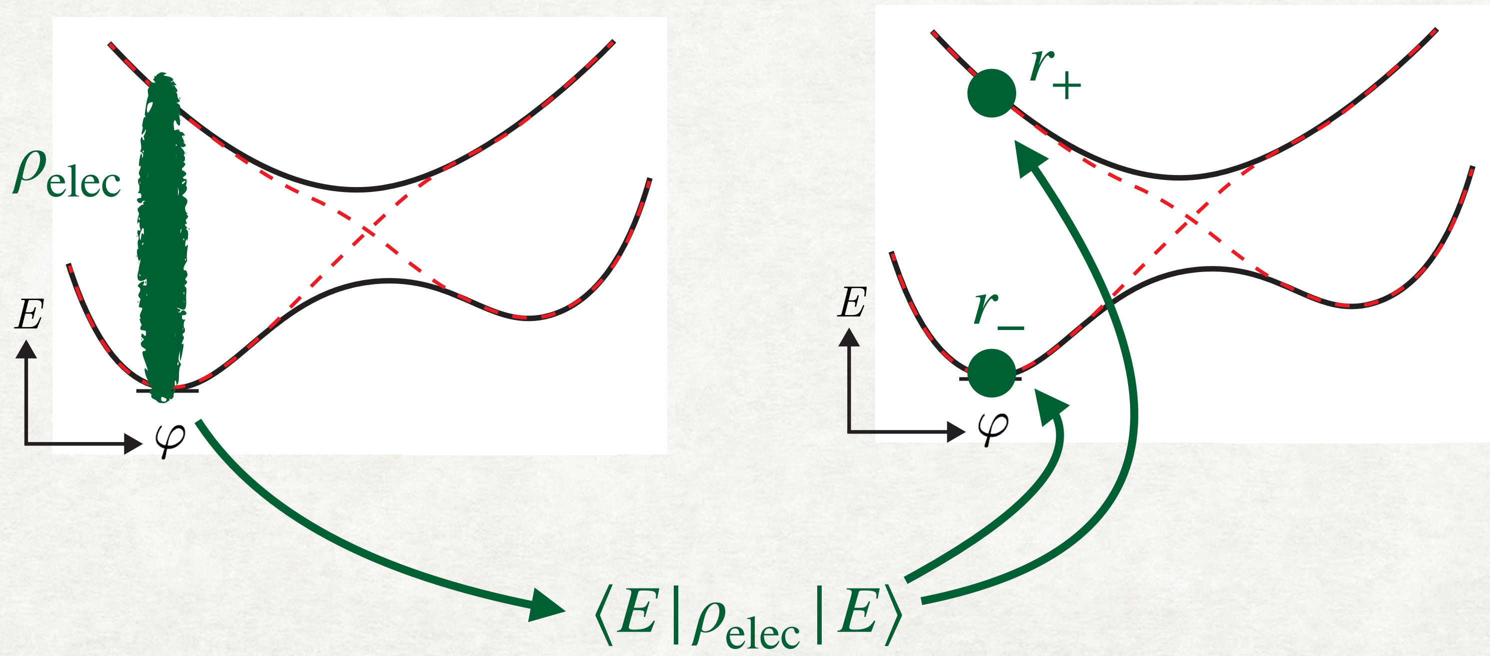

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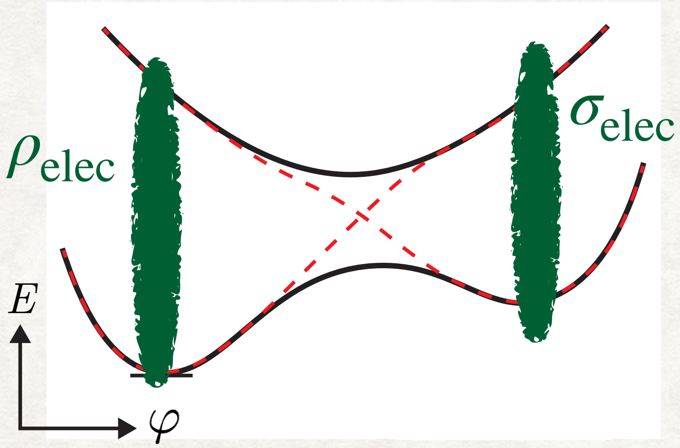

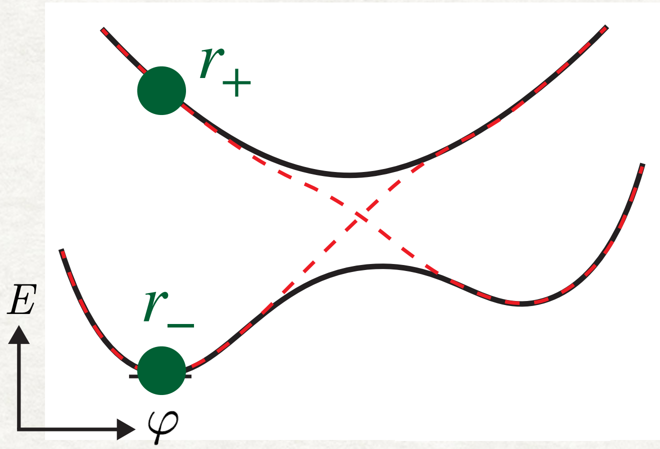

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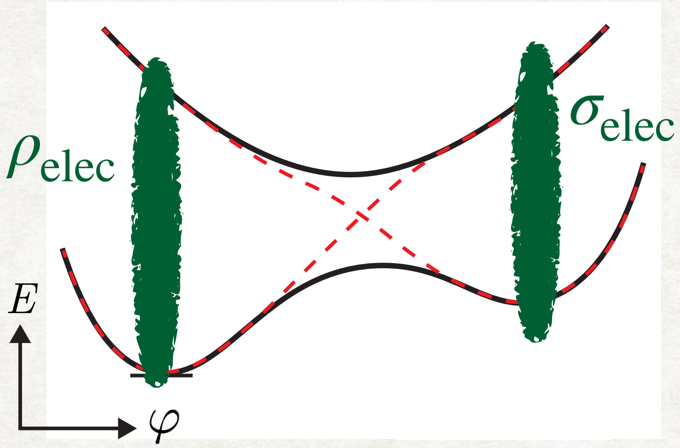

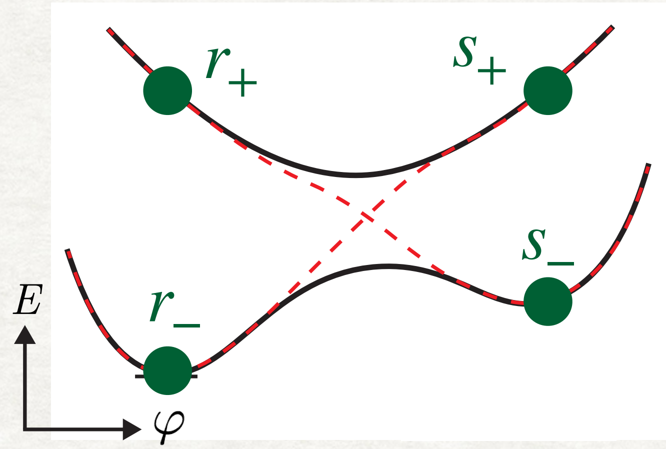

Second laws of thermodynamics for the energy diagonal

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

- Order the rescaled probabilities from greatest to least.

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

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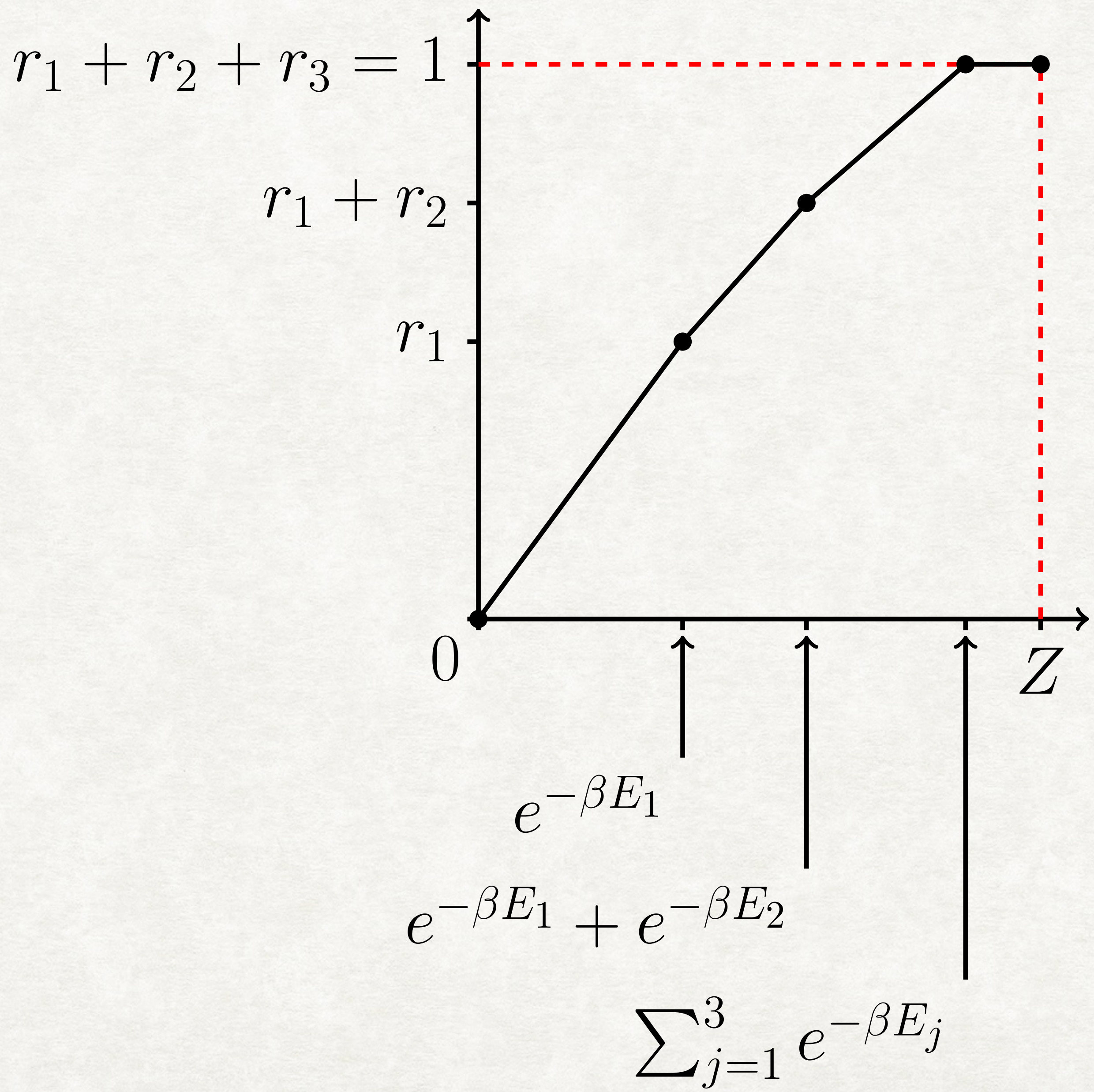
- Plot partial sums.

Second laws of thermodynamics

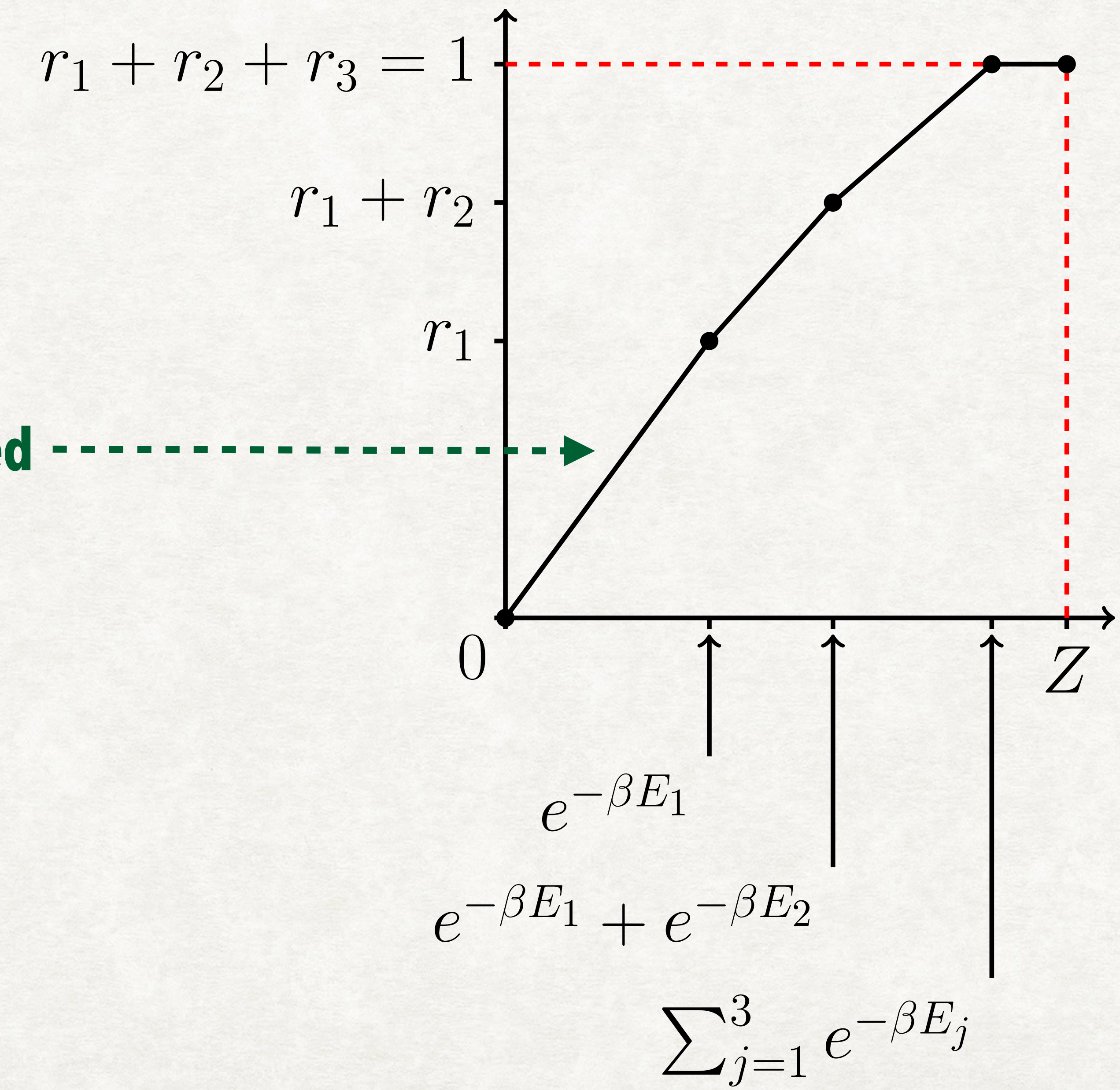
How to check whether $(\rho, H) \mapsto (\sigma, H)$ for free



Second laws of thermodynamics

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

- **Gibbs-rescaled Lorenz curve**



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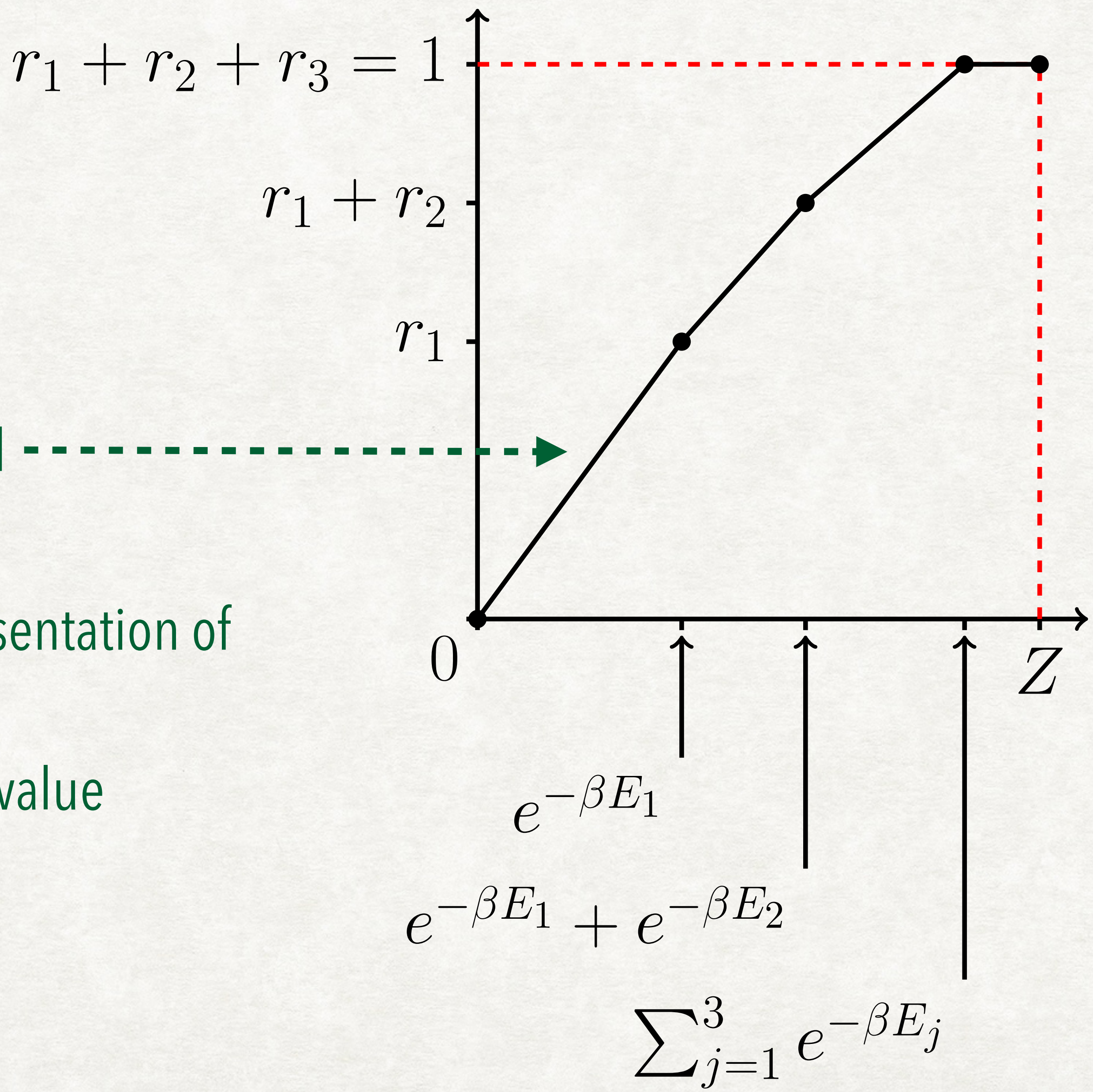
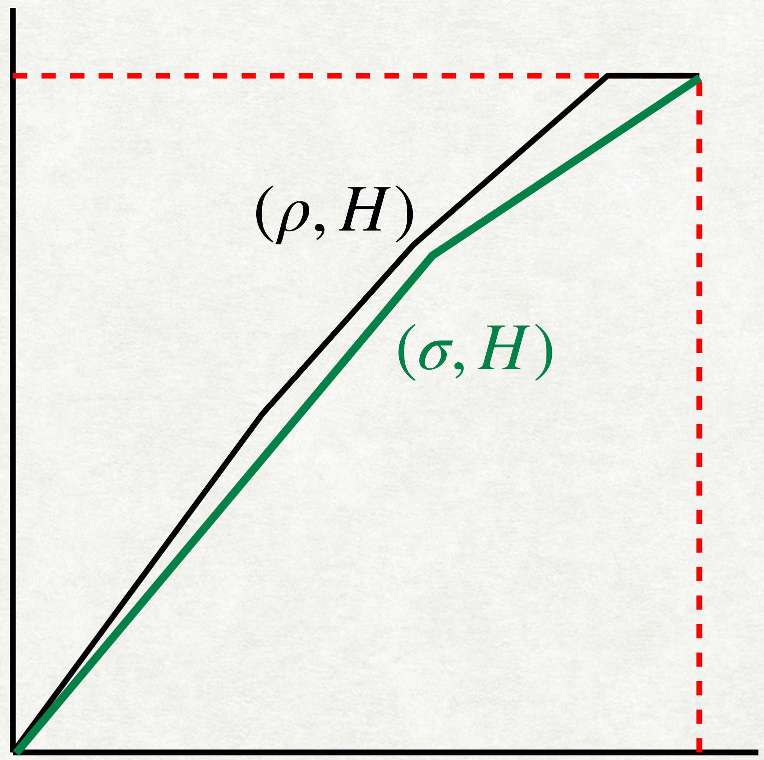


- **Gibbs-rescaled Lorenz curve**
- Geometric representation of the system's thermodynamic value

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.



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.

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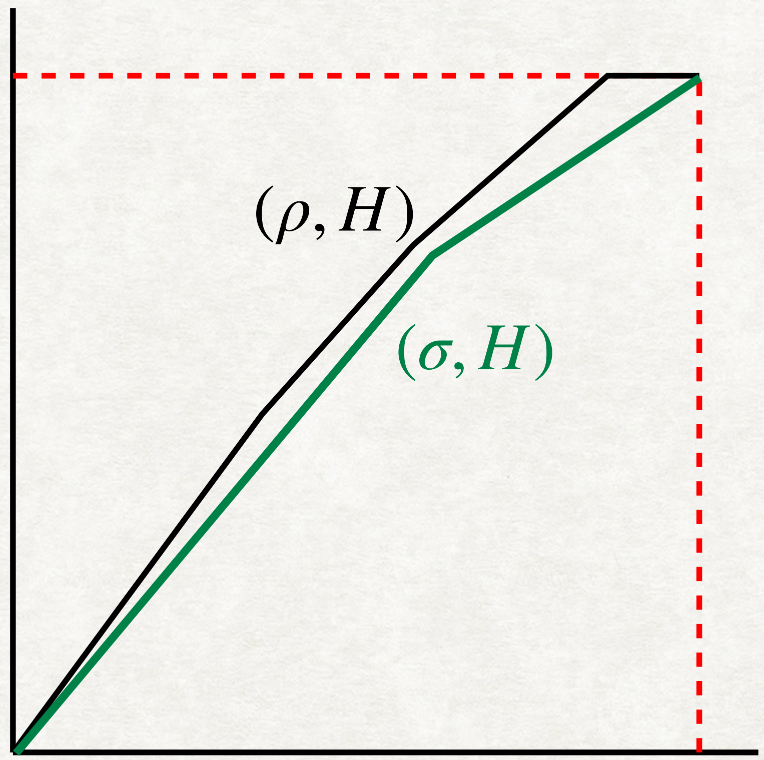

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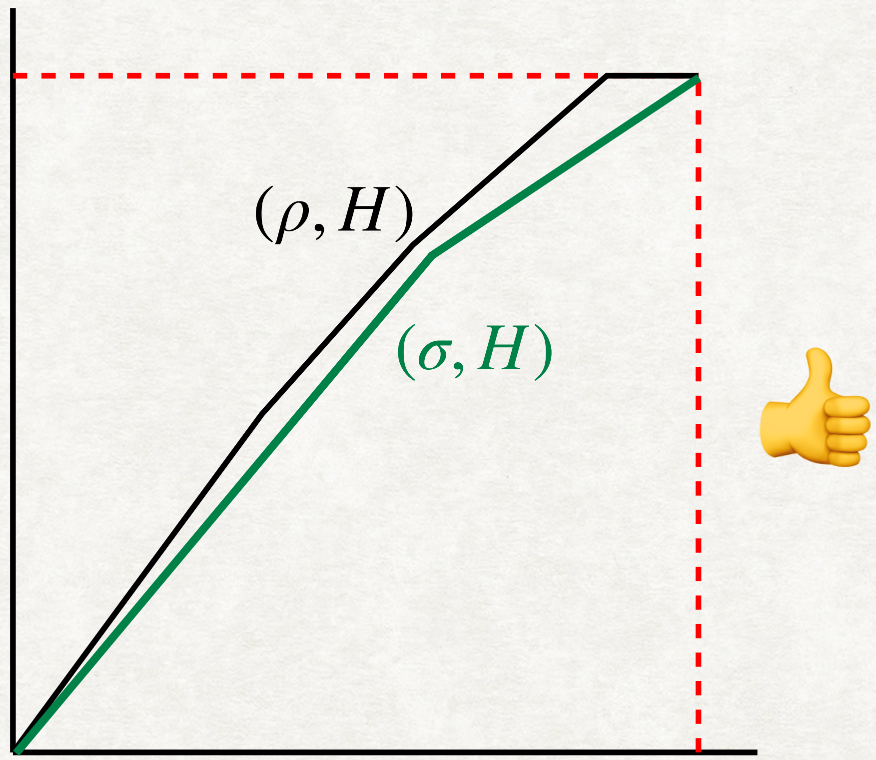

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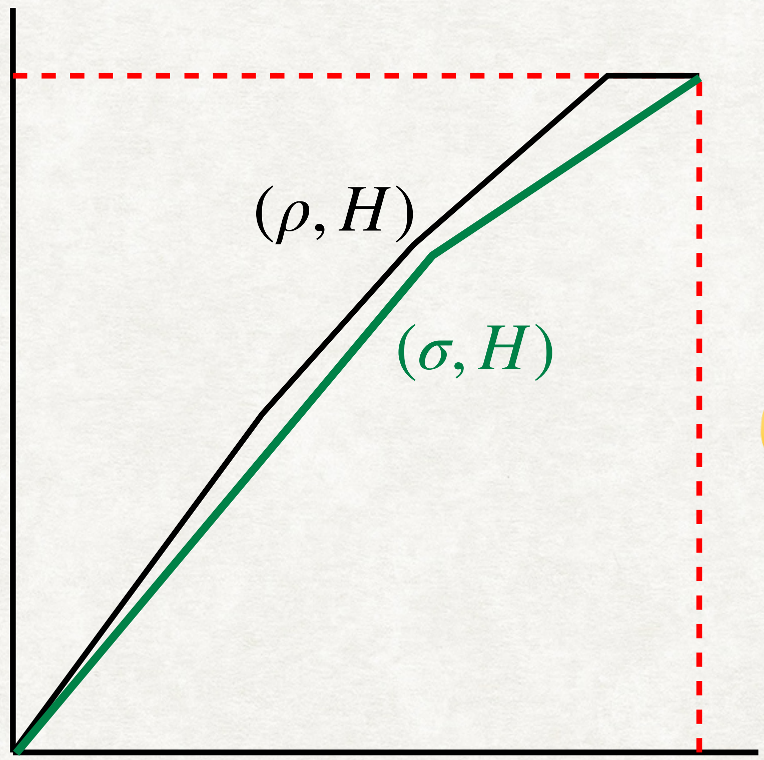

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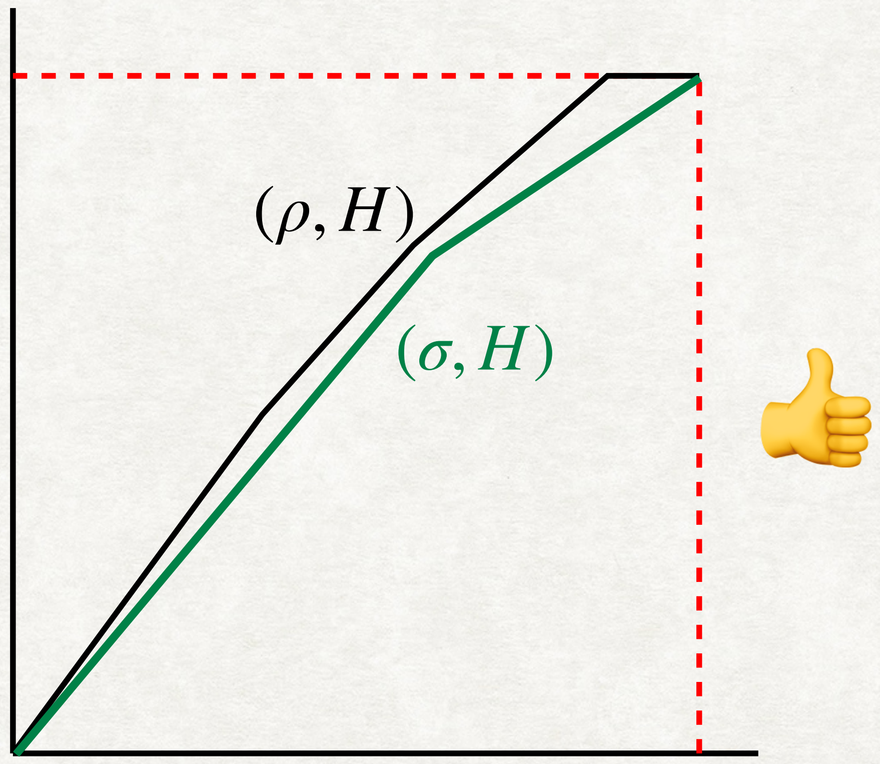
Encodes a bunch of inequalities



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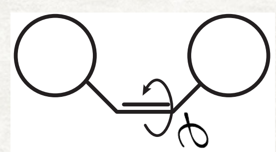
Apply the second laws of thermodynamics
to the photoisomer.

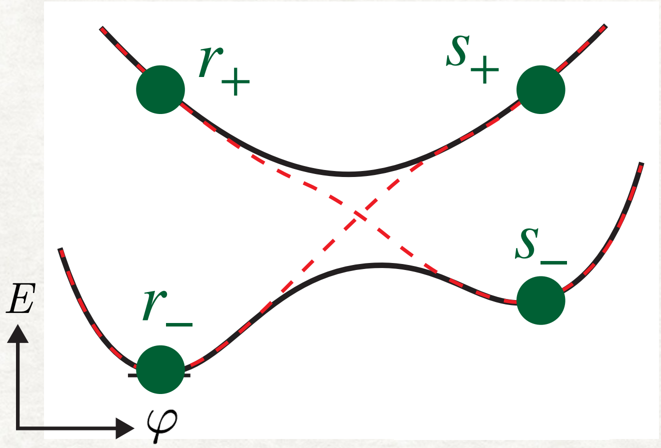


+

NYH and Limmer, arXiv:1811.06551 (2018).

Applying the second laws to the photoisomer

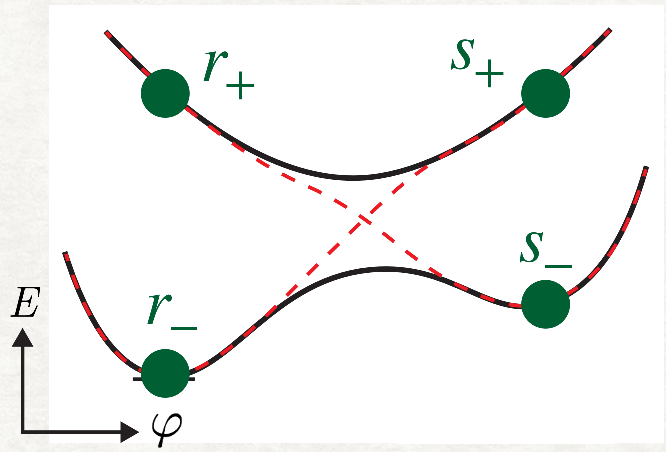
Strategy



Applying the second laws to the photoisomer

Strategy

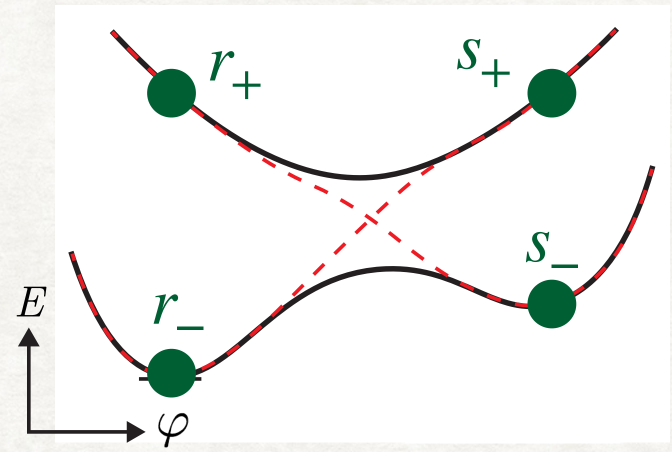
- Construct a post-laser state ρ of the molecule.



Applying the second laws to the photoisomer

Strategy

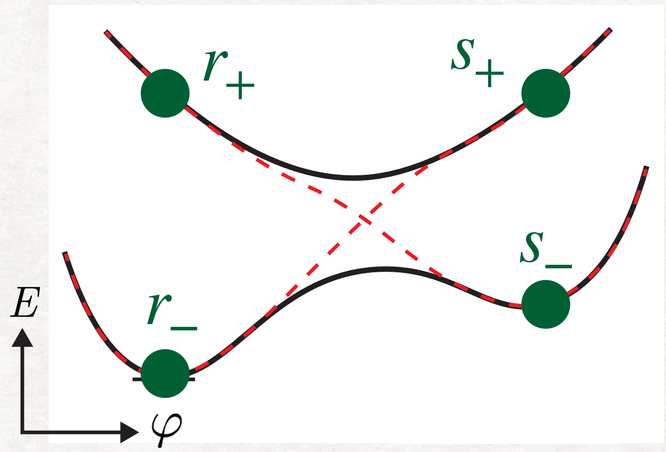
- Construct a post-laser state ρ of the molecule.
- $s_+ = 1 - s_-$



Applying the second laws to the photoisomer

<u>Strategy</u>

- Construct a post-laser state ρ of the molecule.
- $s_+ = 1 - s_-$
- Plug into the second laws.



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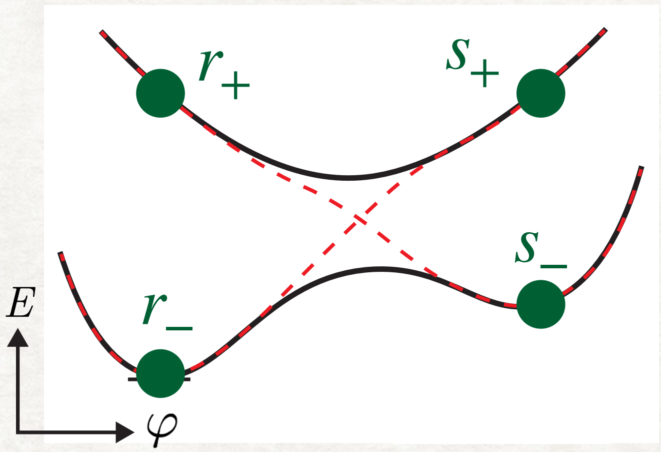

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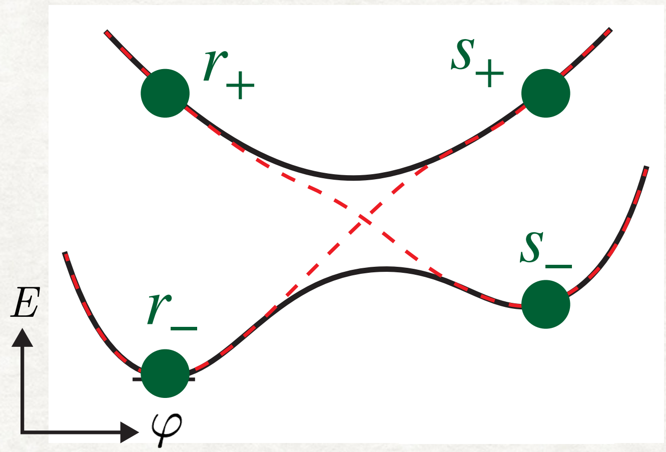
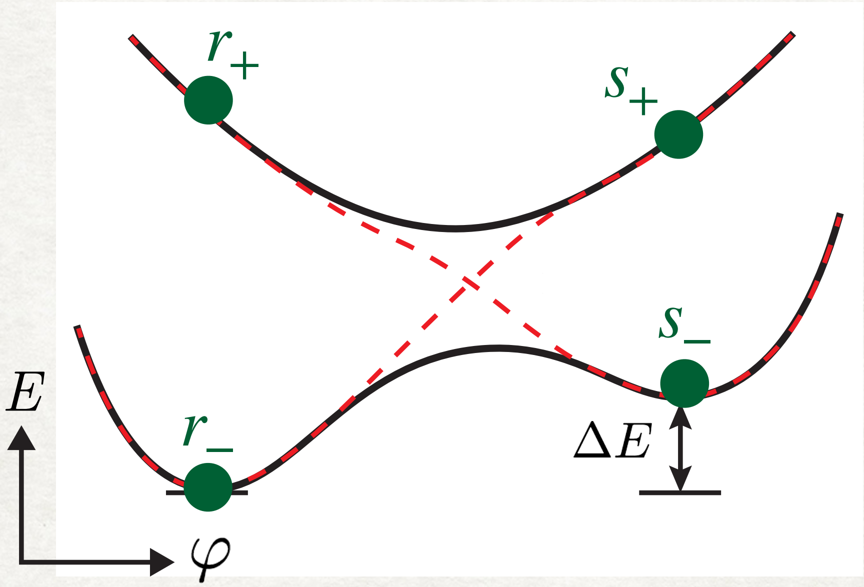
- Solve for the greatest s_- for which the ρ curve lies above/on the σ curve.



Bounds on photoisomerization yield



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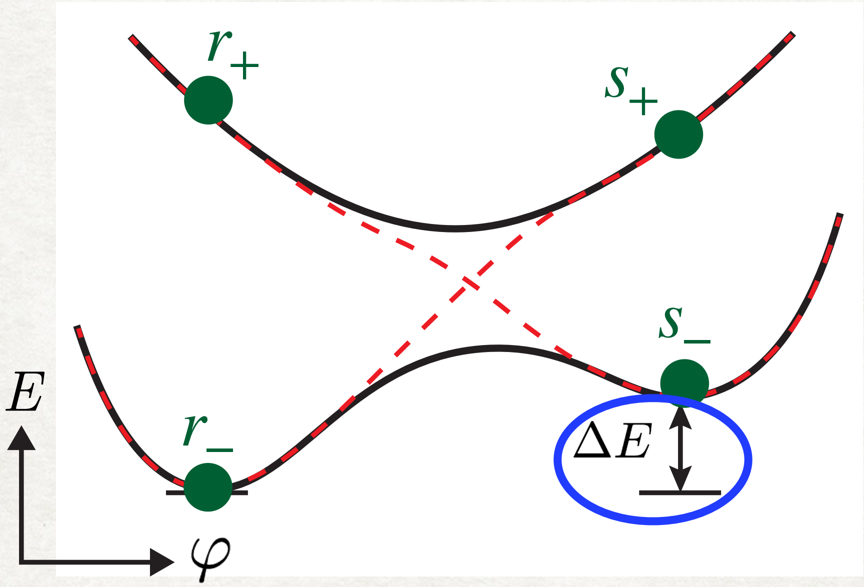

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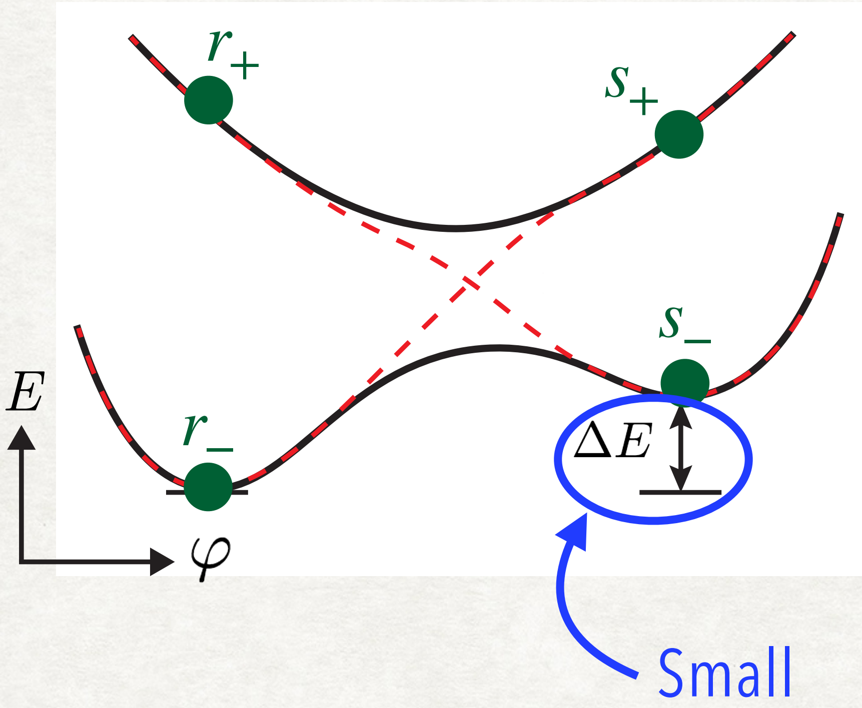

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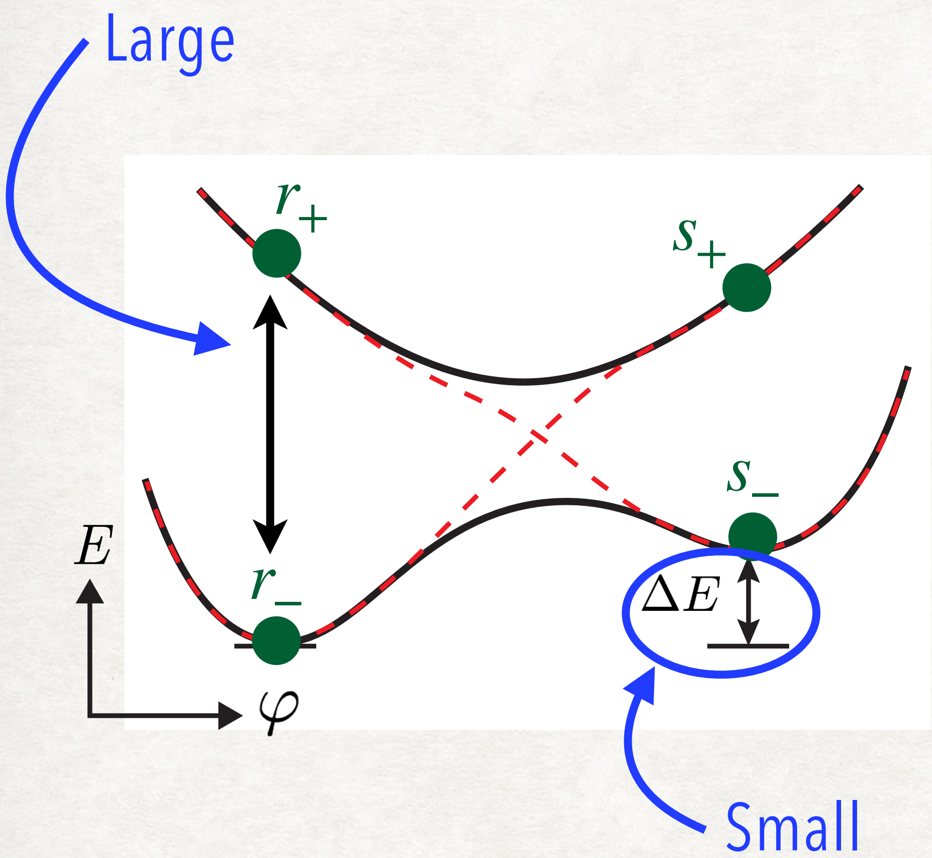

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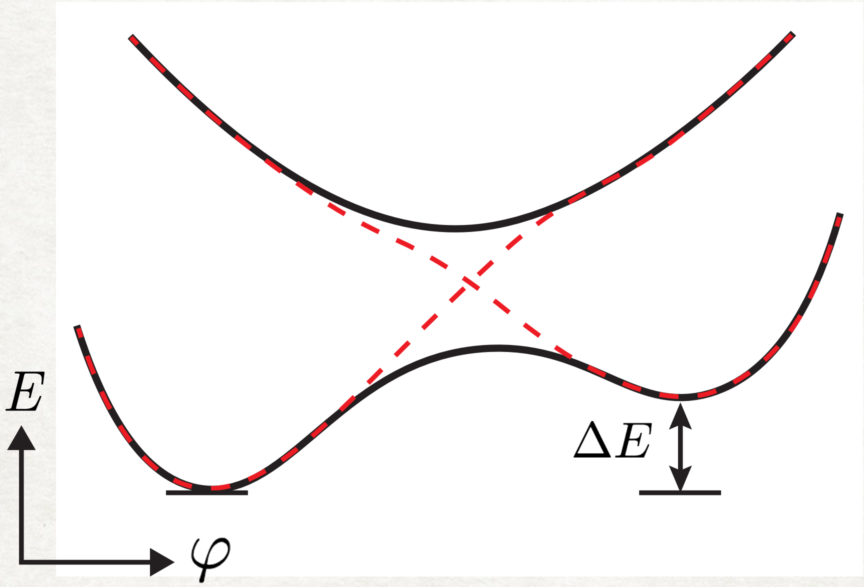

$\beta \Delta E$

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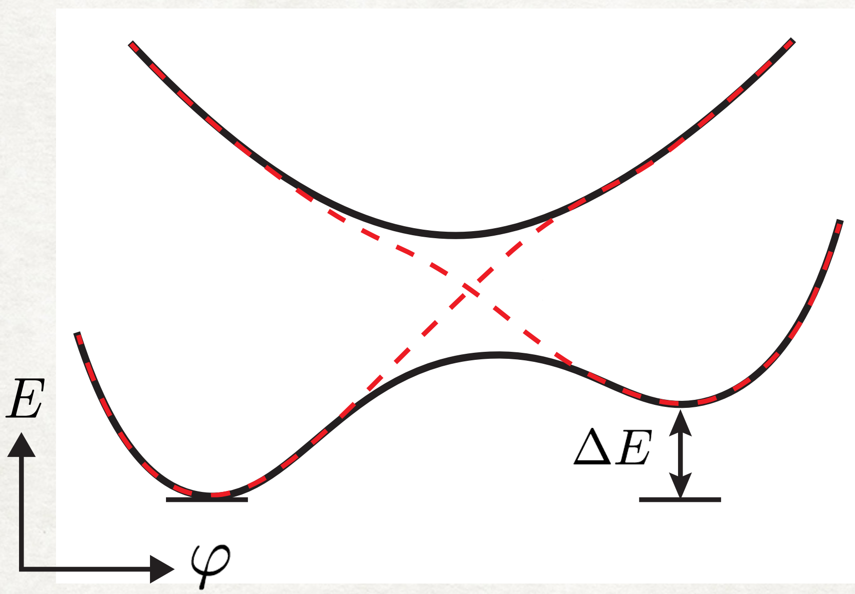

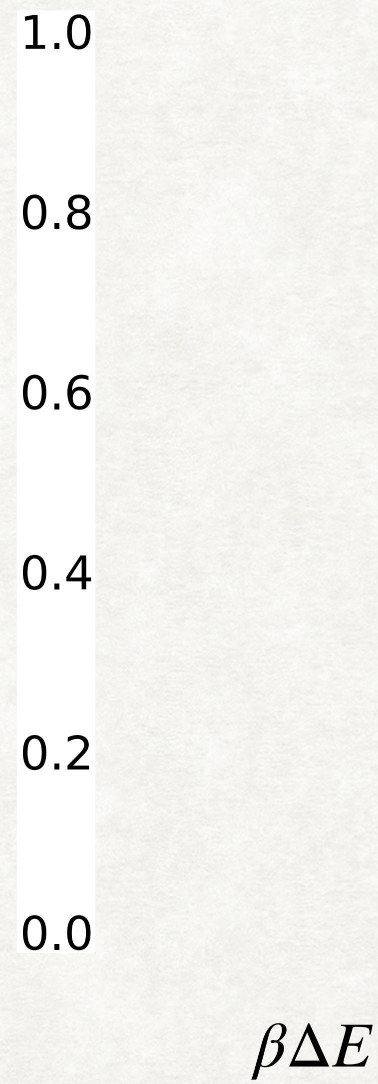

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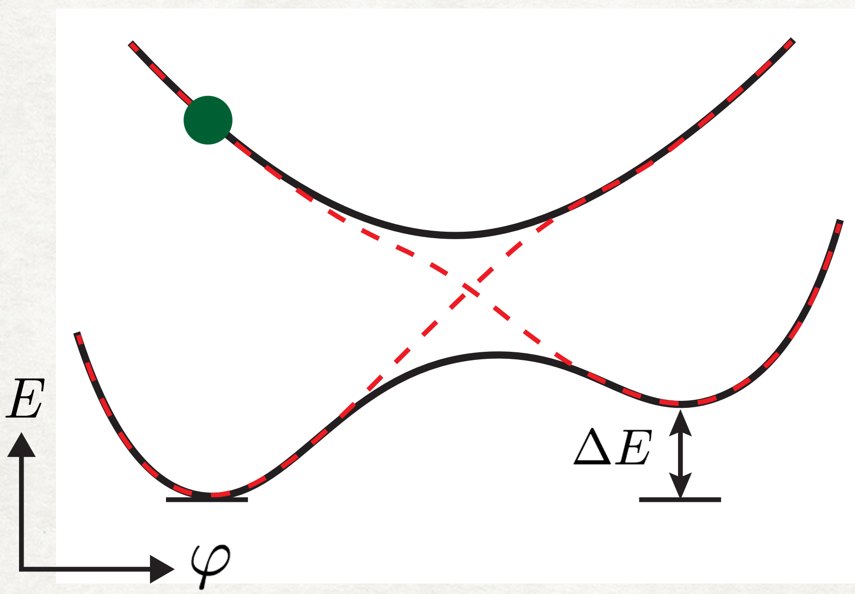
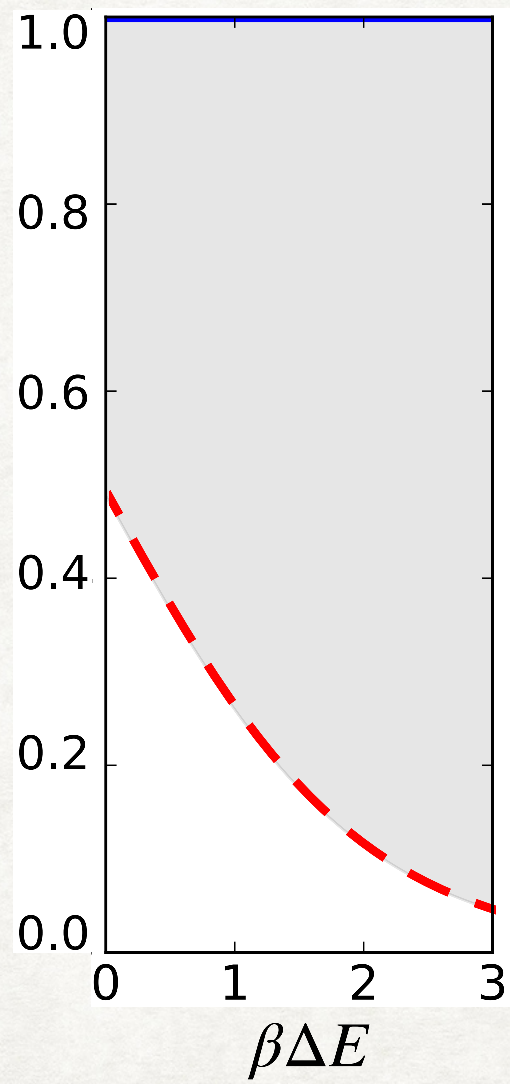


Good-laser regime



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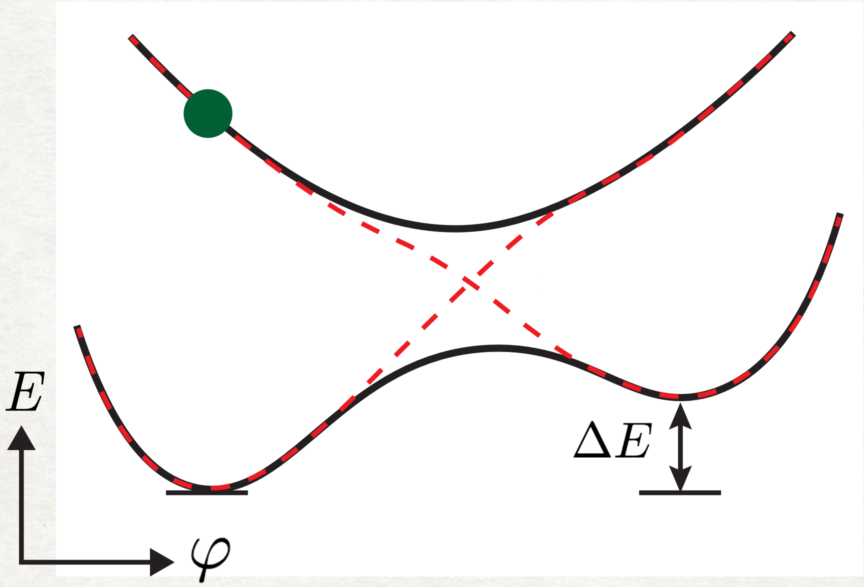

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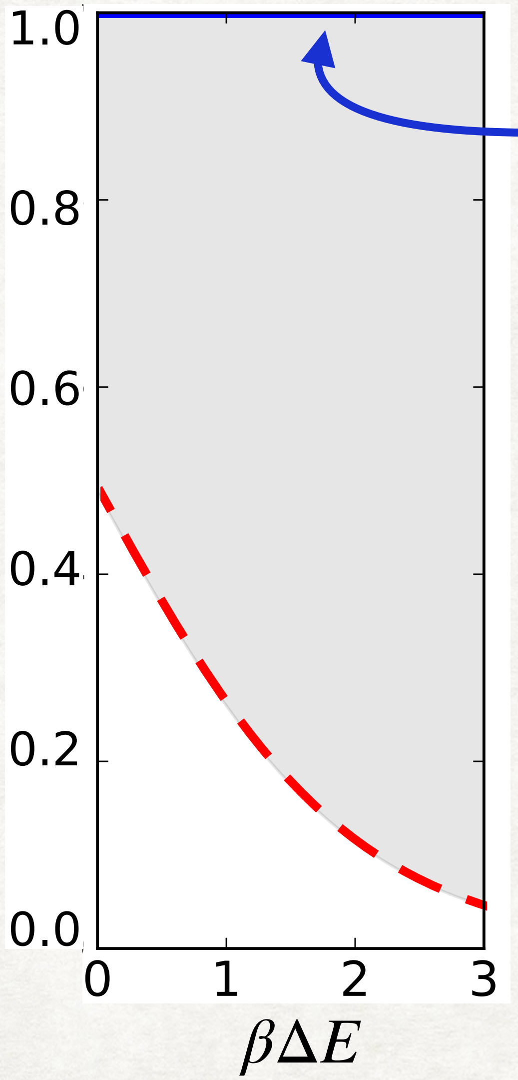
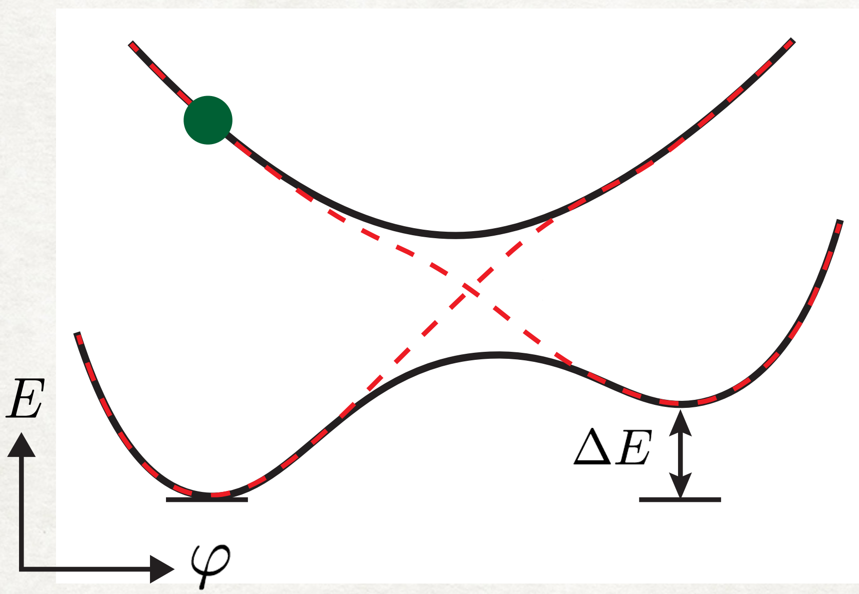


Upper bound from resource theory

Bounds on photoisomerization yield



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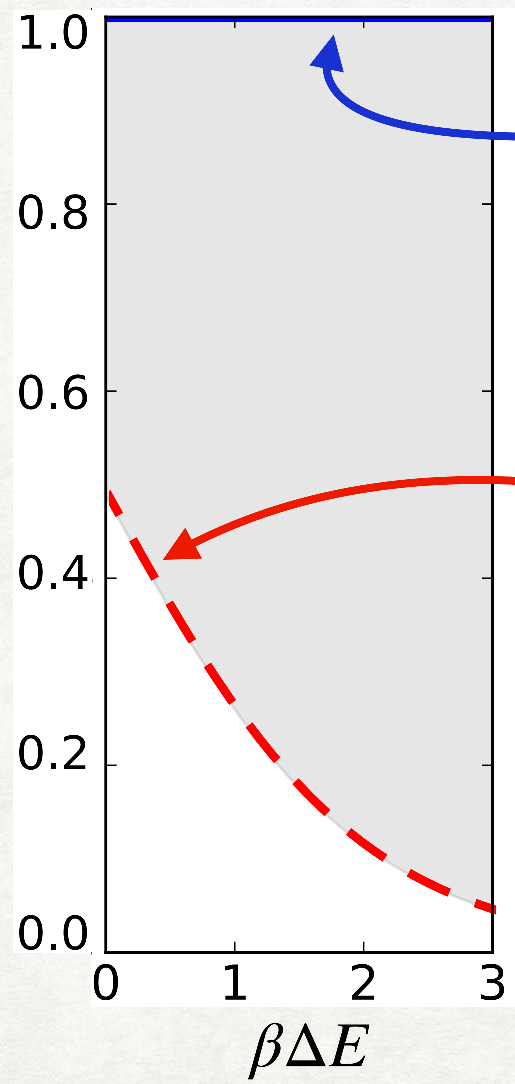
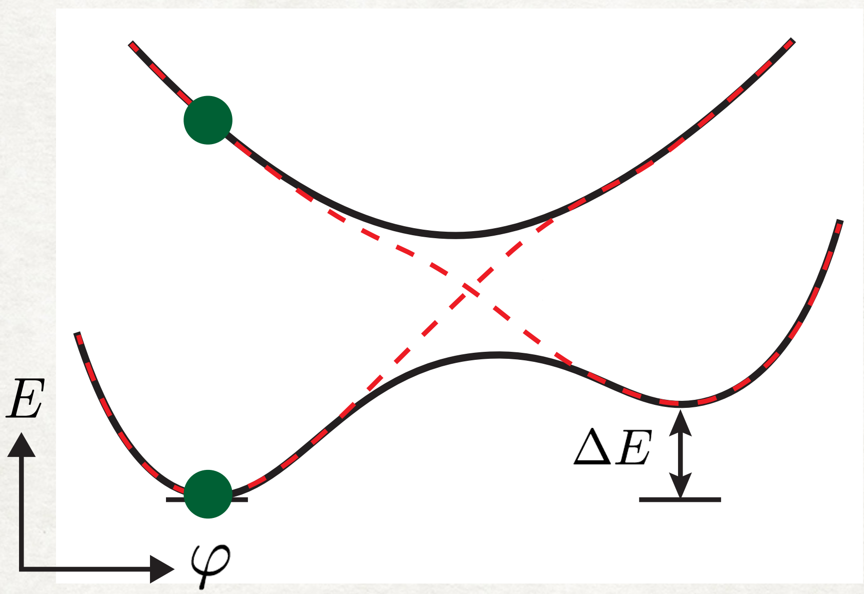
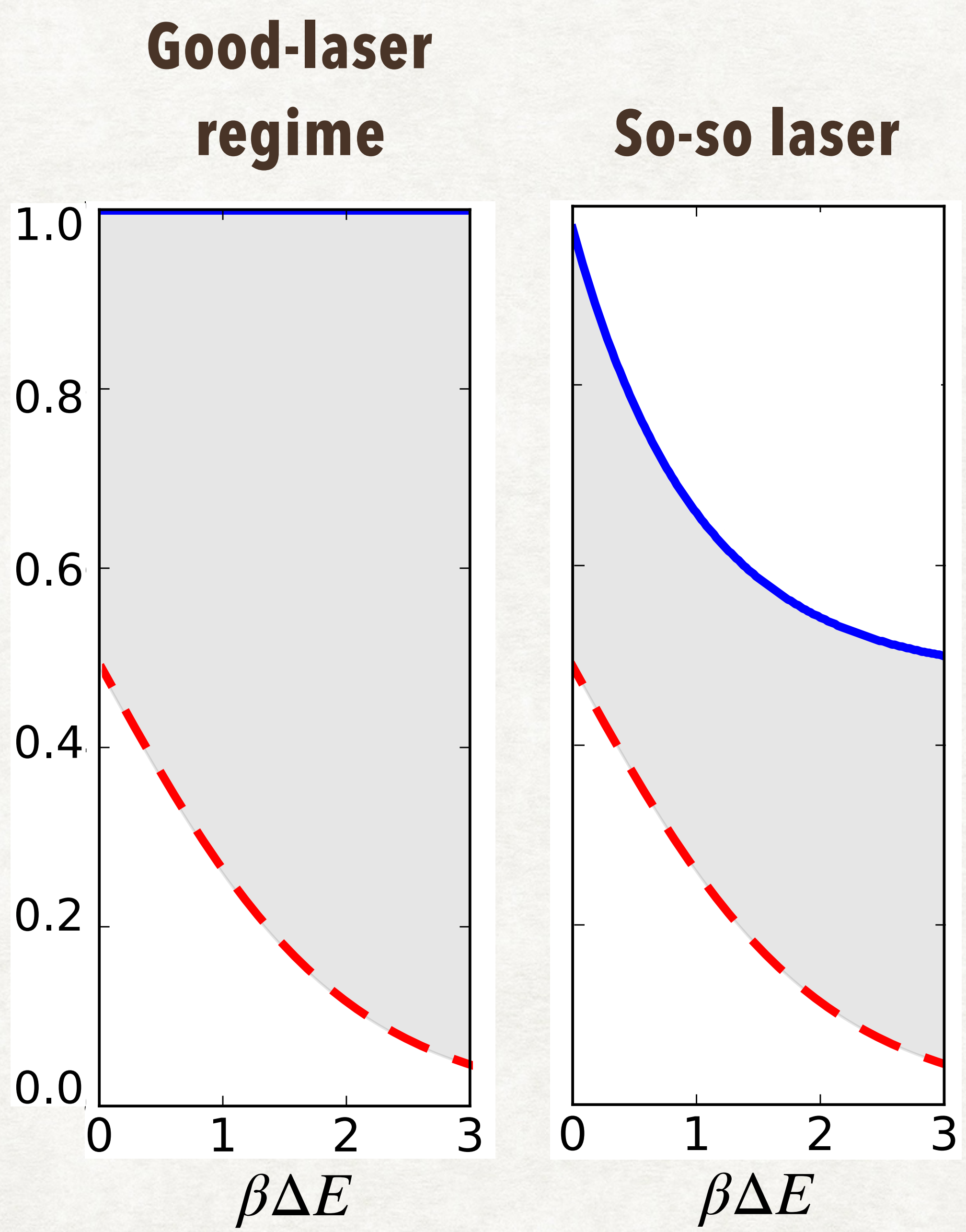


Upper bound from resource theory

Lower bound from detailed balance

Bounds on photoisomerization yield





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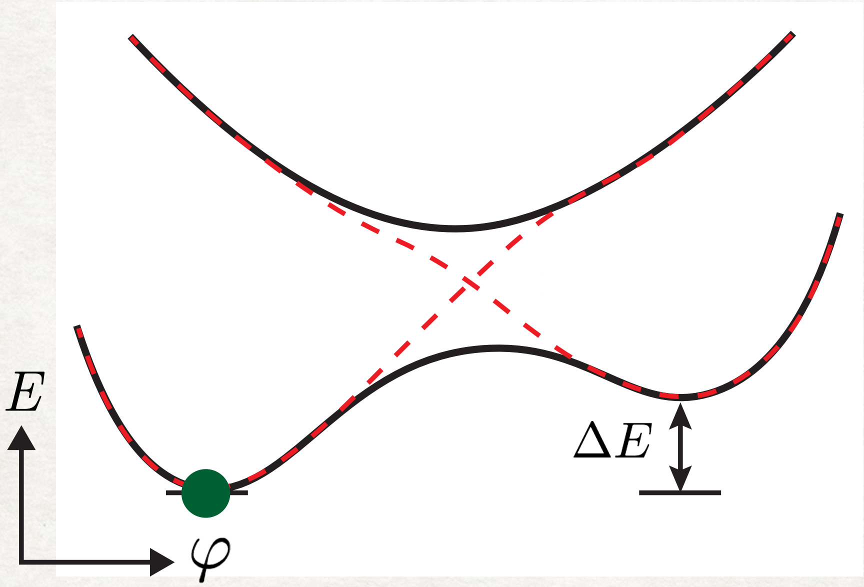

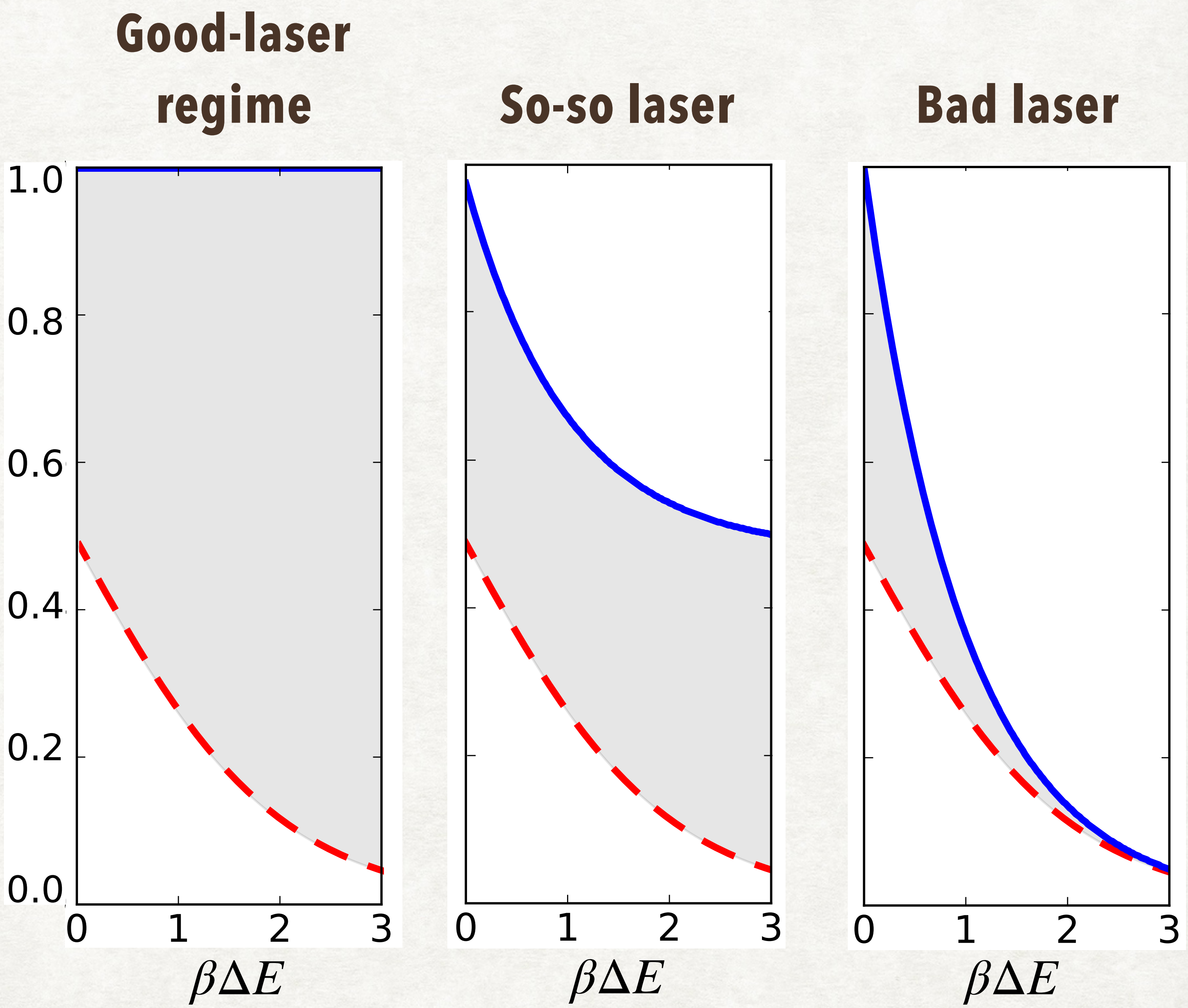

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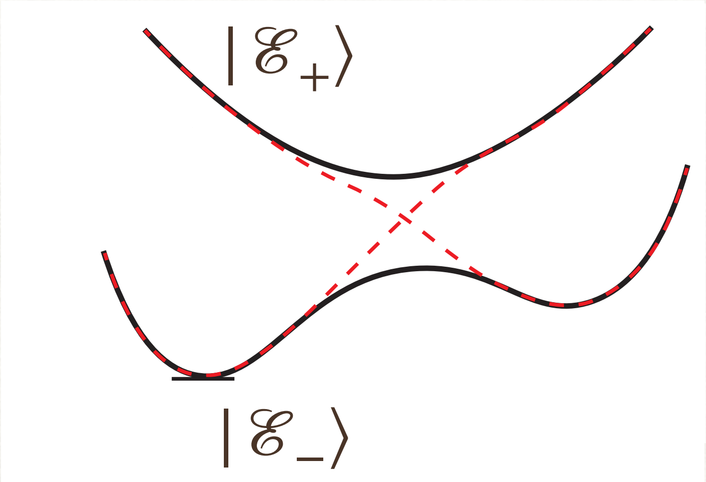

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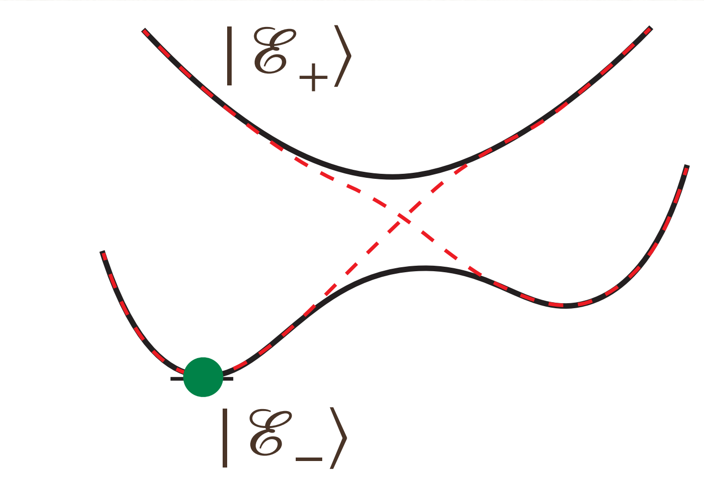

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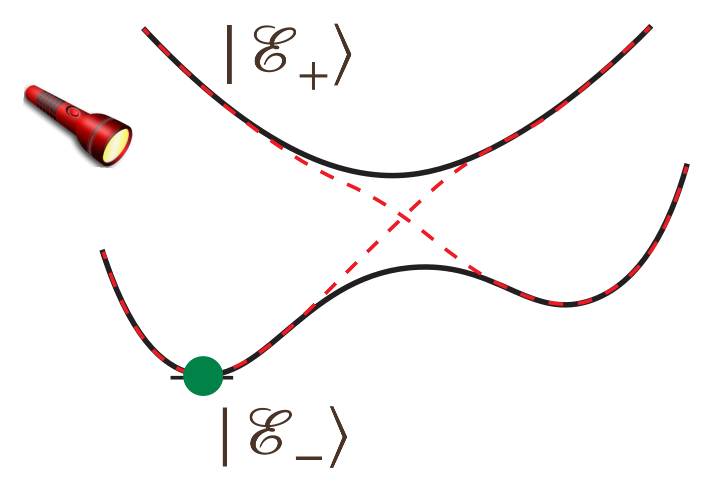

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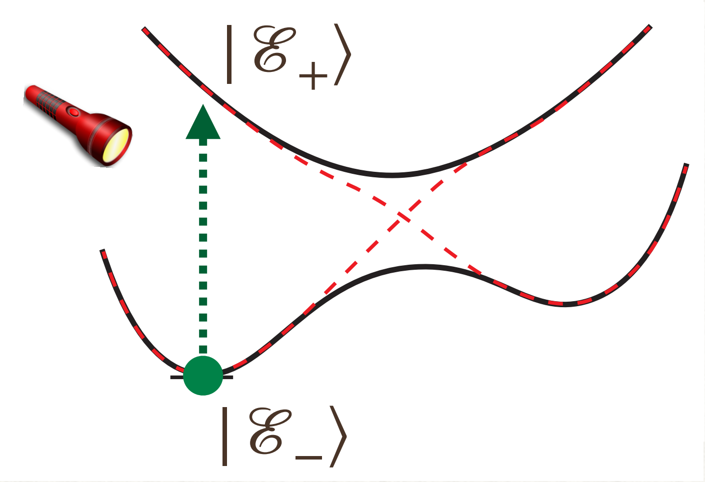

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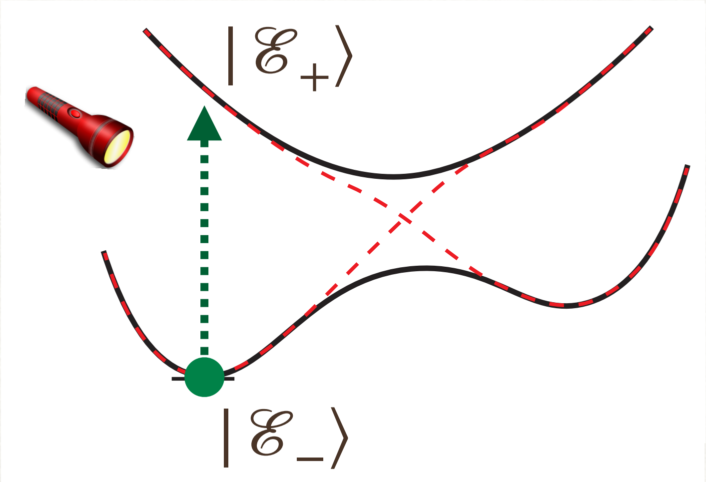

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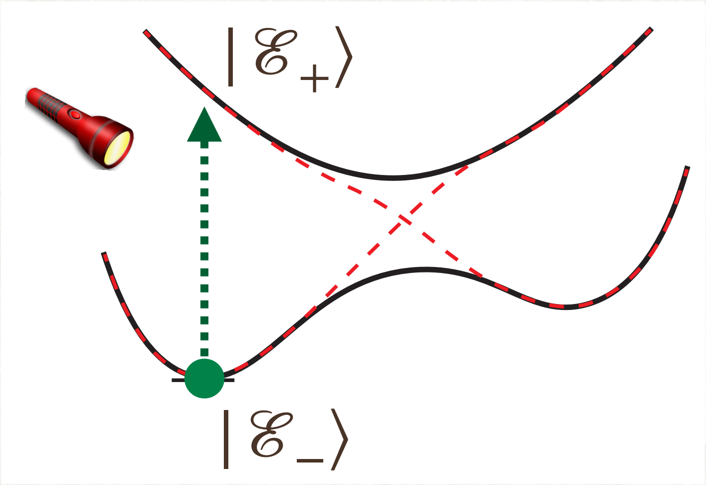

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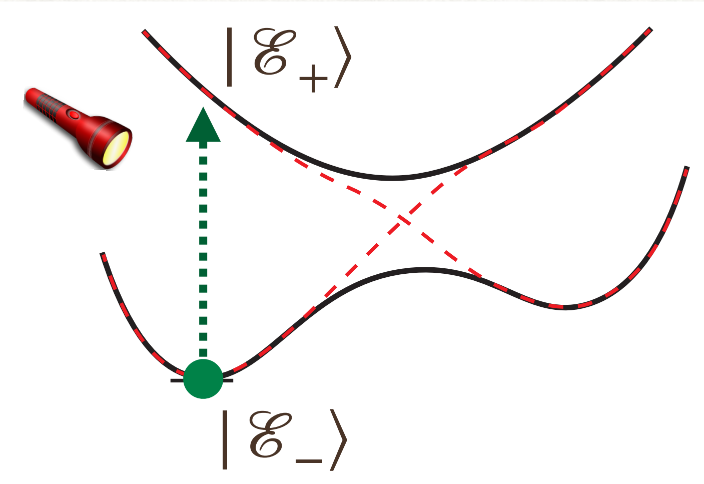

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- **Extraction of work from coherences**

Recap

NYH and Limmer, arXiv:1811.06551 (2018).

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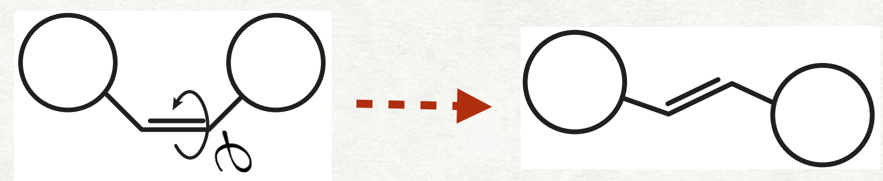
-  **The photoisomer** 

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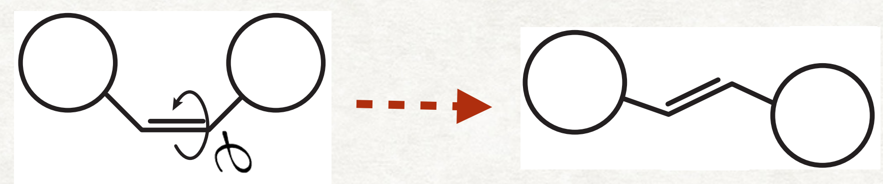
-  **The photoisomer** 
- **Thermodynamic resource theories**

Recap

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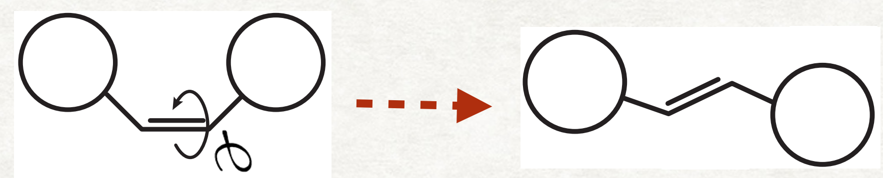
-  **The photoisomer** 

- **Thermodynamic resource theories**
  - How to model your favorite system

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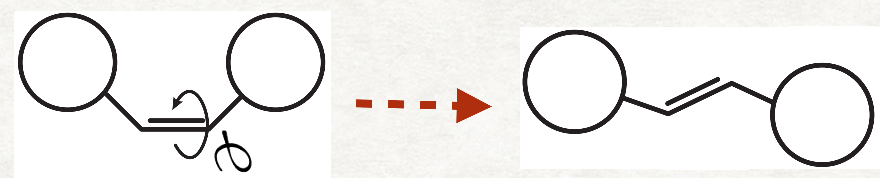
-  **The photoisomer** 

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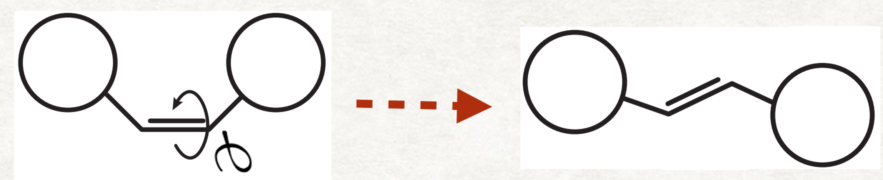
-  **The photoisomer** 

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- **Results**

Recap

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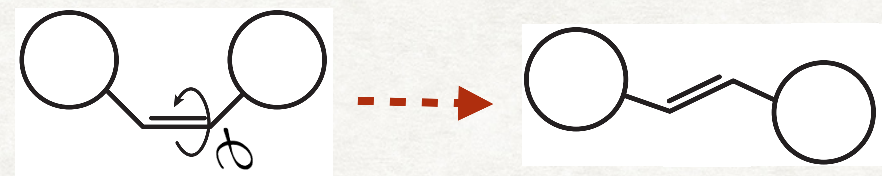
-  **The photoisomer** 

- **Thermodynamic resource theories**
  - How to model your favorite system
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  - Modeled the photoisomer in a resource theory

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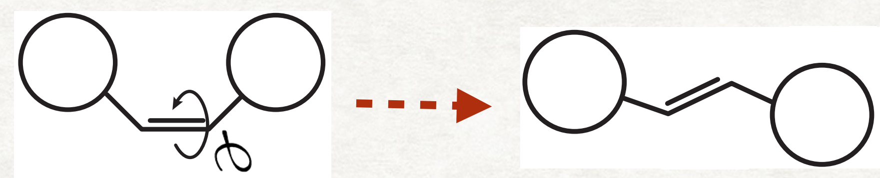
-  **The photoisomer** 

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  - How to model your favorite system
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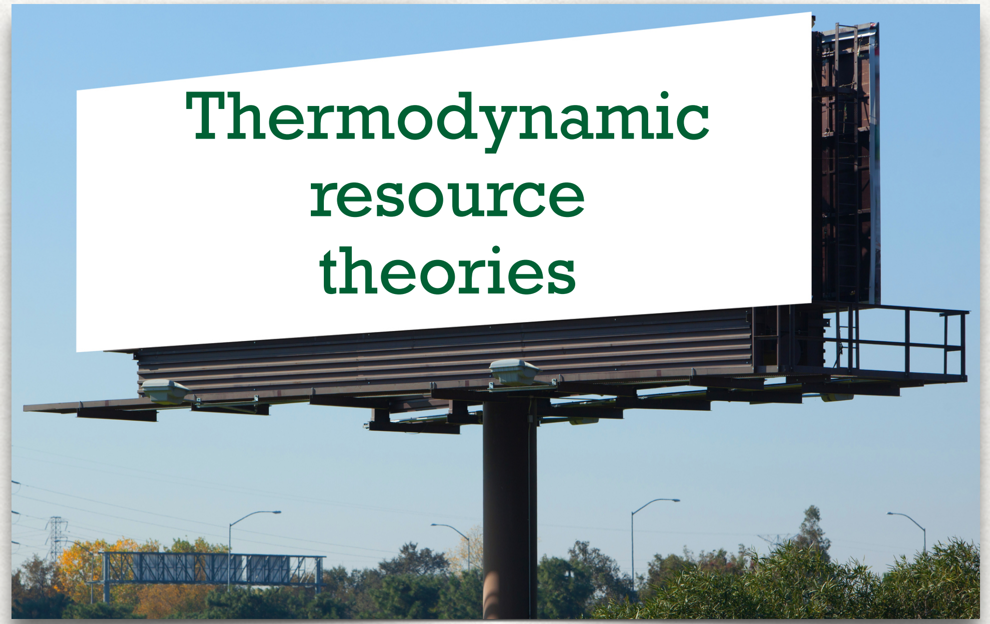
- **Results**
  - Modeled the photoisomer in a resource theory
  - Bounded the photoisomerization probability, using second laws

Open questions

NYH and Limmer, arXiv:1811.06551 (2018).

Open questions



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Open questions

Toolkit for operations on open quantum systems

NYH and Limmer, arXiv:1811.06551 (2018).

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Toolkit for operations on open quantum systems

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NYH and Limmer, arXiv:1811.06551 (2018).

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  - Exciton transport in quantum-dot films
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