HOW EFFECTIVELY CAN A MOLECULAR SWITCH SWITCH? A BOUND FROM THERMODYNAMIC RESOURCE THEORIES

NICOLE YUNGER HALPERN

Harvard-Smithsonian ITAMP

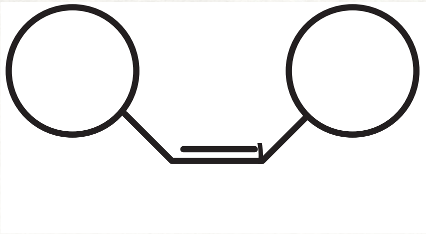
Harvard University Department of Physics

NYH and Limmer, arXiv:1811.06551 (2018).

"Algebraic and Statistical Ways into Quantum Resource Theories," BIRS, 23 July 2019

The photoisomer

The photoisomer



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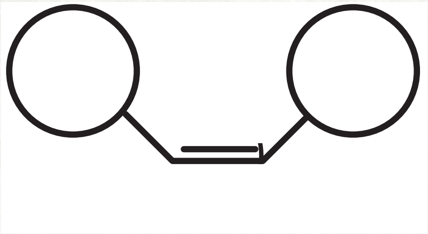
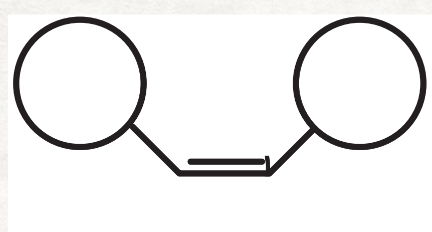


Cis

0°

The photoisomer



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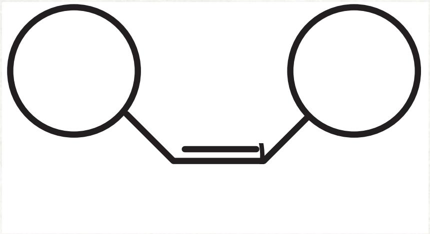

(possible)

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0°

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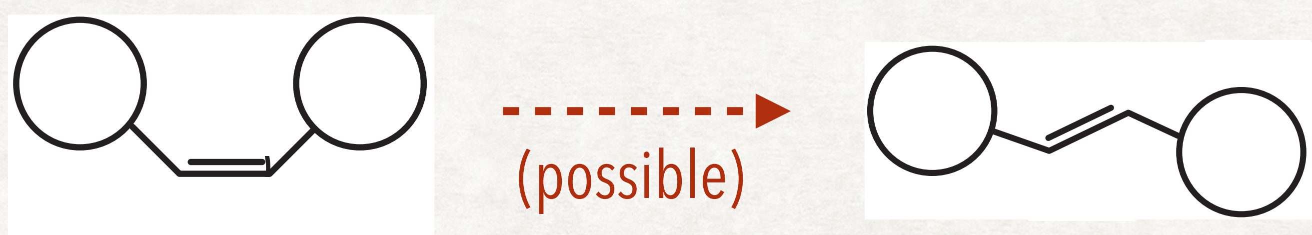

Cis

0°

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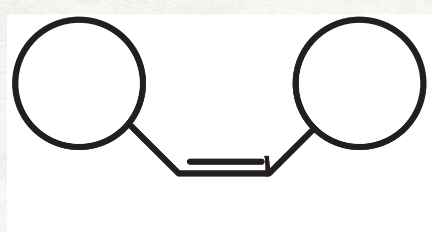

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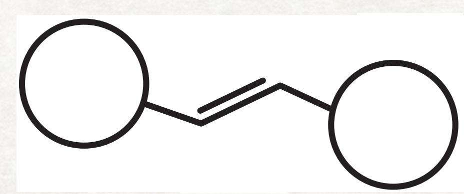


Cis

0º

Trans

180º

Photoisomers surface across nature and technologies.

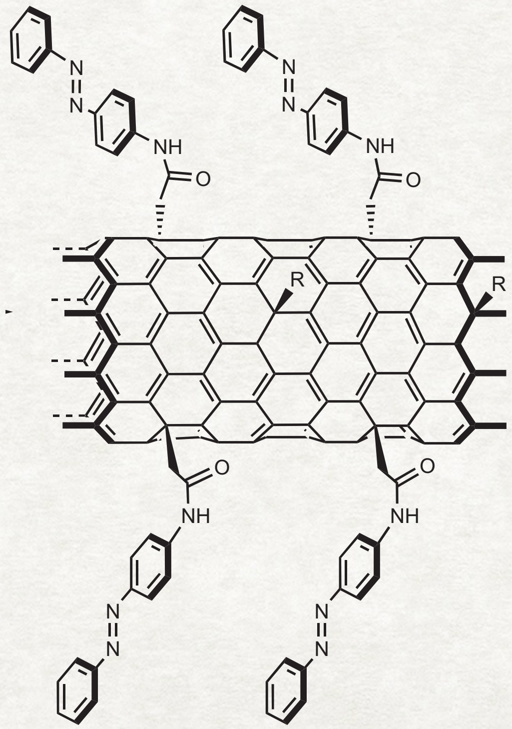
Photoisomers surface across nature and technologies.

- **Retinal**

Photoisomers surface across nature and technologies.

- **Retinal**

- **Solar-fuel storage**



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

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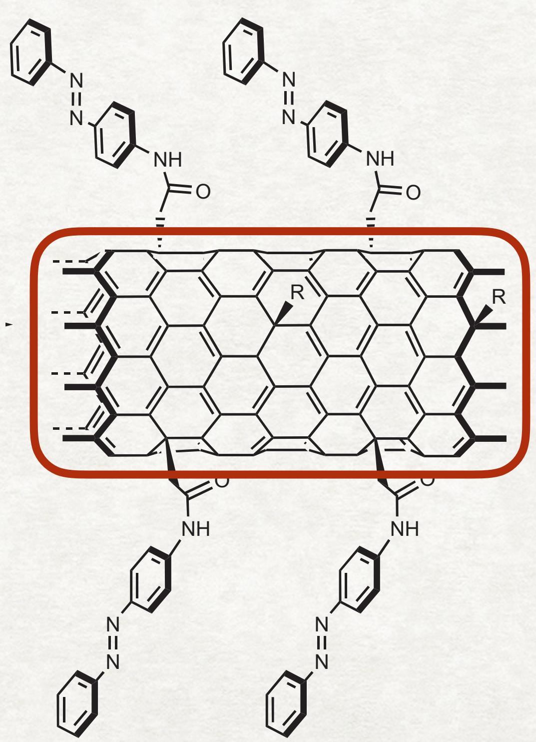

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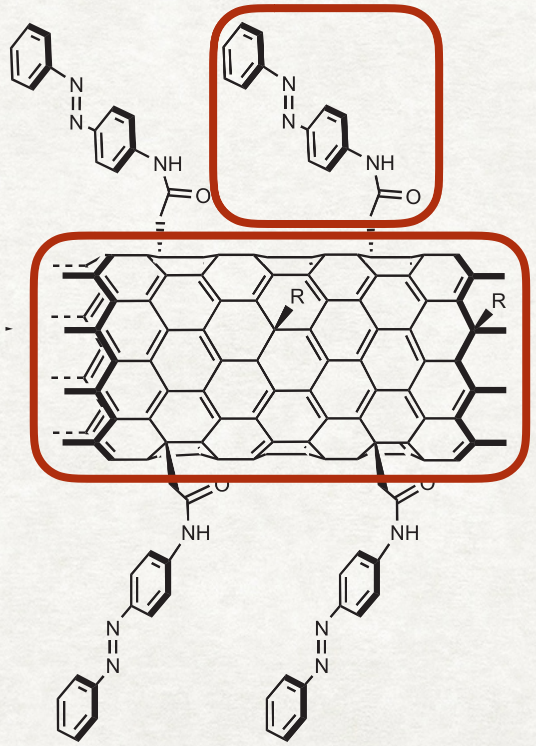

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Photoisomers surface across nature and technologies.

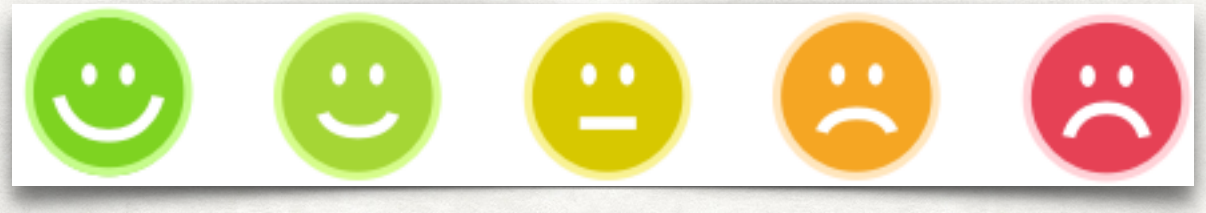
$$\Downarrow$$

Photoisomers surface across nature and technologies.

⇓

Worth asking,

"How effectively can these molecular switches switch?"



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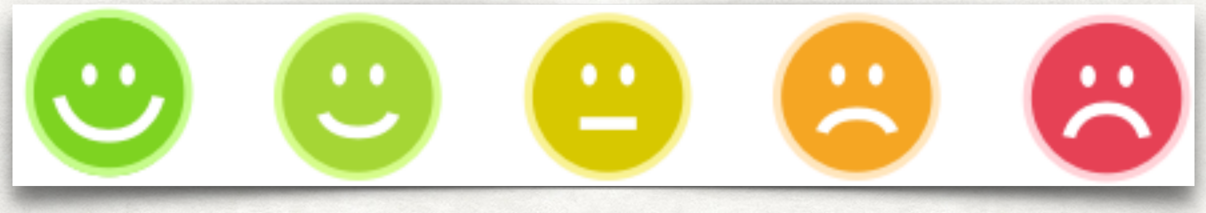

But photoisomers are small, quantum, and far from equilibrium.

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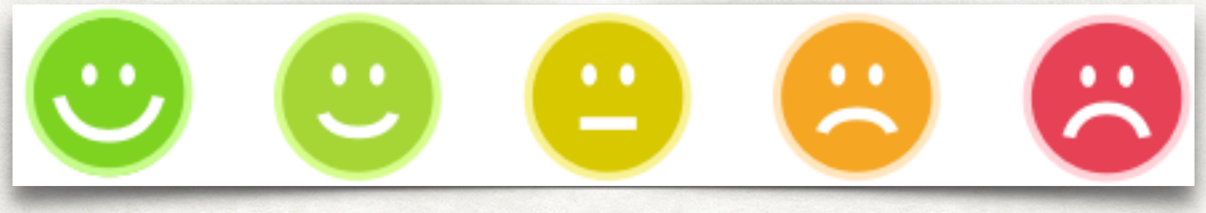

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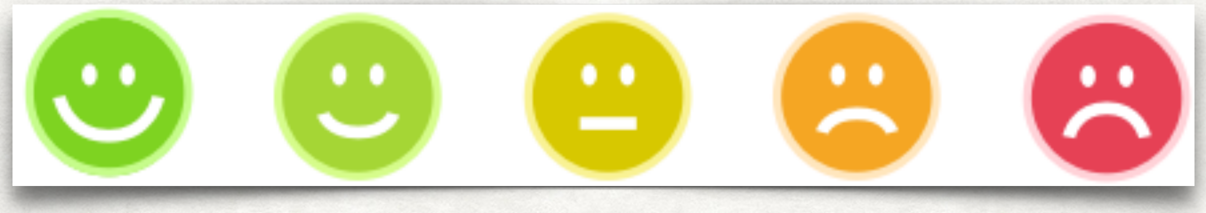

But photoisomers are small, quantum, and far from equilibrium.

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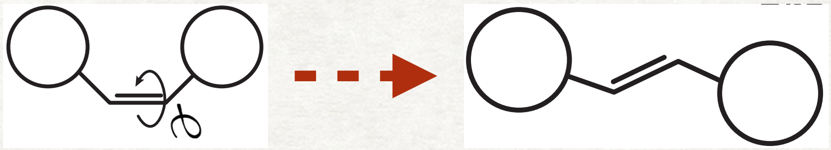
Headway seems to require assumptions,

some of which can be distasteful.

Wanted

General, simple bounds
on photoisomers' switching probability



Wanted

General, simple bounds
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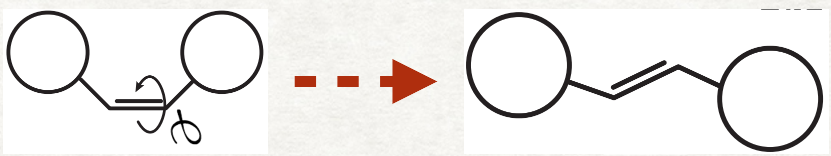
Photoisomerization
yield



Resource theories for thermodynamics

Resource theories for thermodynamics

-Being used to extend the laws of thermodynamics…

- to small scales

Resource theories for thermodynamics

-Being used to extend the laws of thermodynamics…

- to small scales
- to coherent quantum states

Resource theories for thermodynamics

-Being used to extend the laws of thermodynamics…

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

Resource theories for thermodynamics

-<u>Assumptions</u>

Resource theories for thermodynamics

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- Energy conservation

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- Environmental temperature

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-Style: abstract quantum information theory

Resource theories for thermodynamics

-<u>Assumptions</u>

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-<u>Style</u>: abstract quantum information theory ⟶

⋮

Theorem

Theorem

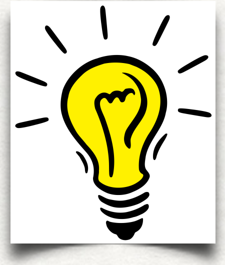
`Corollary`

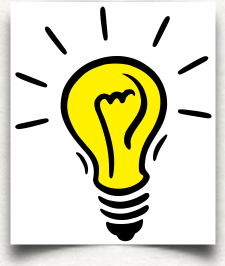
Theorem

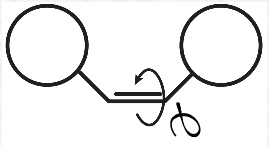
Theorem

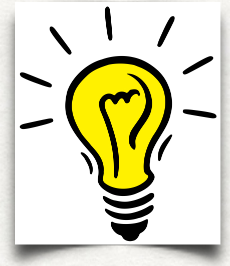
`Lemma`

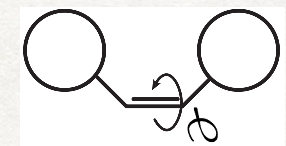
Lemma





Model a photoisomer within a thermodynamic resource theory. →  +



Model a photoisomer within a thermodynamic resource theory. →  +

⋮

Theorem

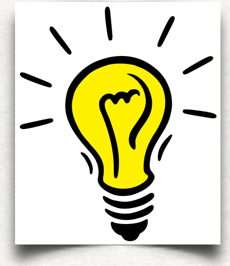
Corollary

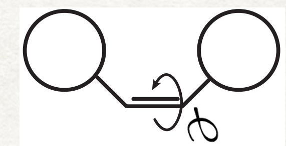
Theorem

Theorem

Lemma

Evaluate resource-theory theorems on the photoisomer. →



Model a photoisomer within a thermodynamic resource theory. →  +

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Theorem

Corollary

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Theorem

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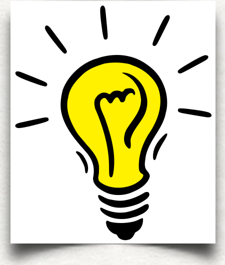
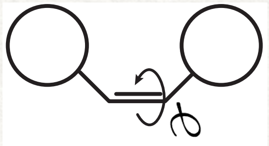
Evaluate resource-theory theorems on the photoisomer. →

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



Model a photoisomer within a thermodynamic resource theory. →



\+

⋮

Theorem

Corollary

Theorem

Theorem

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NYH and Limmer, arXiv:1811.06551 (2018).

Game plan

Game plan

- **Photoisomer background**

Game plan

- Photoisomer background
- Quick review: thermodynamic resource theories

Game plan

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- Results

Game plan

- **Photoisomer background**
- **Quick review: thermodynamic resource theories**
- **Results**
  - Model photoisomer in resource theory

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    - Model photoisomer in resource theory
    - Bound photoisomerization probability

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  - Model photoisomer in resource theory
  - Bound photoisomerization probability
  - Electronic energy coherences can't increase the probability.

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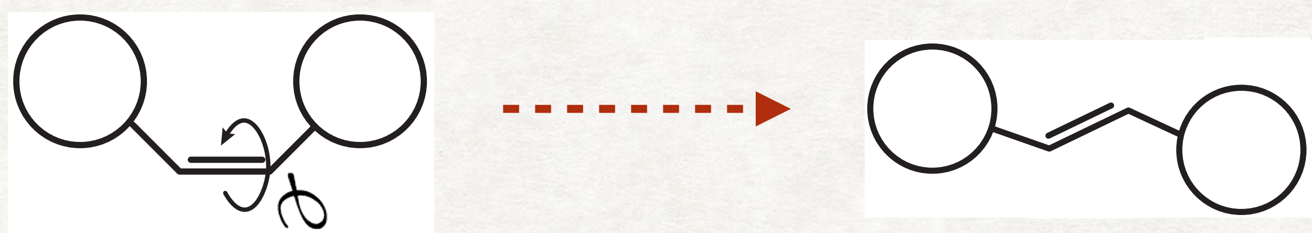
Photoisomer background

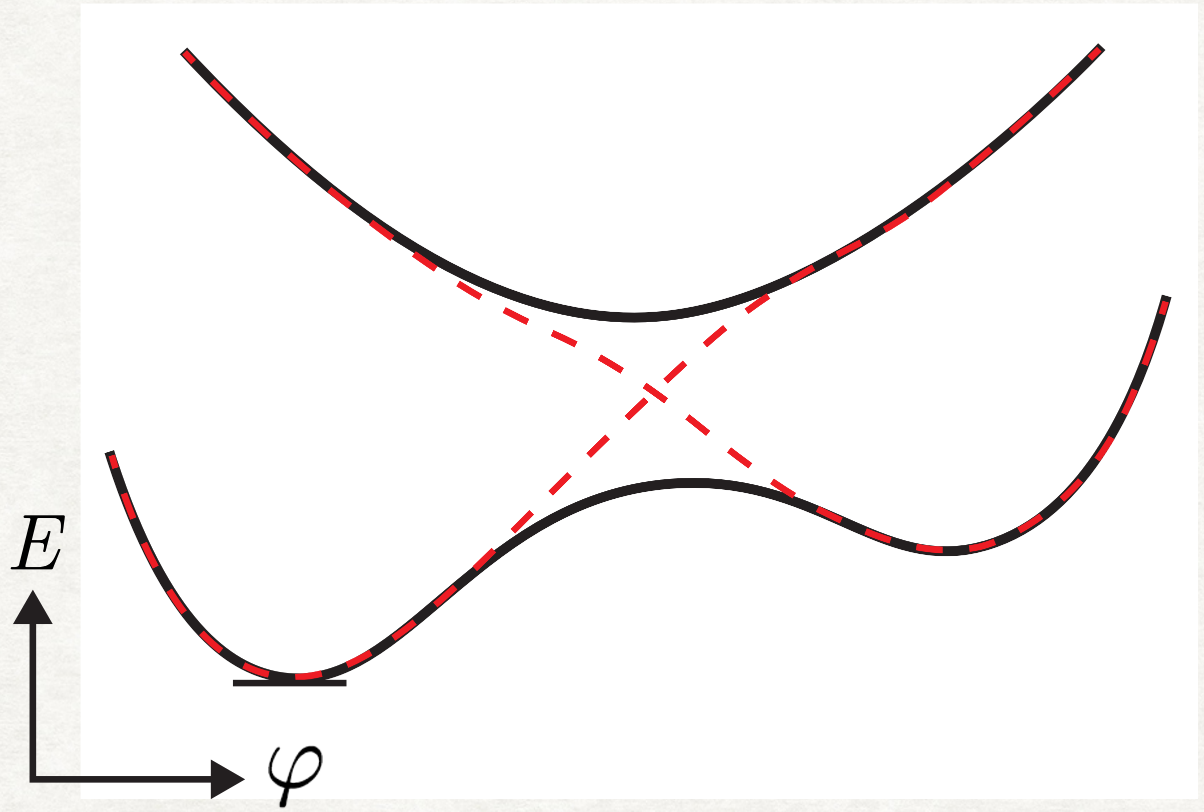


Cis *Trans*

Energy landscape

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

Energy landscape



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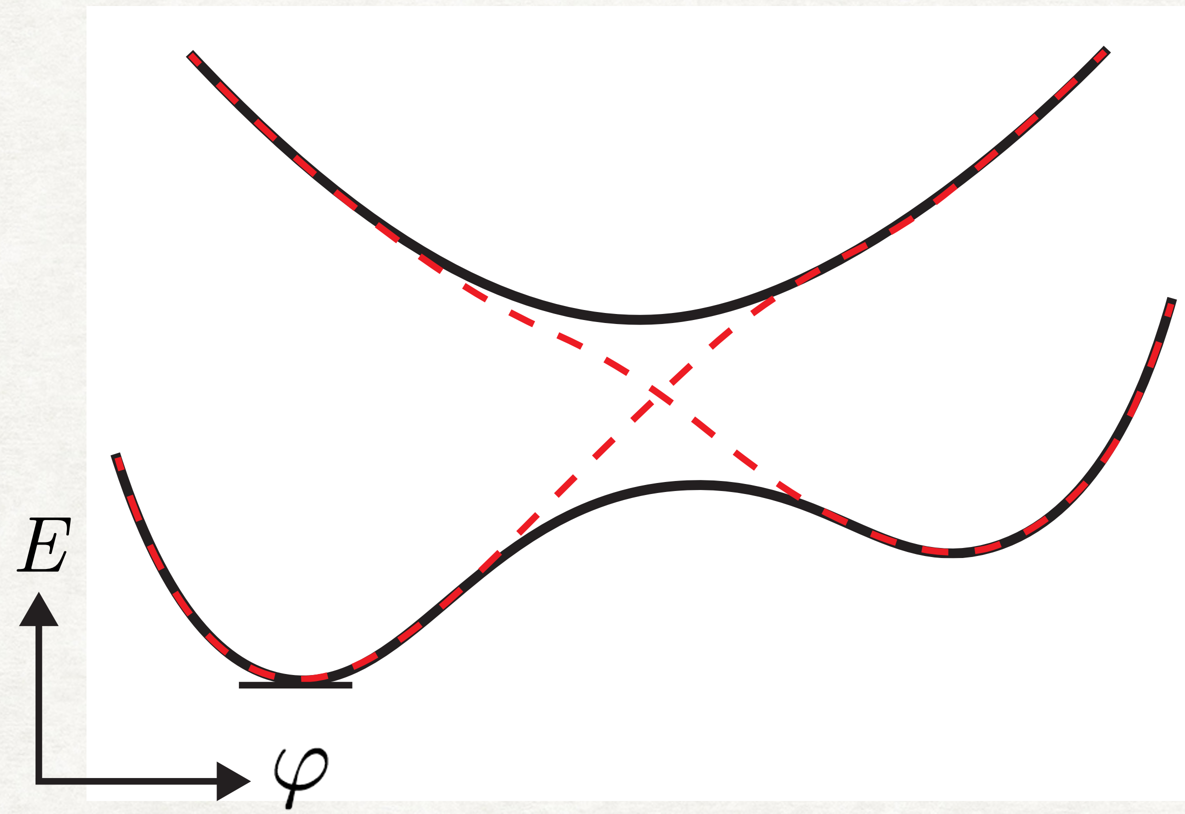

-Rotational coordinate

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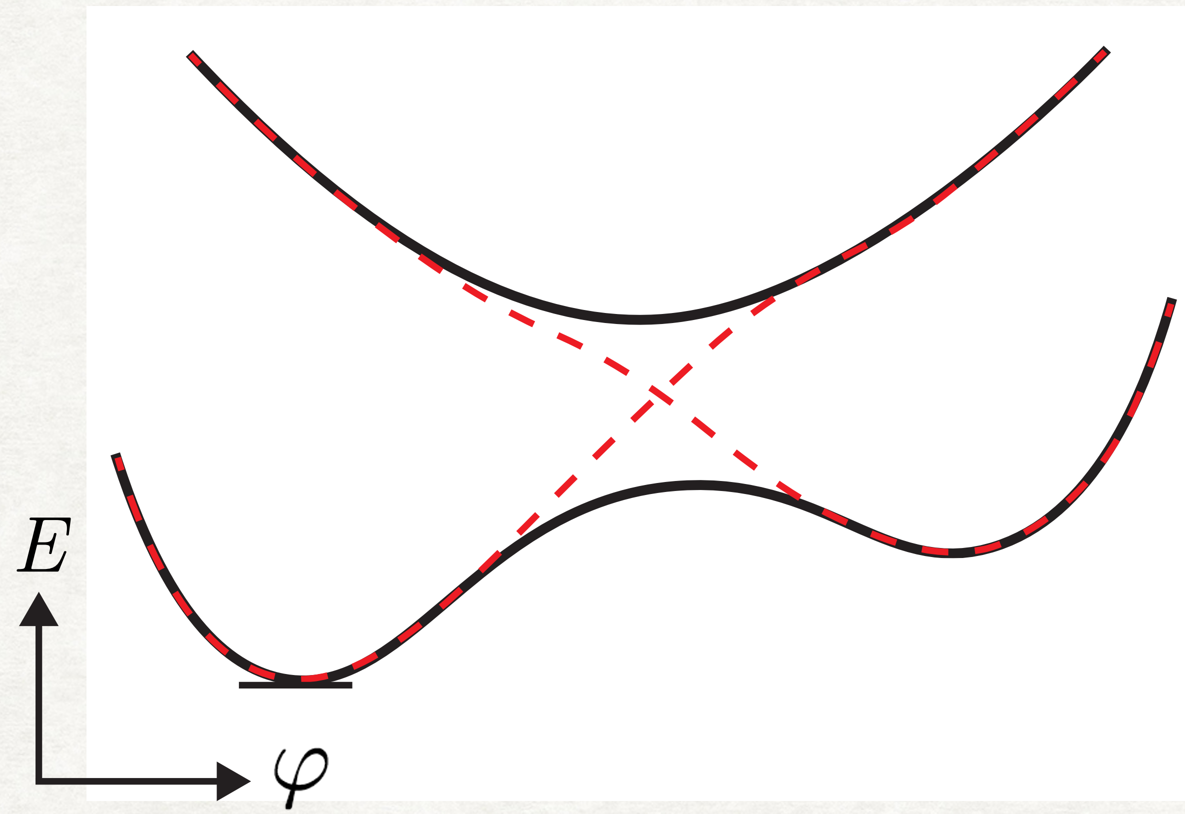
Energy landscape



-Rotational coordinate

0º

Cis

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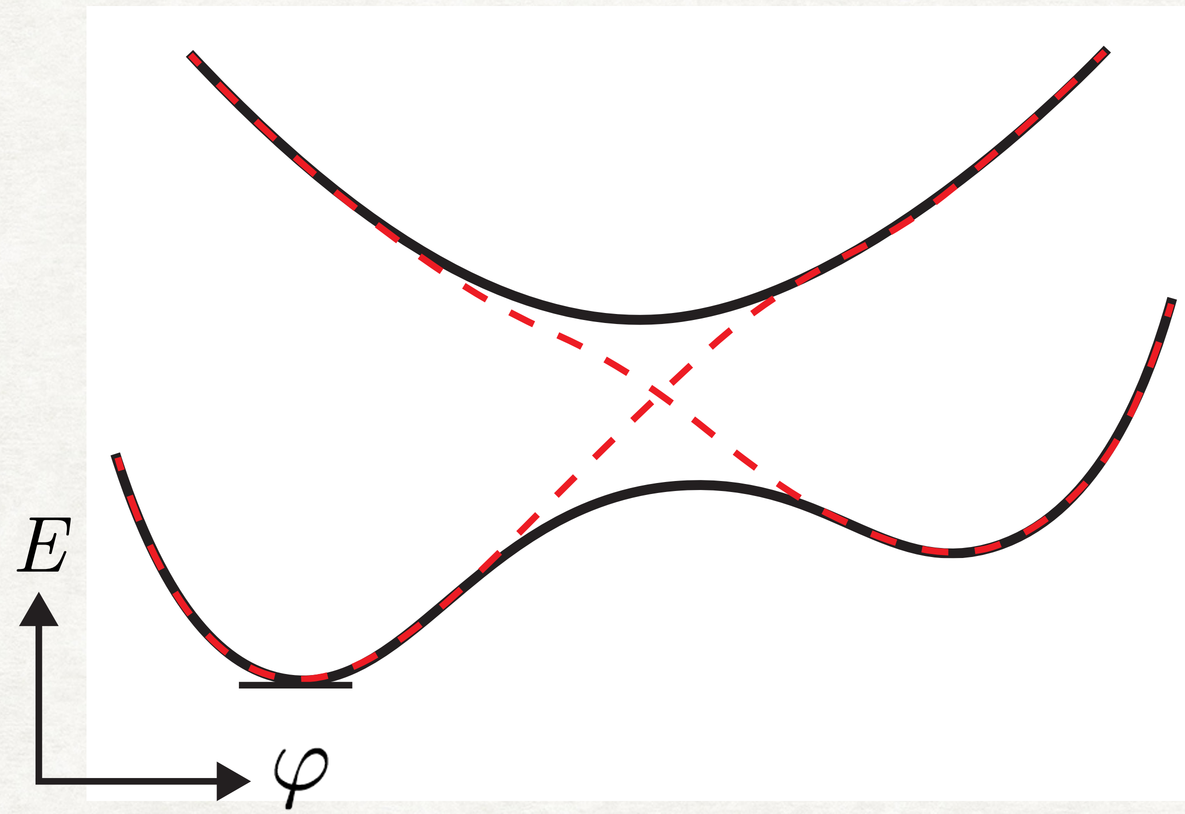

-Rotational coordinate

0º

Cis

180º

Trans

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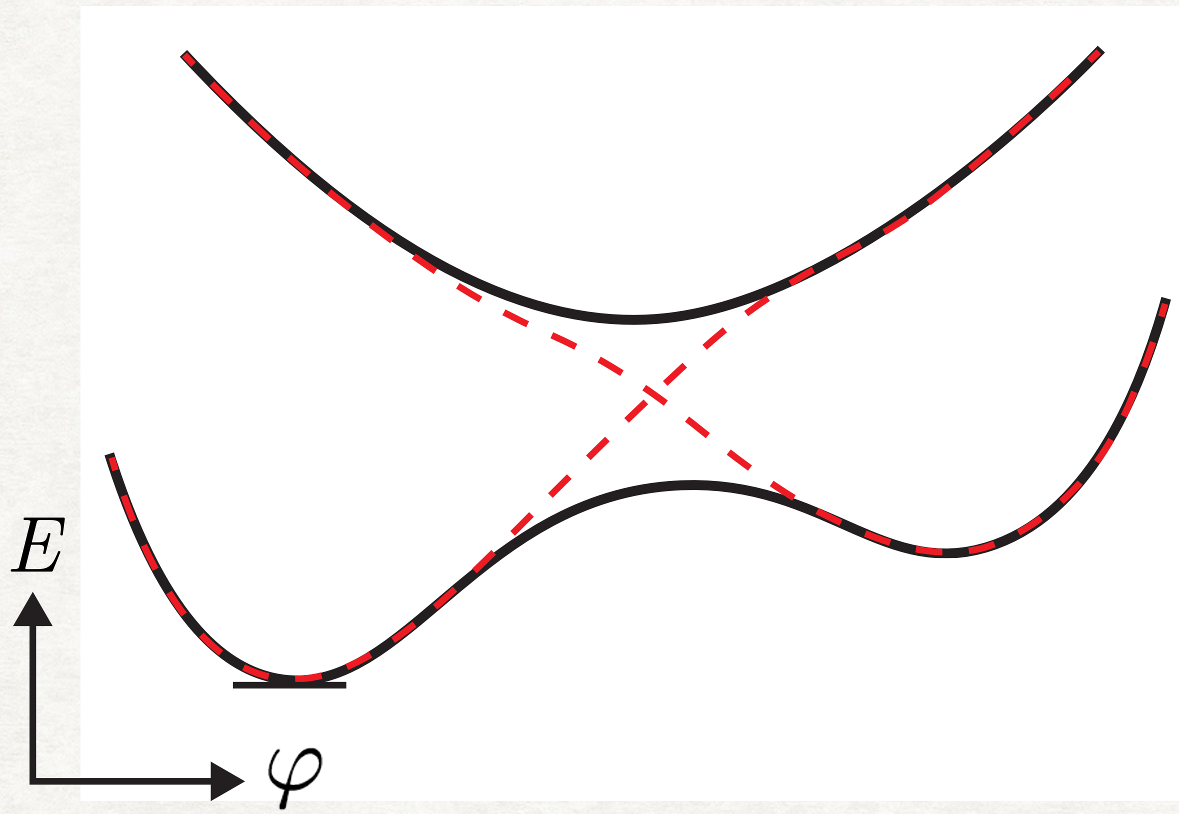

-Rotational coordinate
-Nuclear degree of freedom

0º
Cis

180º
Trans

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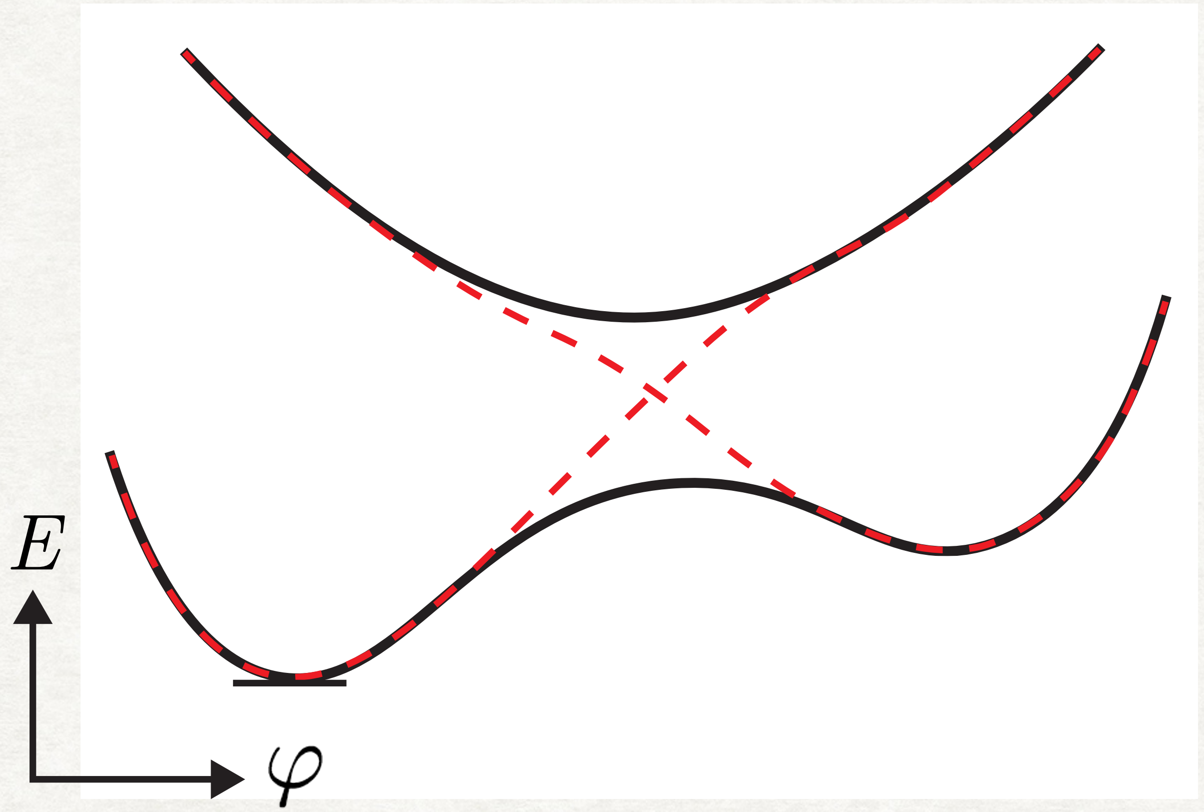
Energy landscape



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

0º
Cis

180º
Trans

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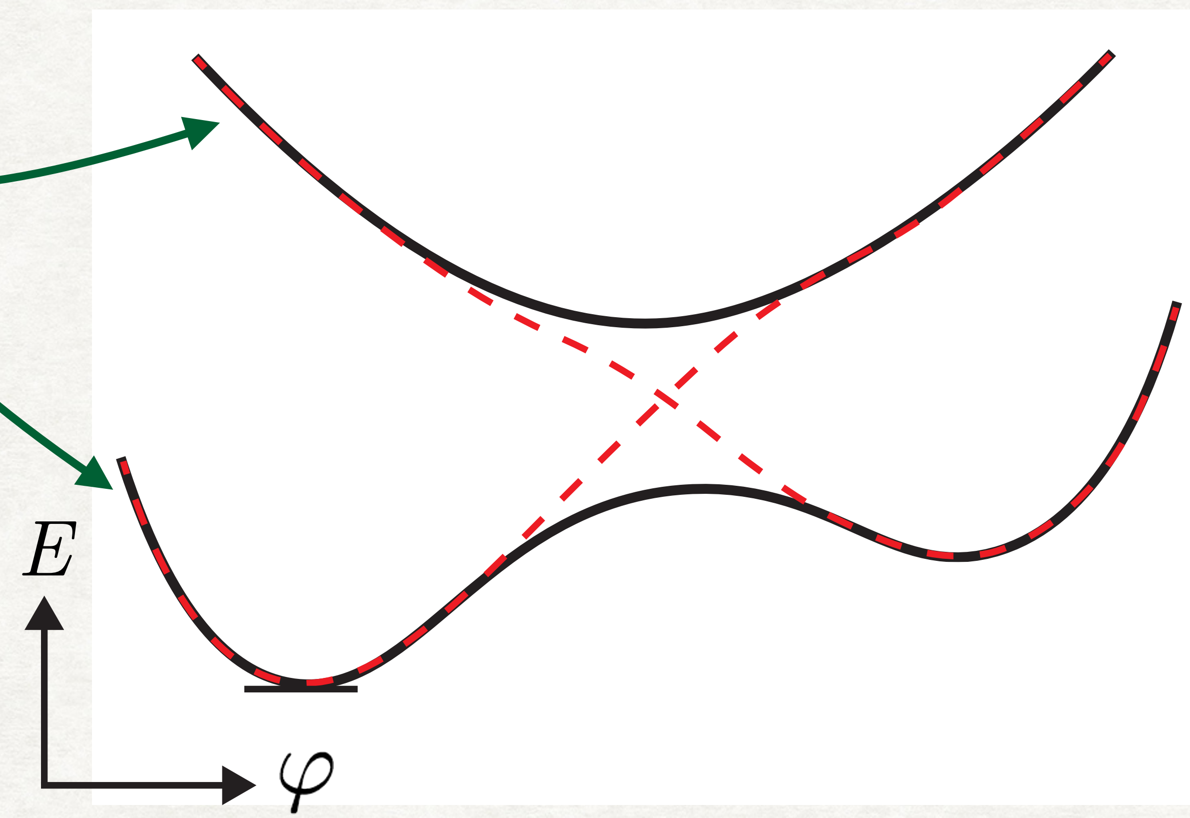
Energy landscape

-Electronic degree of freedom



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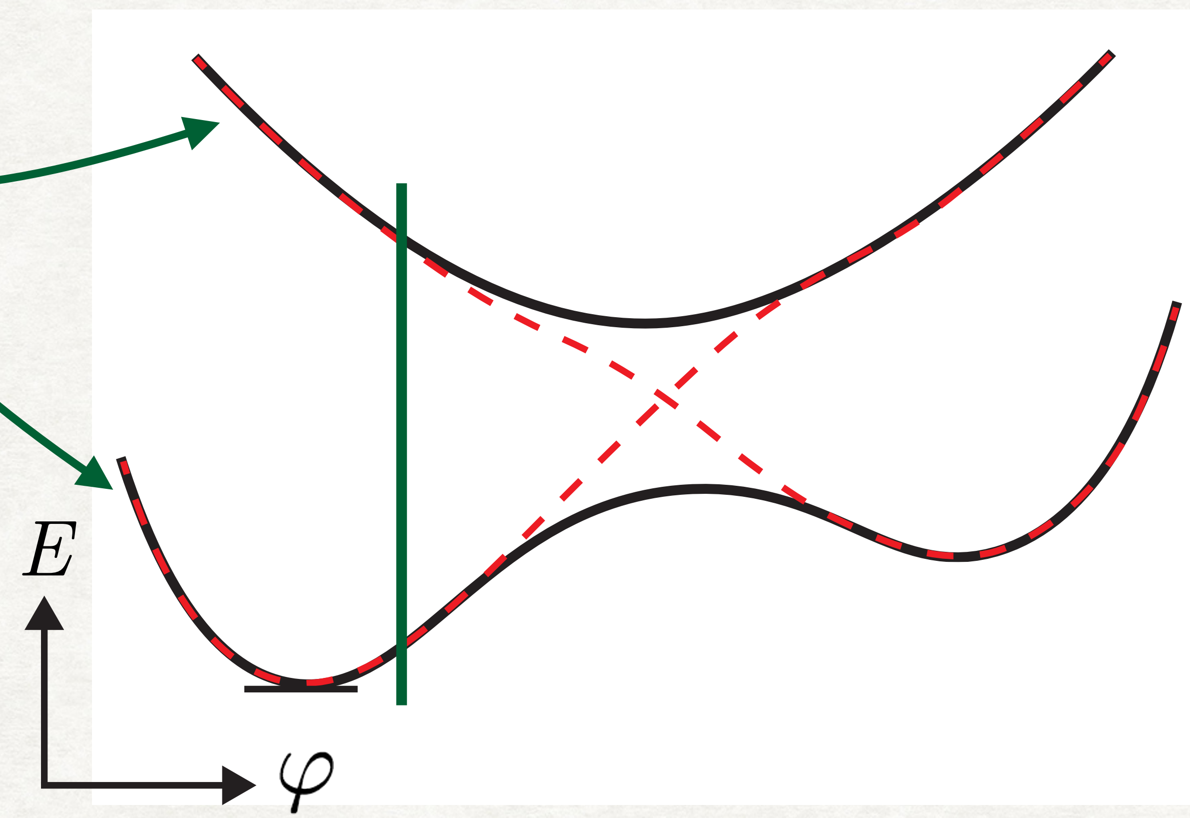

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0º
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180º
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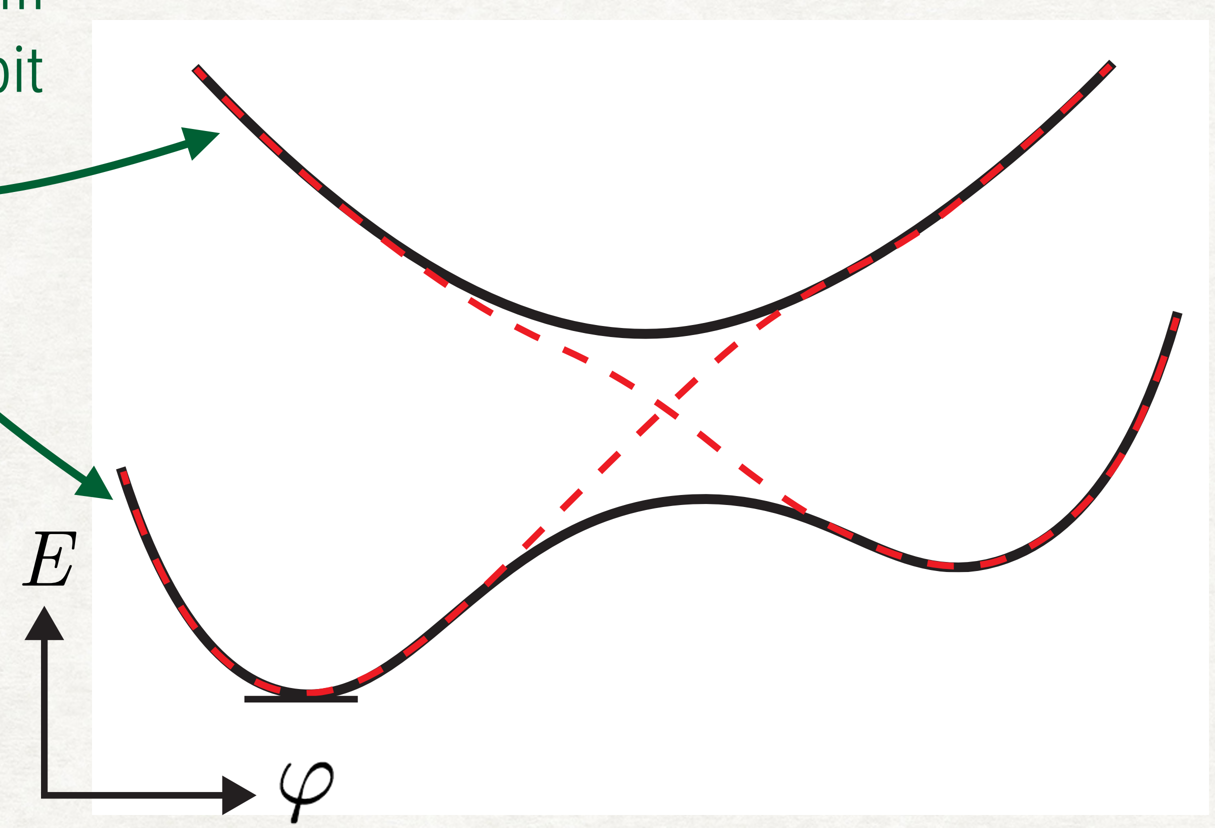
Energy landscape

-Electronic degree of freedom
-Effective qubit



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Cis

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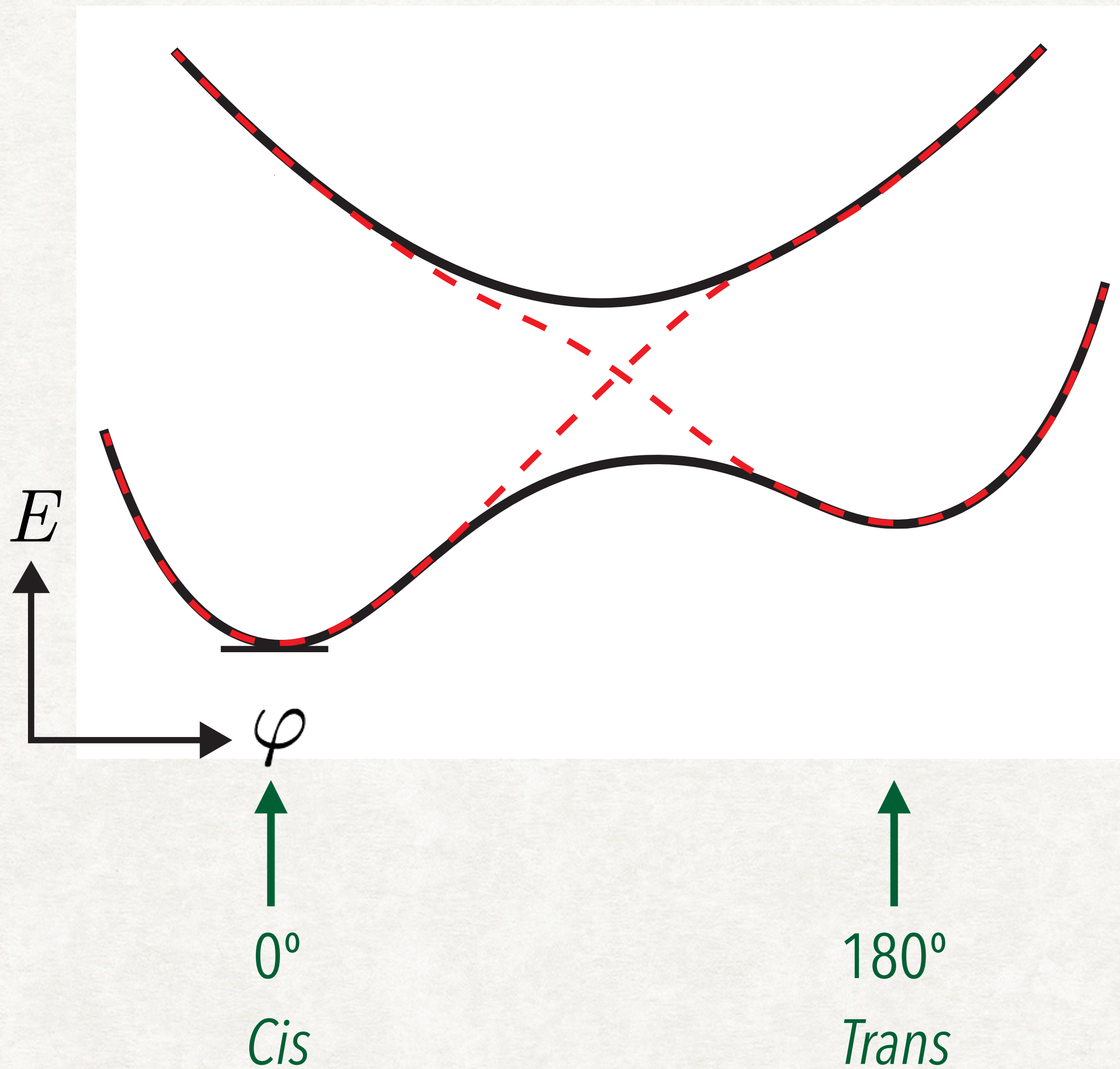
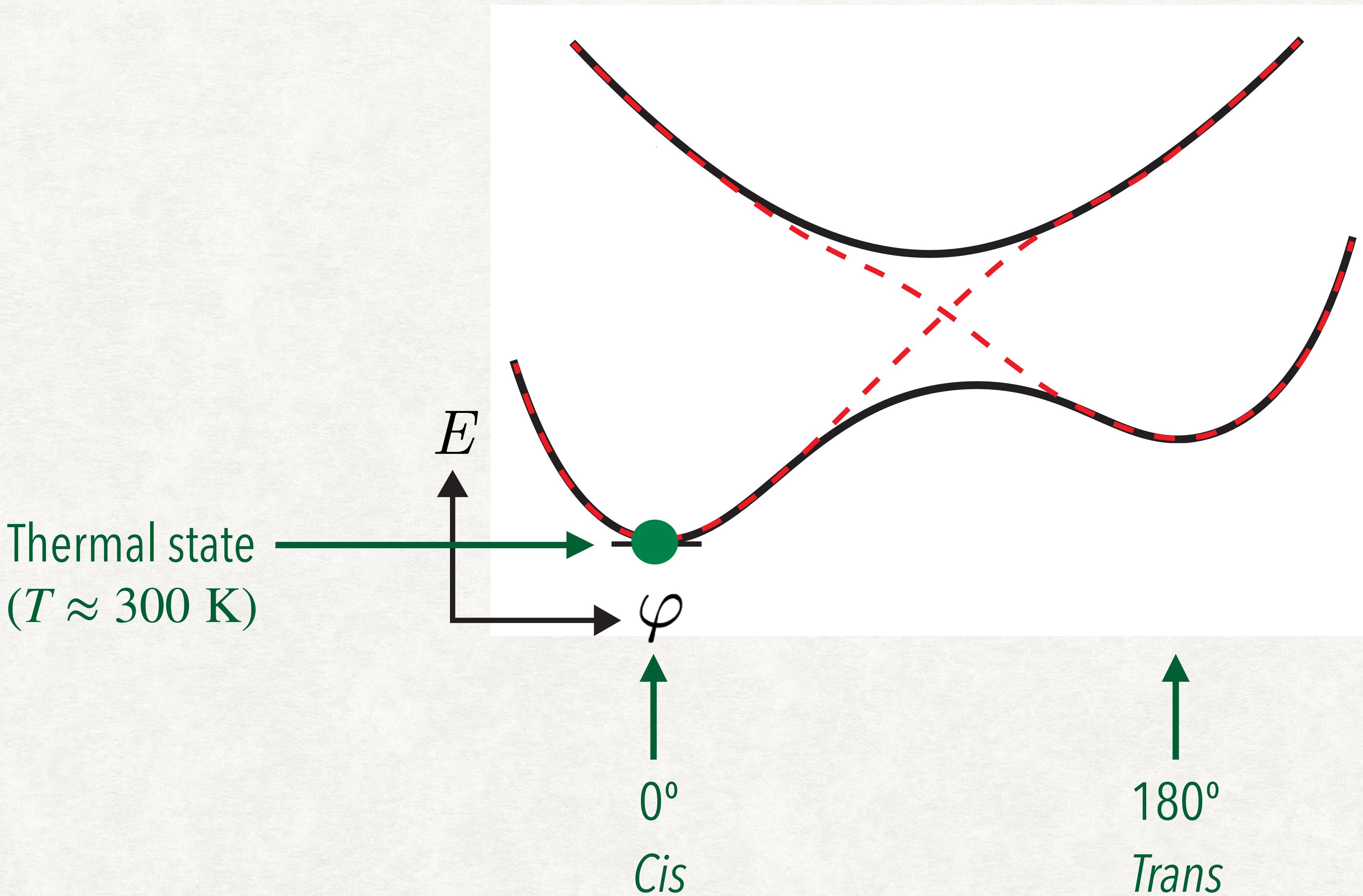
Photoisomerization



Photoisomerization



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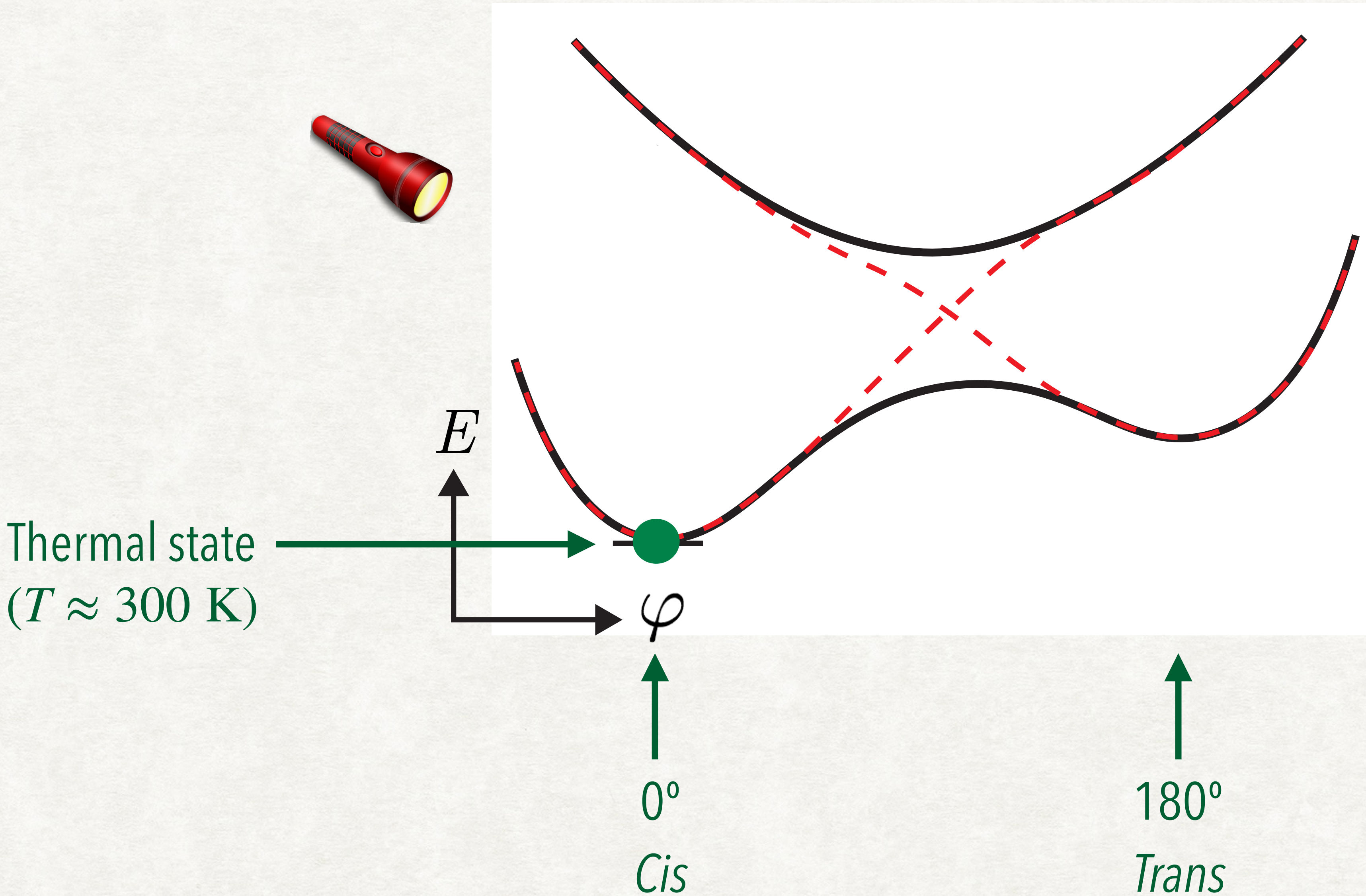

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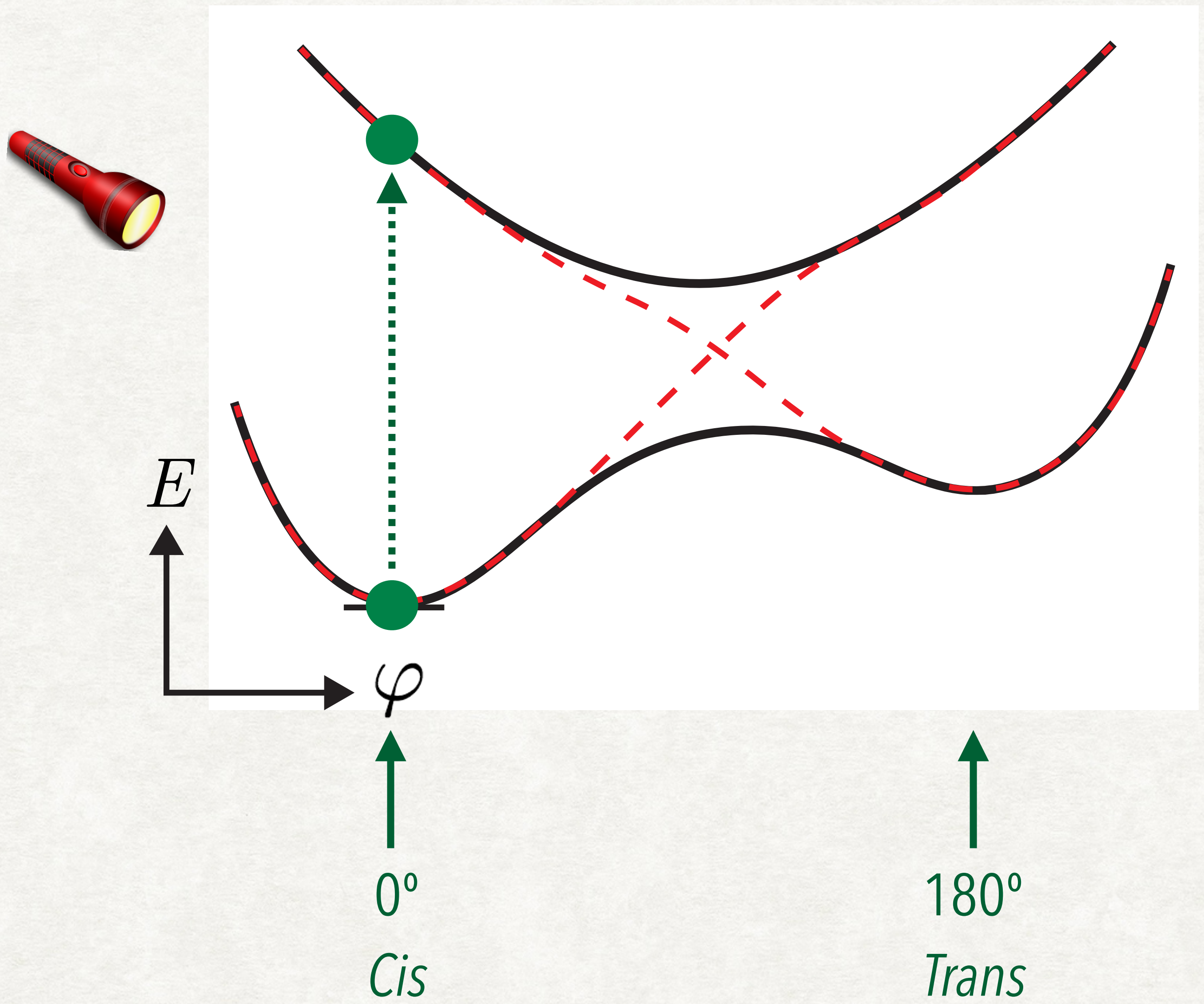

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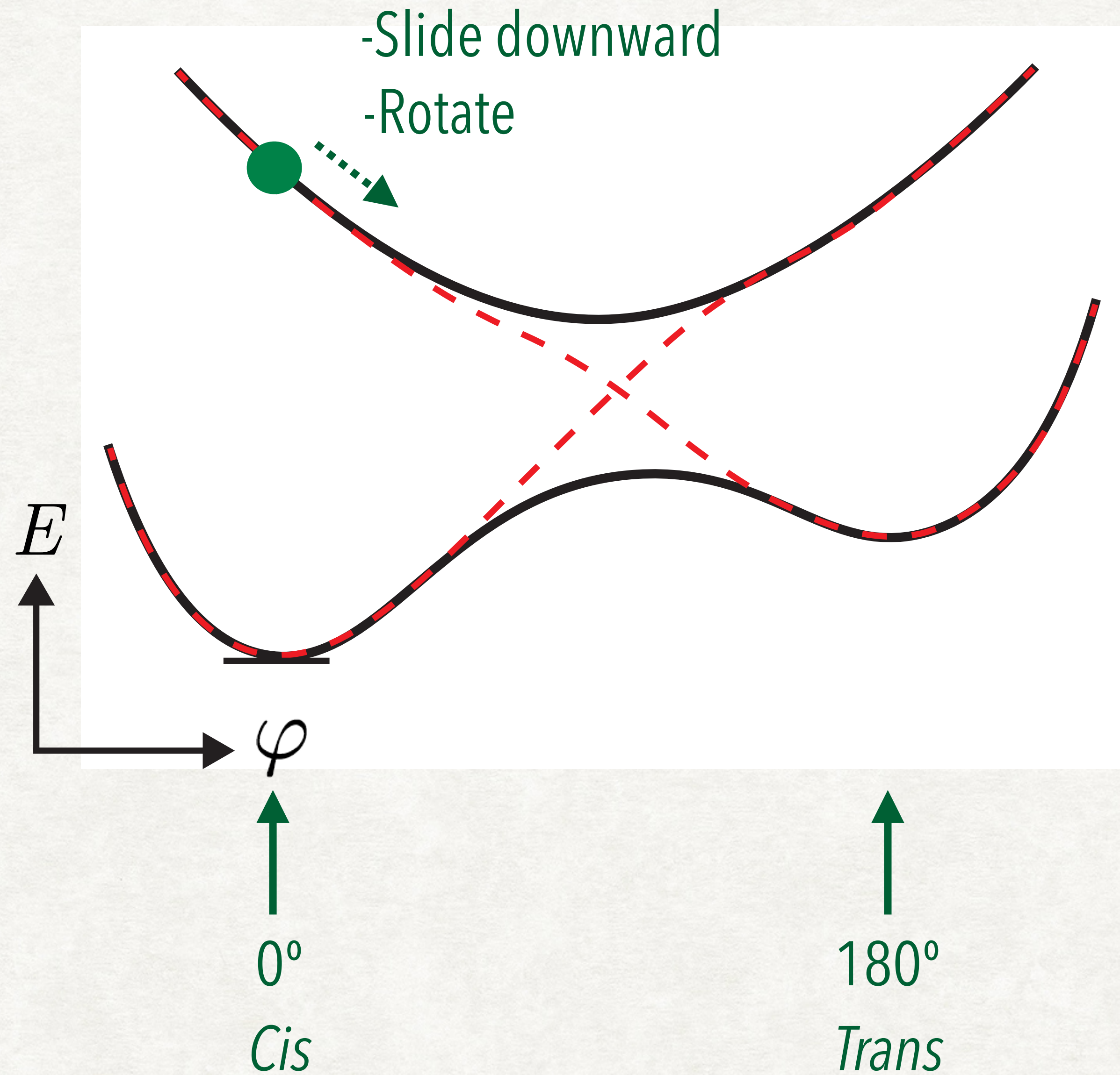

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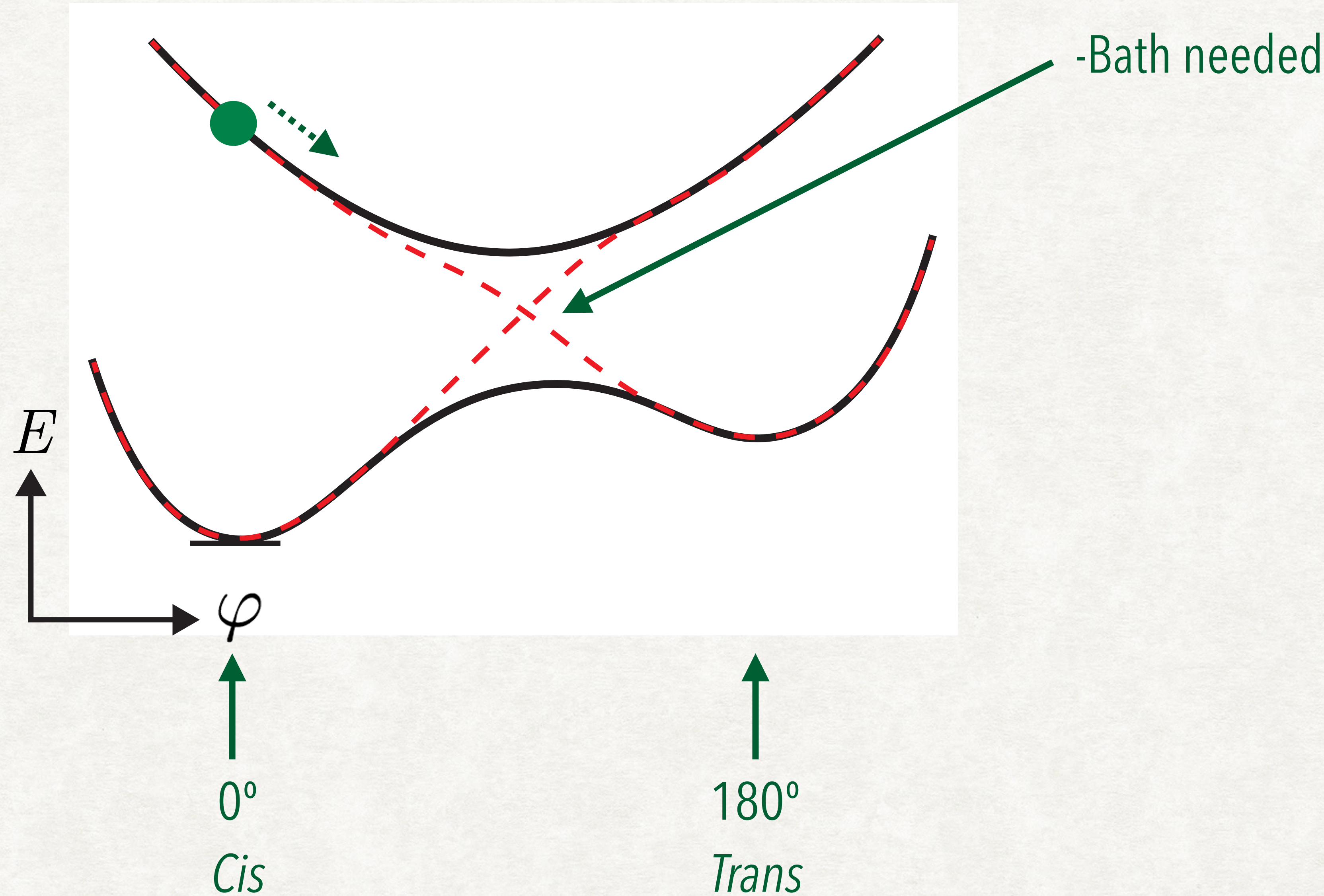

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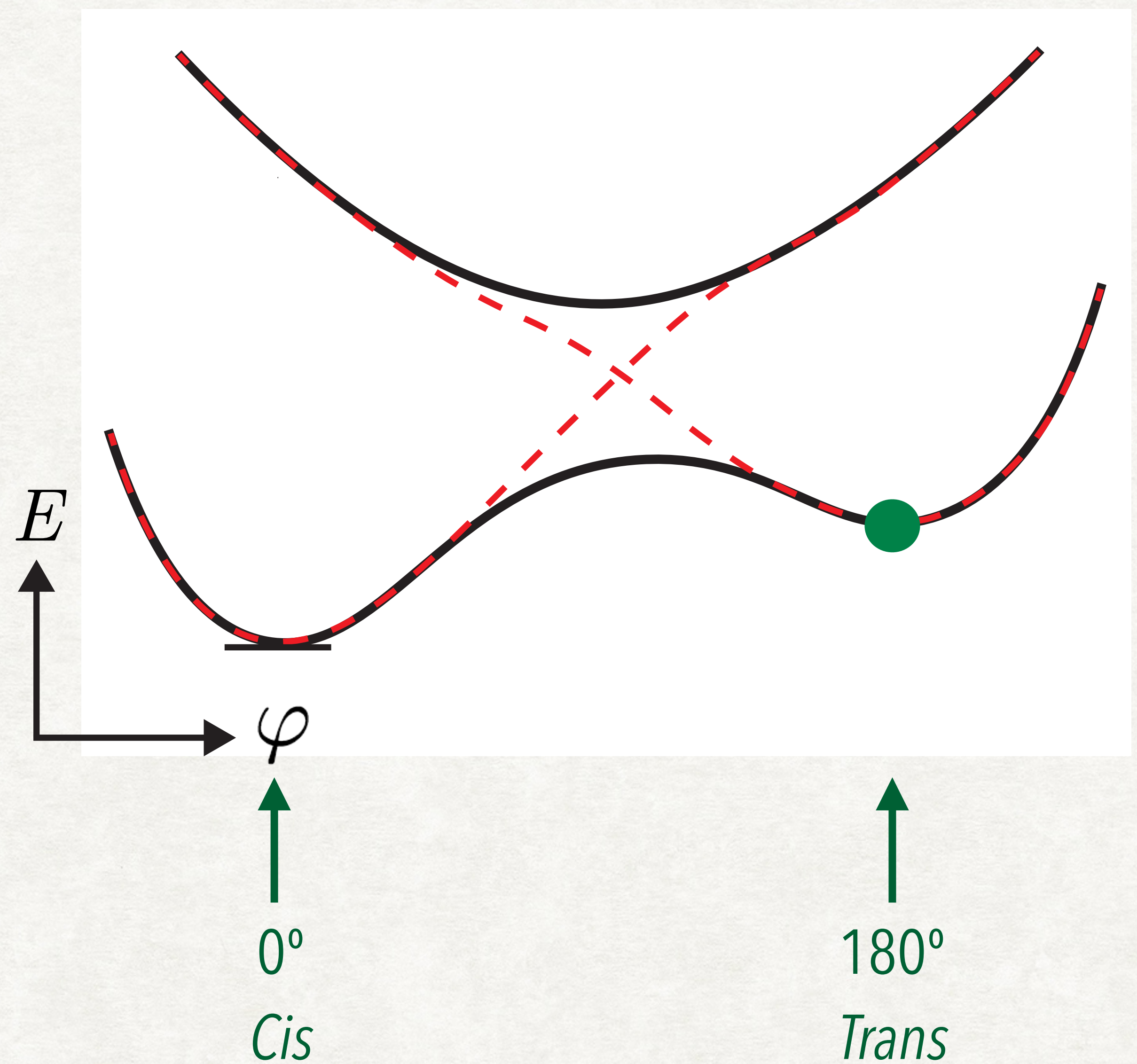

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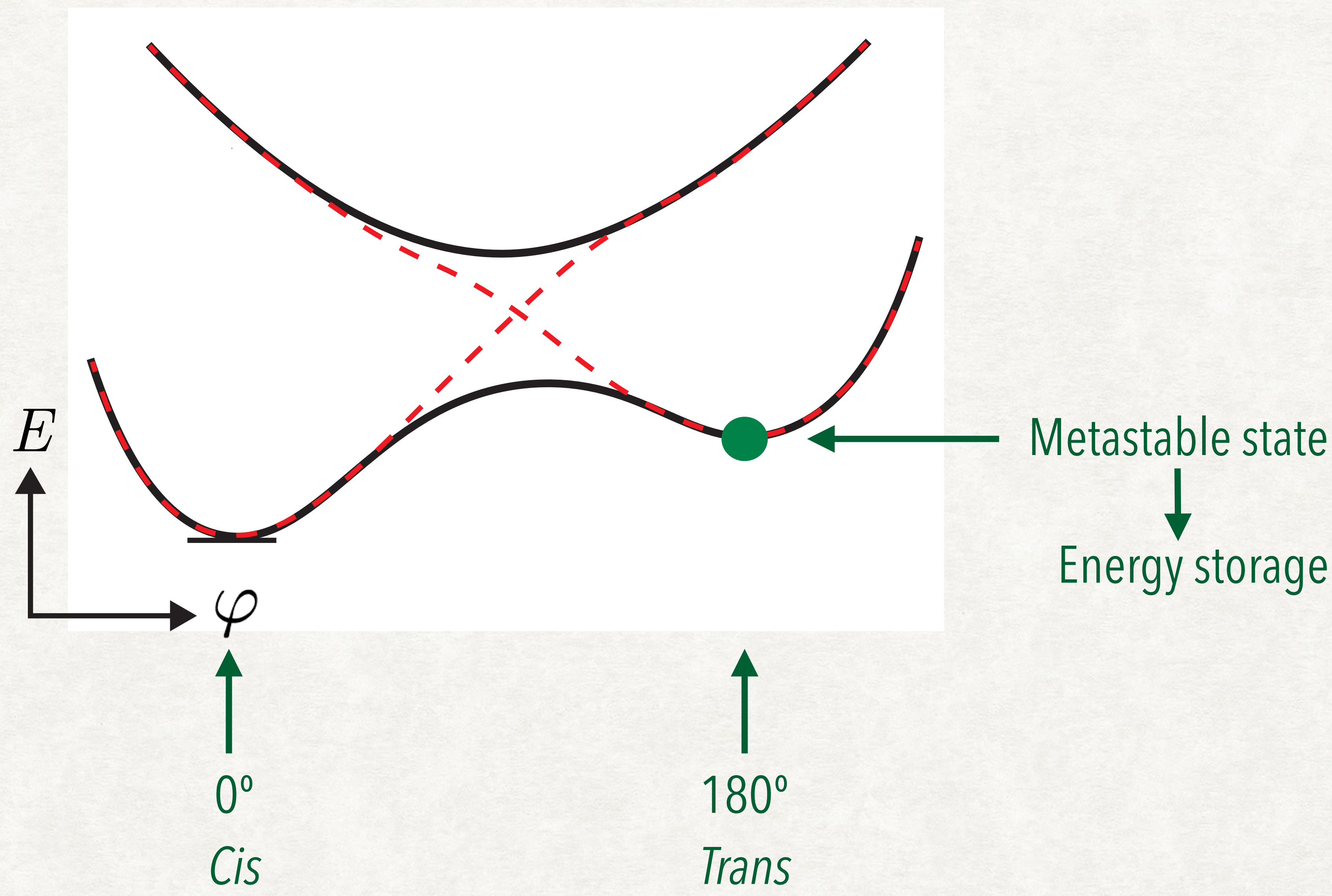

Quick review: Thermodynamic resource theories that model heat exchanges

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- <u>How to specify a system</u>:

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- How to specify a system: $\mathscr{H}$

Hilbert space

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

Hamiltonian

Hilbert space

Density operator

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Hamiltonian

Hilbert space   Density operator

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

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

  Hilbert space ($\mathscr{H}$), Density operator (ρ), Hamiltonian (H)

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

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

Free operations

Free operations

- **Thermal operations**

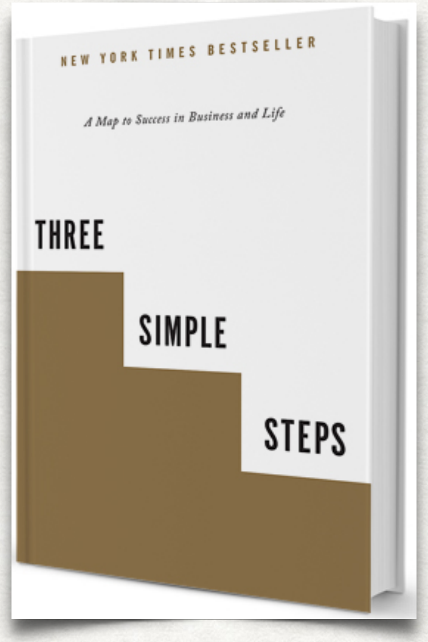
Free operations

- **Thermal operations** (simplest of the options)

Free operations

- **Thermal operations**
- Tend to thermalize states

Free operations

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

Free operations

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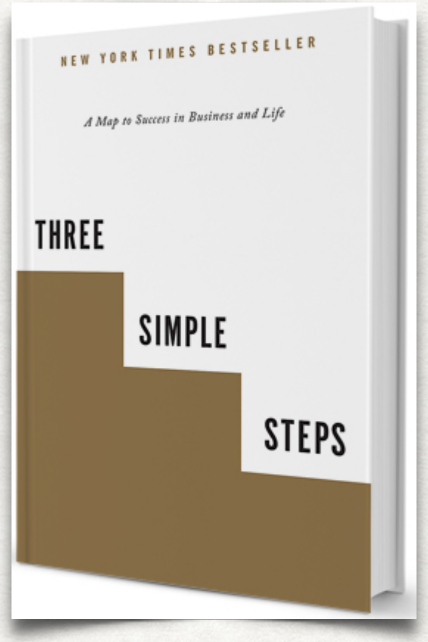
- Each free operation consists of  .

1) Draw any free state from the bath.

Free operations

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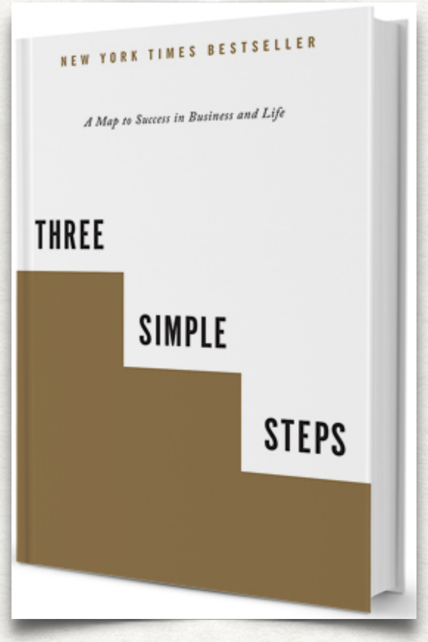
- Each free operation consists of  .

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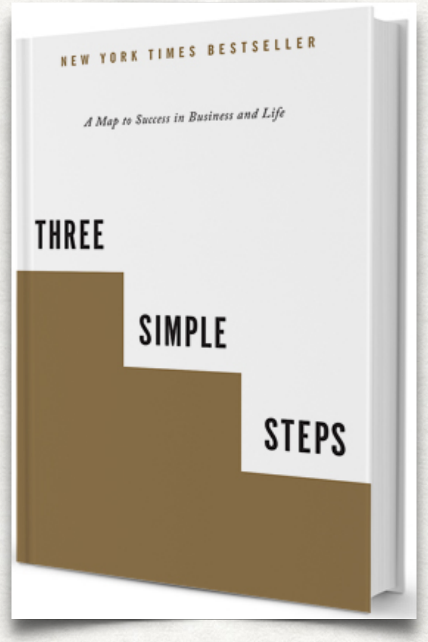
- Each free operation consists of  .

1) Draw any free state from the bath.
2) Perform any unitary that conserves the total energy.
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

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

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~First law of thermodynamics

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~First law of thermodynamics

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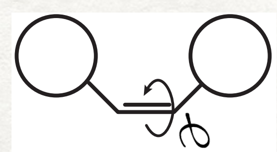
    $\parallel$

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

~First law of thermodynamics

Modeling the photoisomer in the resource theory



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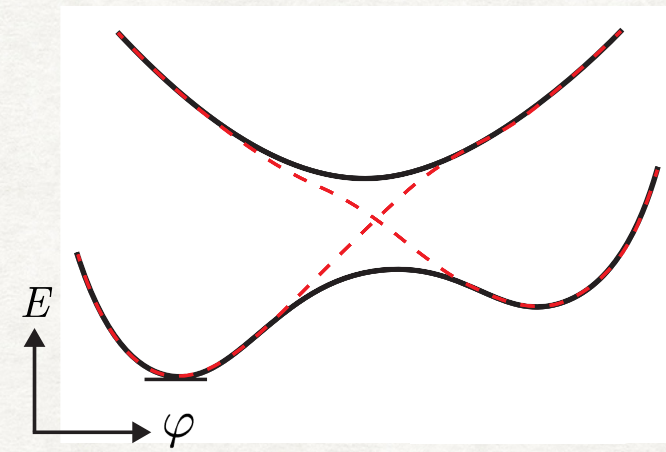
NYH and Limmer, arXiv:1811.06551 (2018).

Modeling the photoisomer in the resource theory

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



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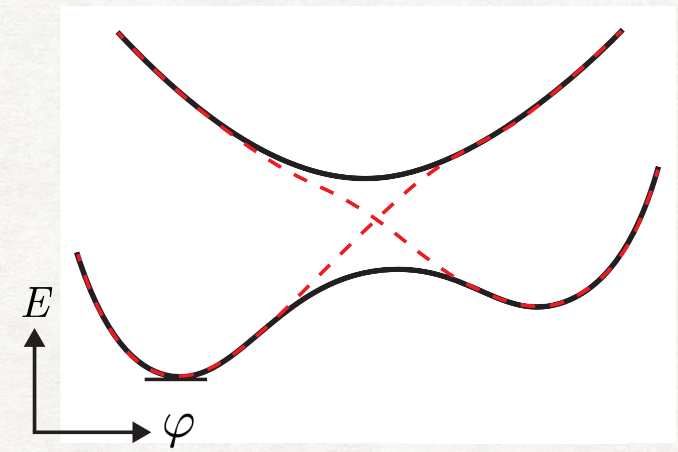

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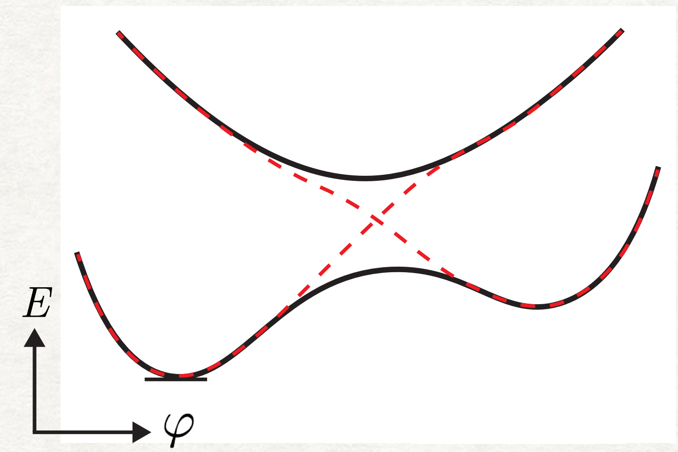

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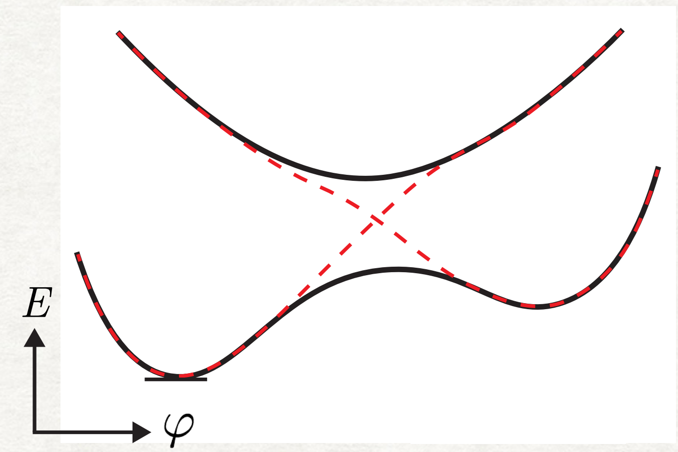

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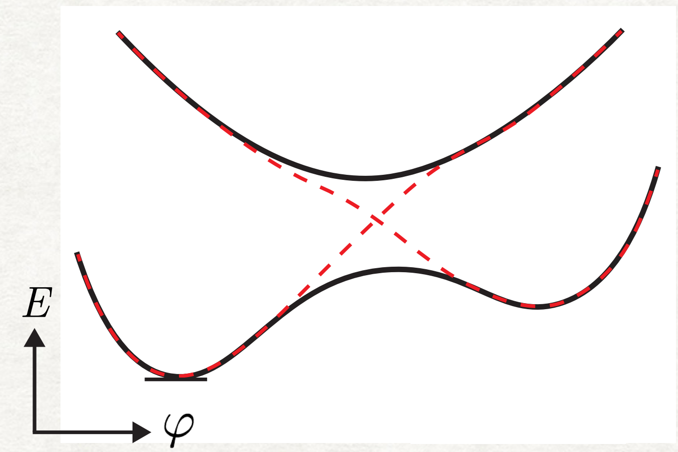

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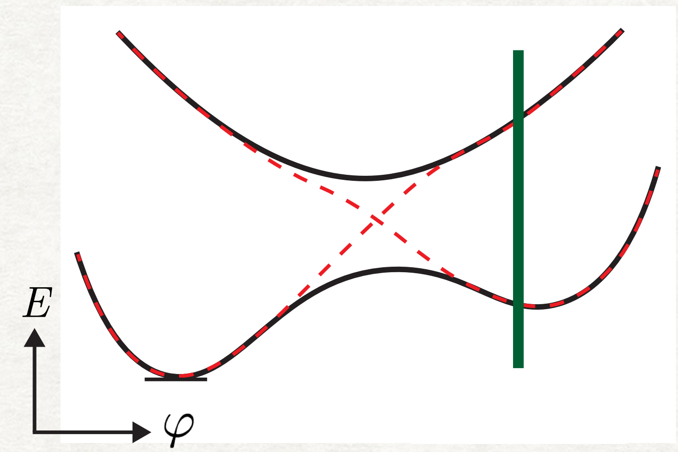

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Modeling photoisomerization's steps with thermal operations

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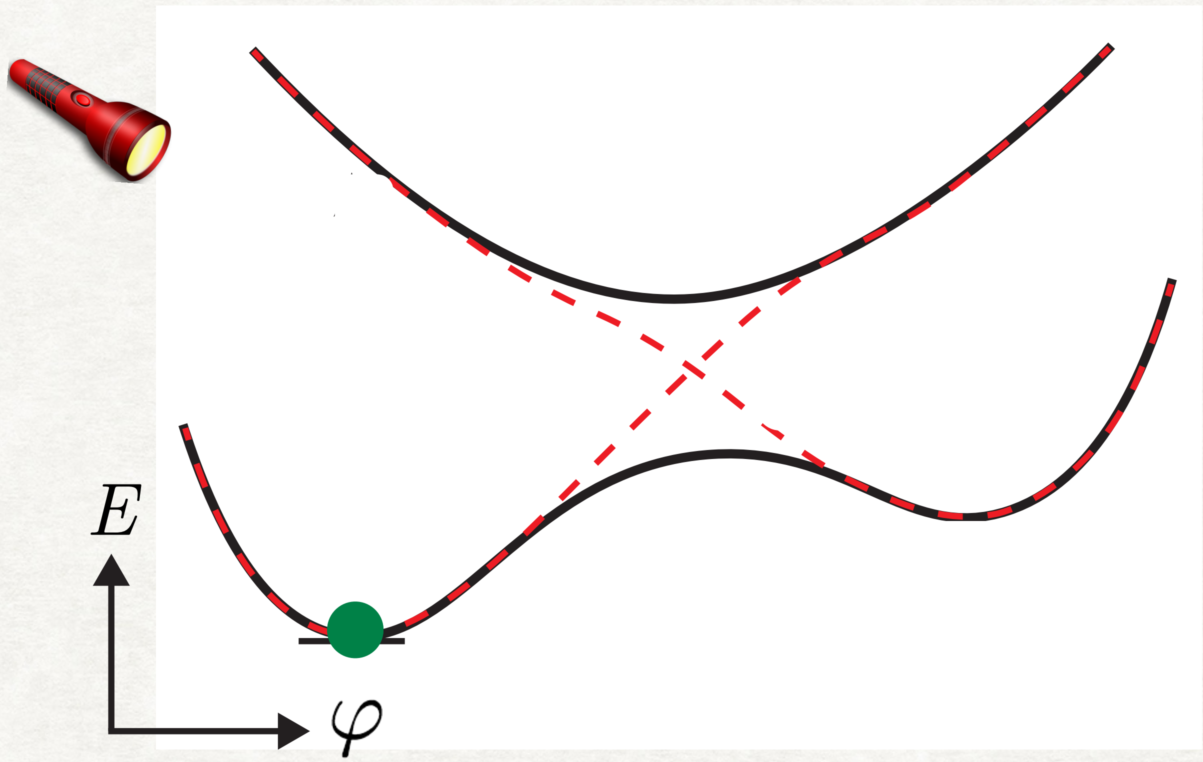

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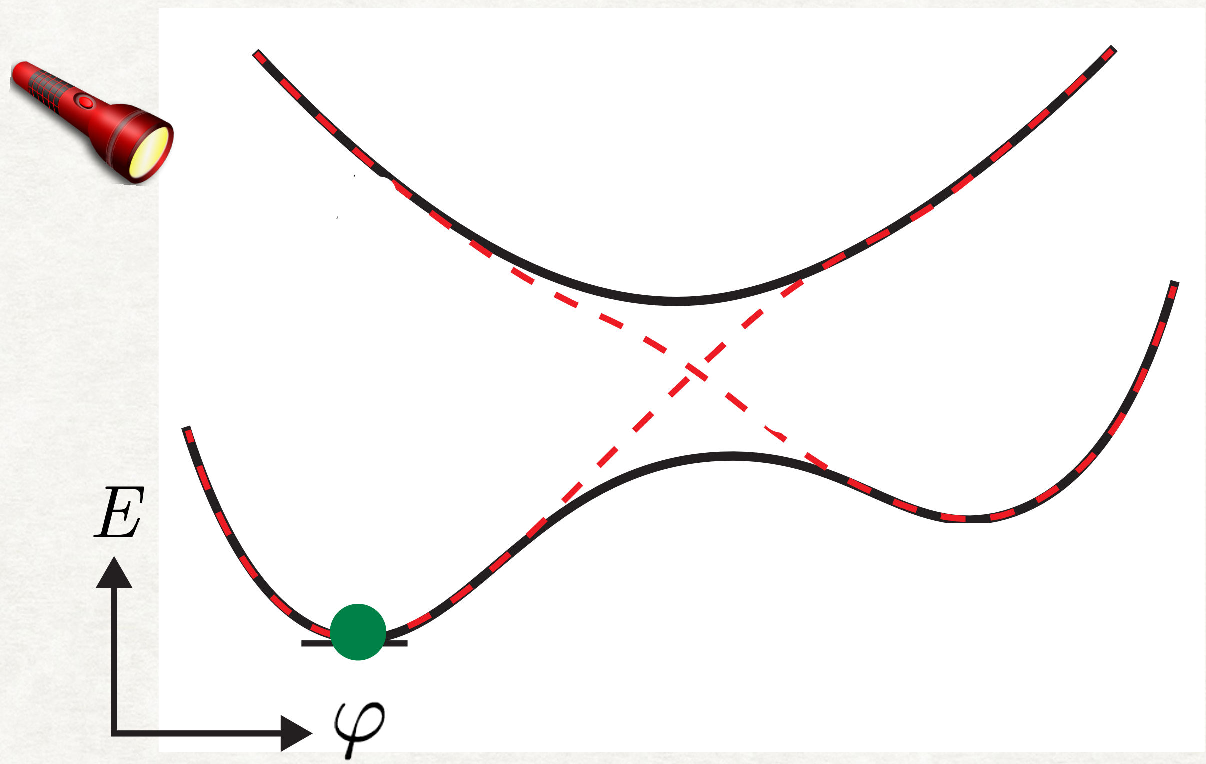
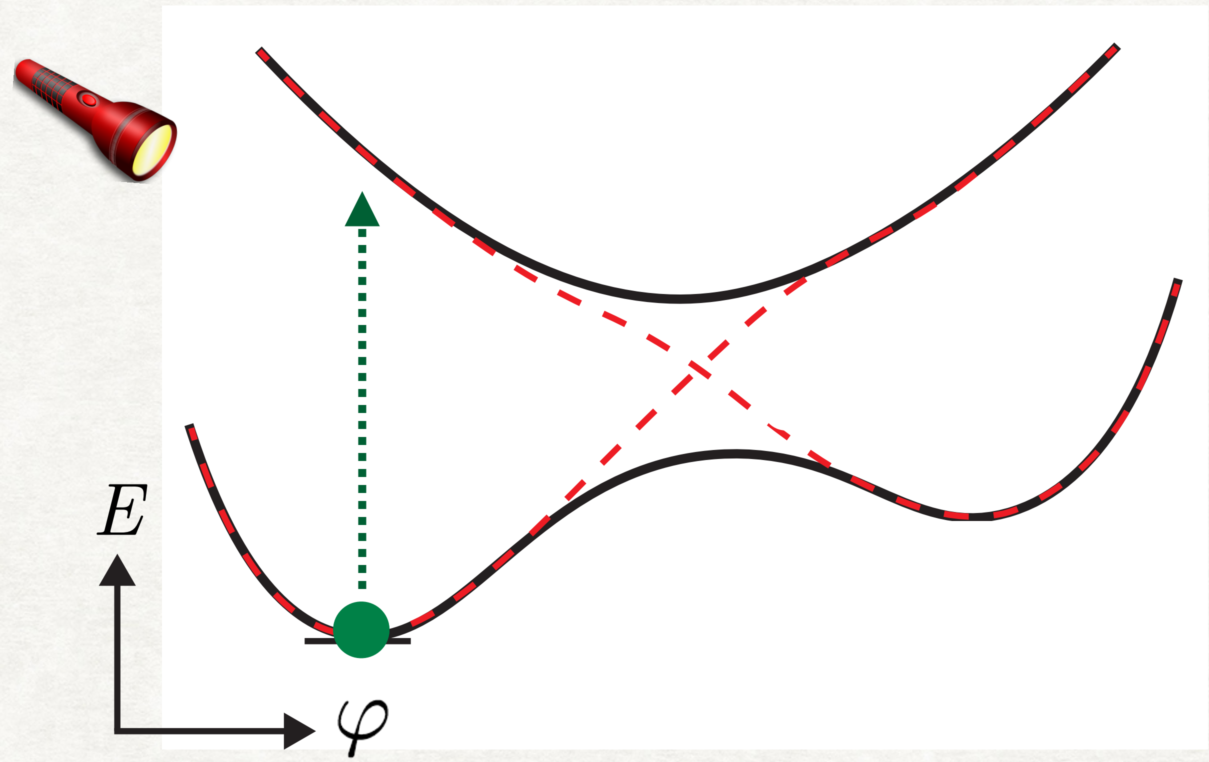


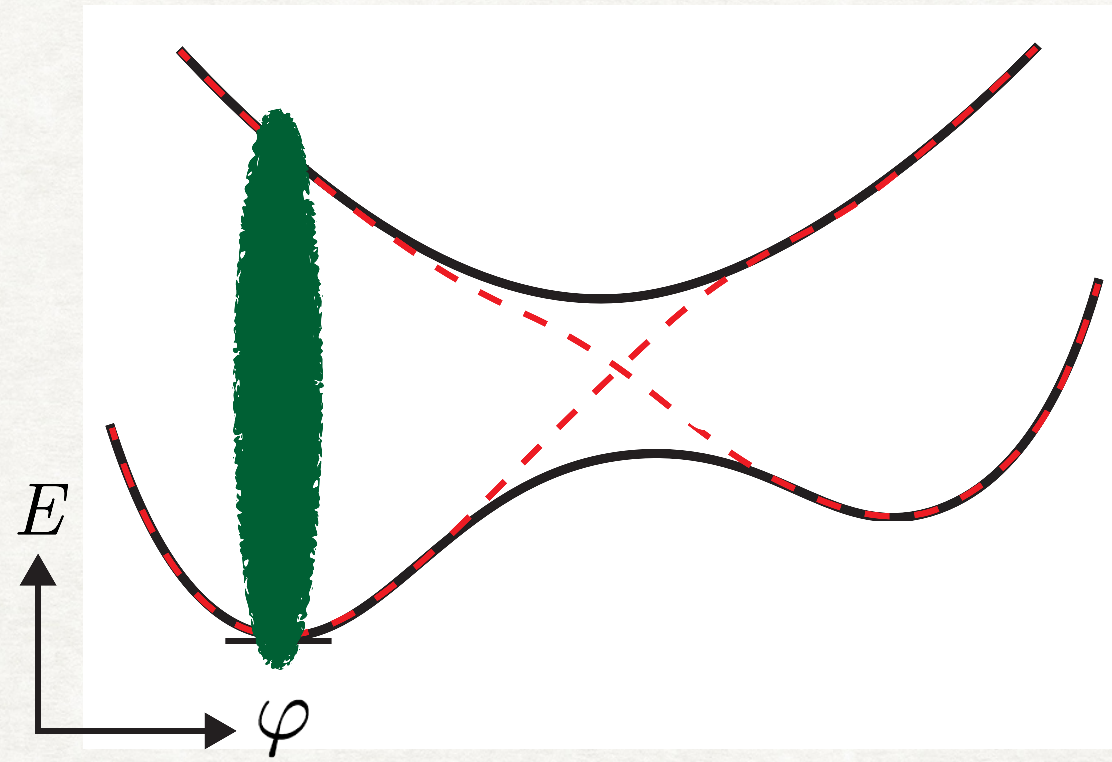
<u>Initial molecule-and-laser state</u>: $e^{-\beta H_{\text{mol}}}/Z_{\text{mol}} \otimes \rho_{\text{laser}}$

Modeling photoisomerization's steps with thermal operations



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

Modeling photoisomerization's steps with thermal operations



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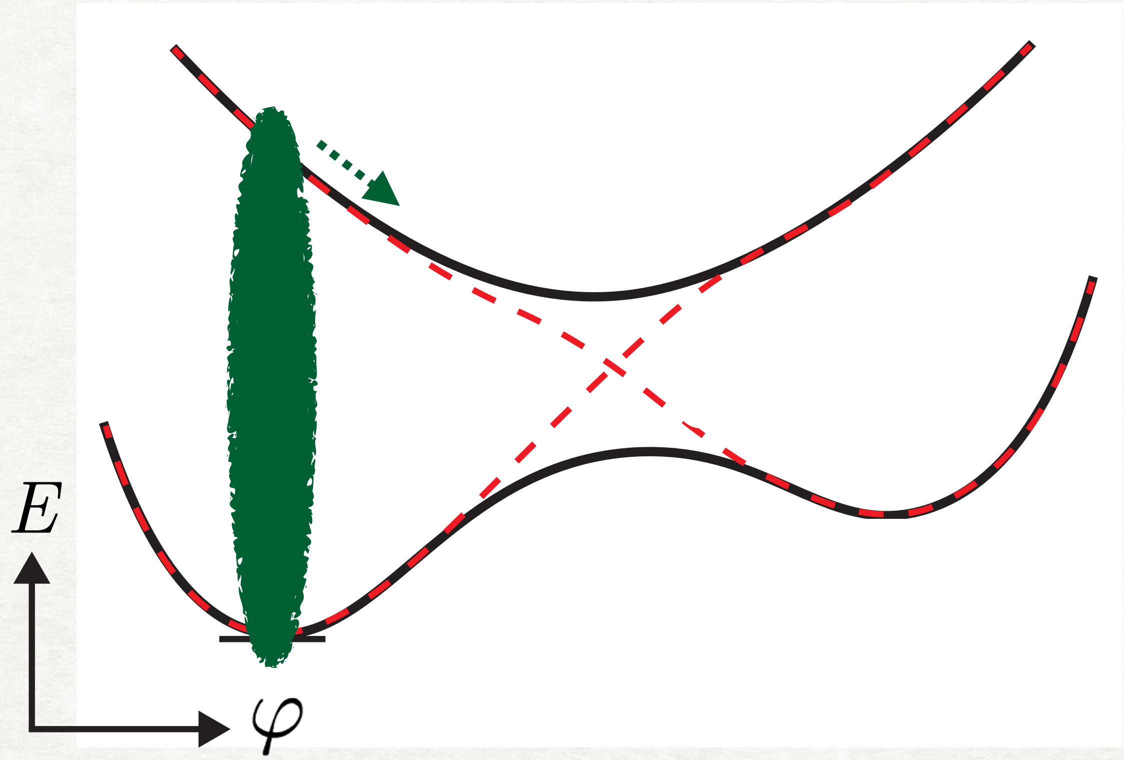

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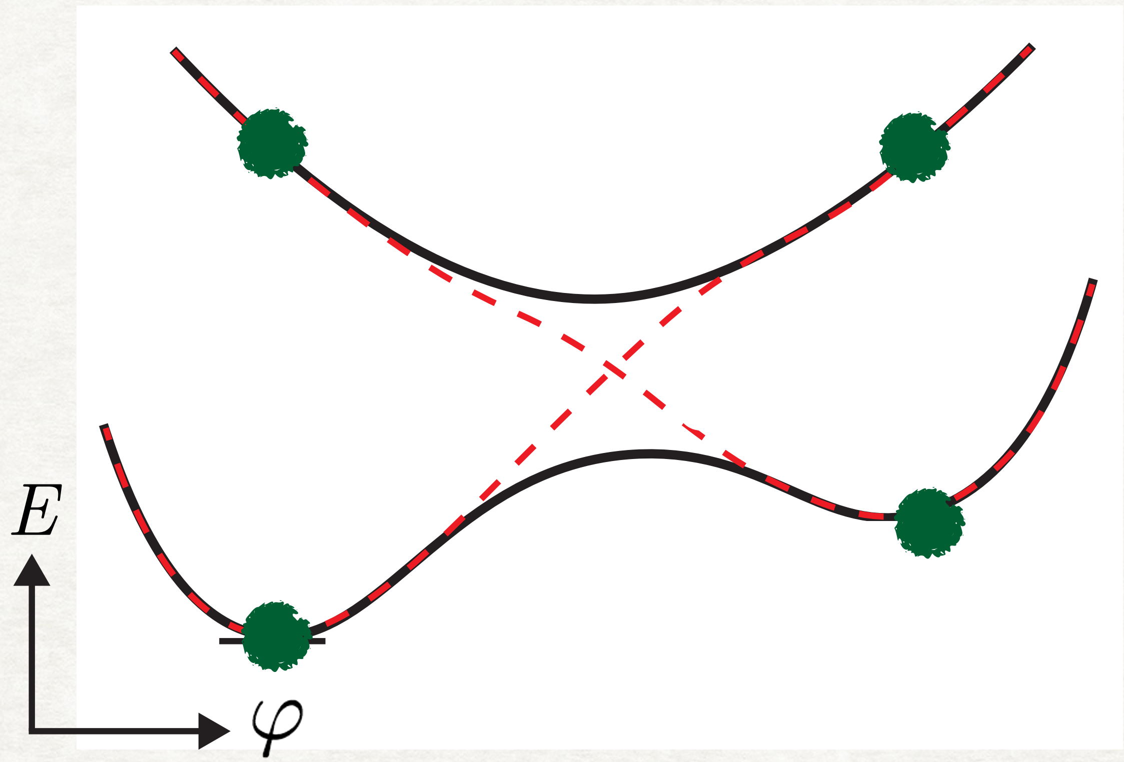

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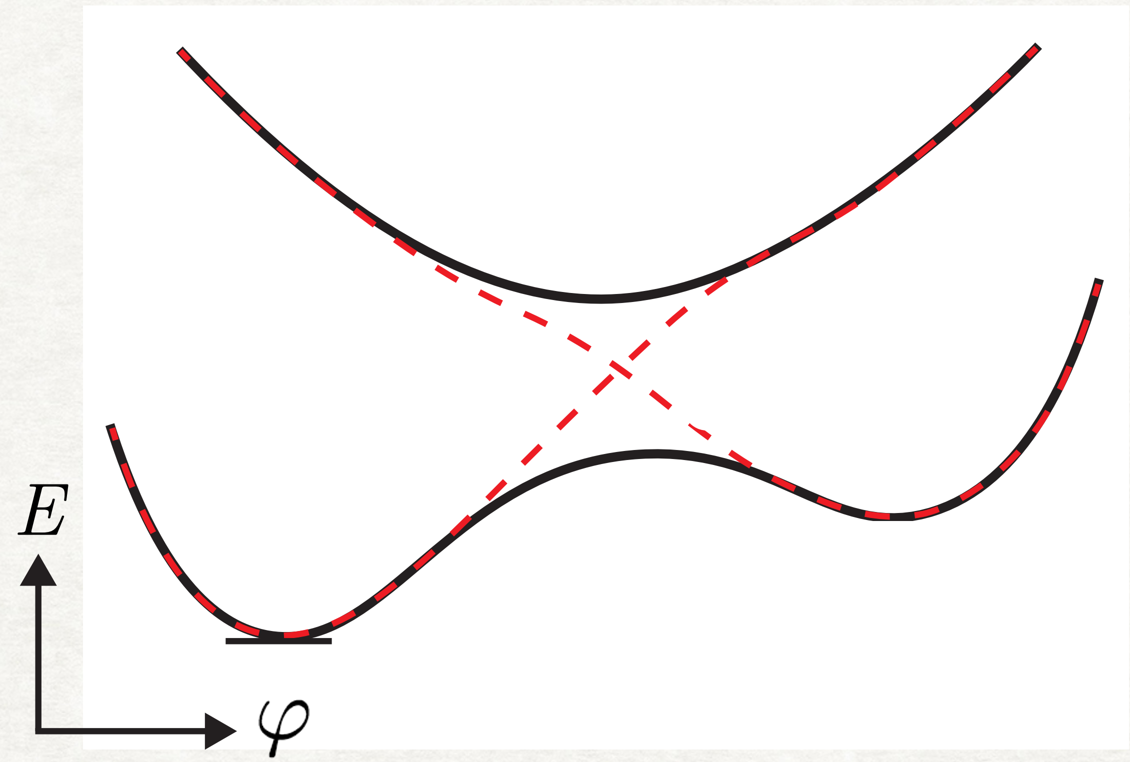
σ

Question



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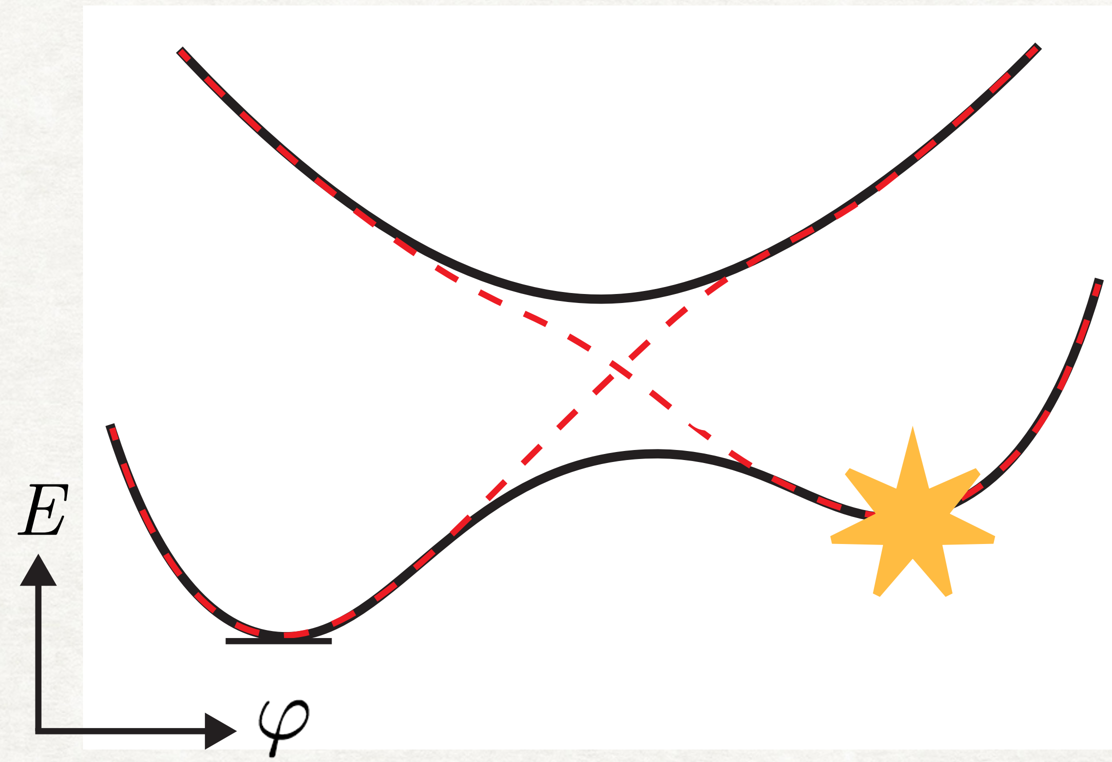

- How large a probability weight can the final state have on the lower level?

Tool:

Second laws of thermodynamics

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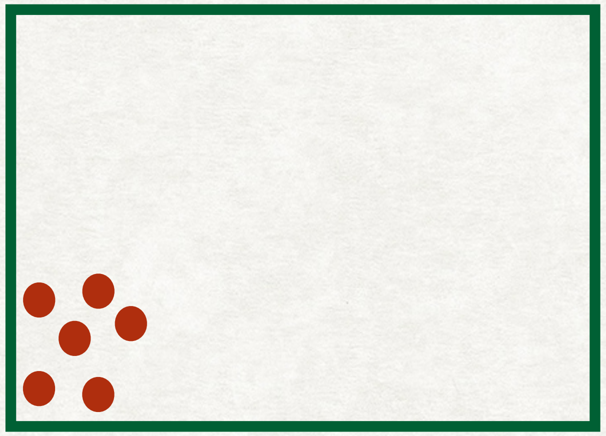
Second laws of thermodynamics

Theorems proved with help from the resource theory

Second law in conventional thermodynamics

Second law in conventional thermodynamics



Second law in conventional thermodynamics

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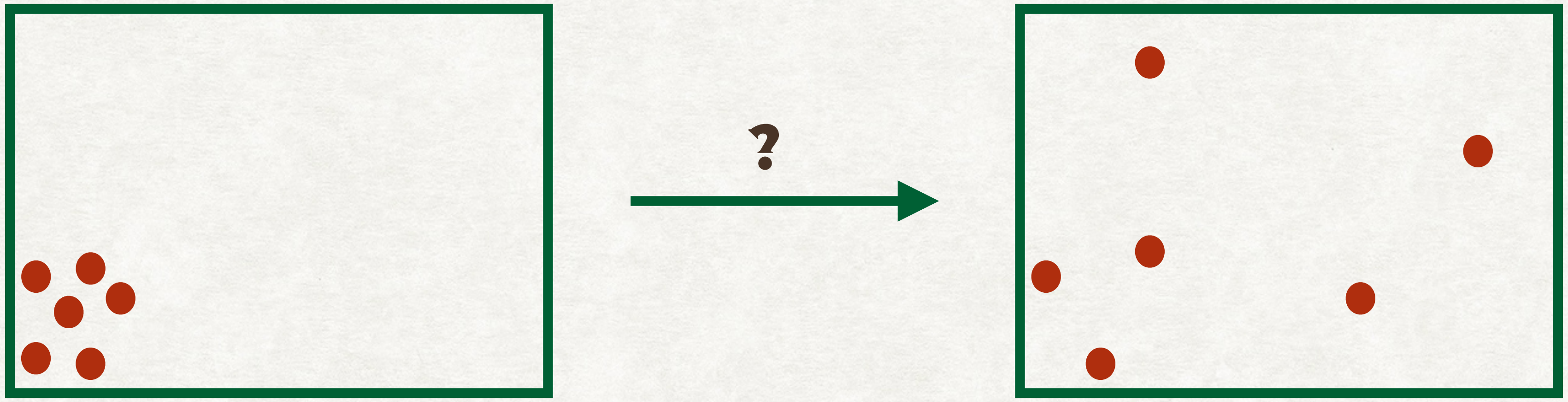
- Can a system transition from one state to another spontaneously?



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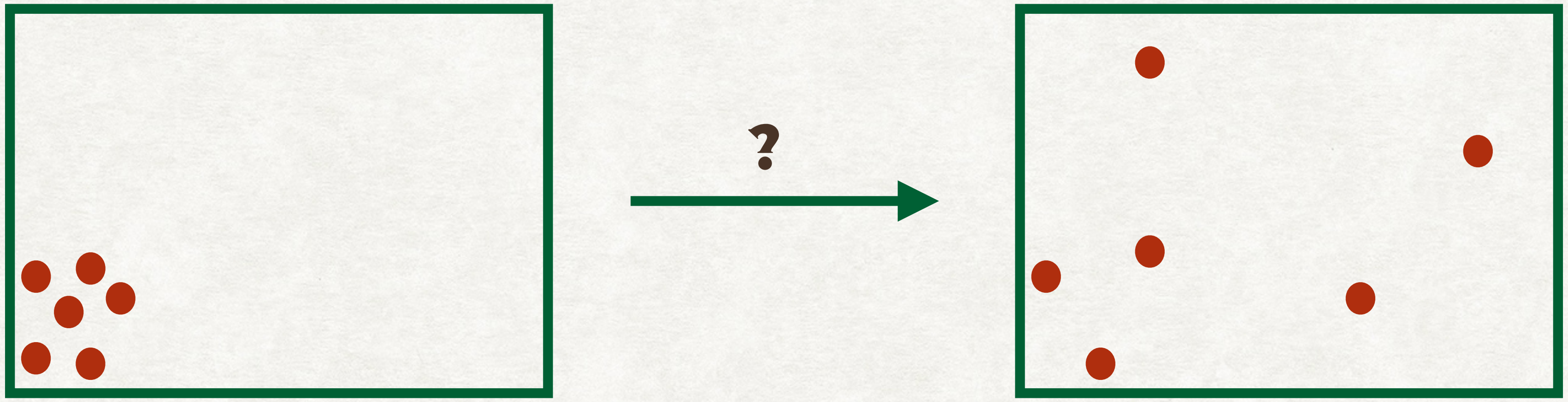

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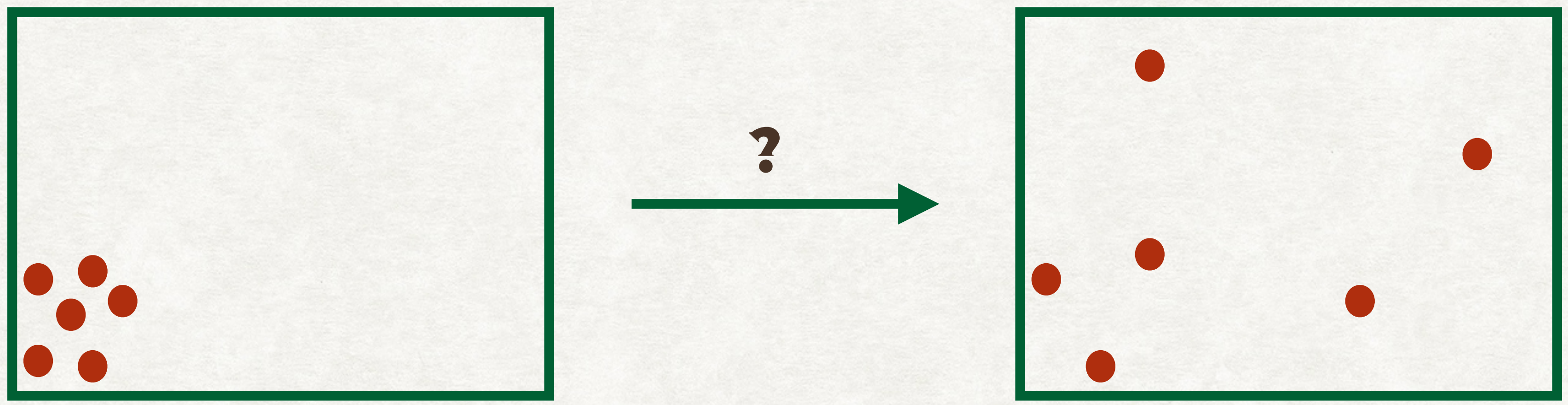

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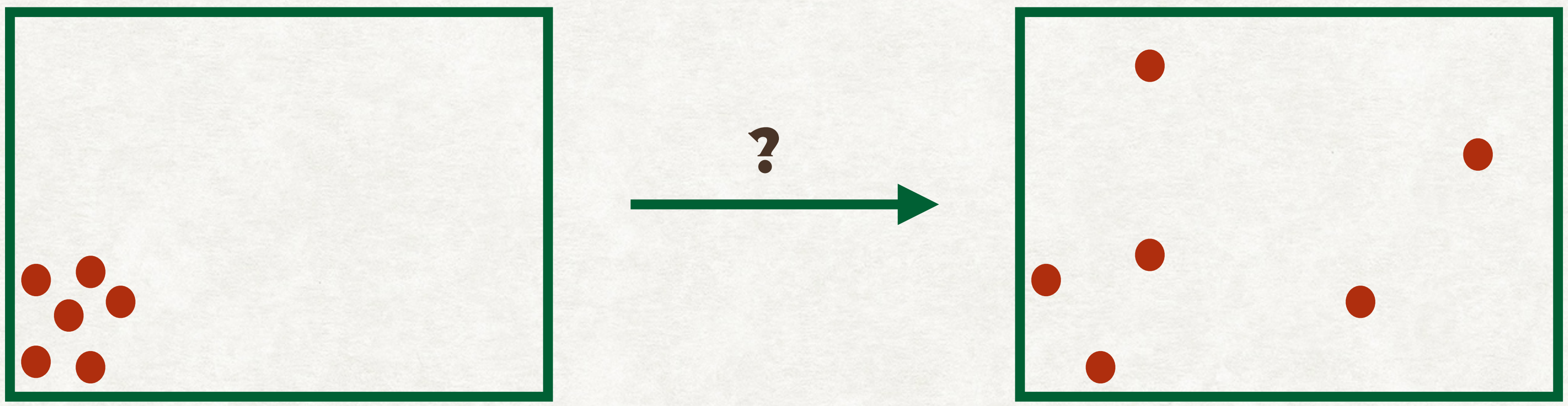
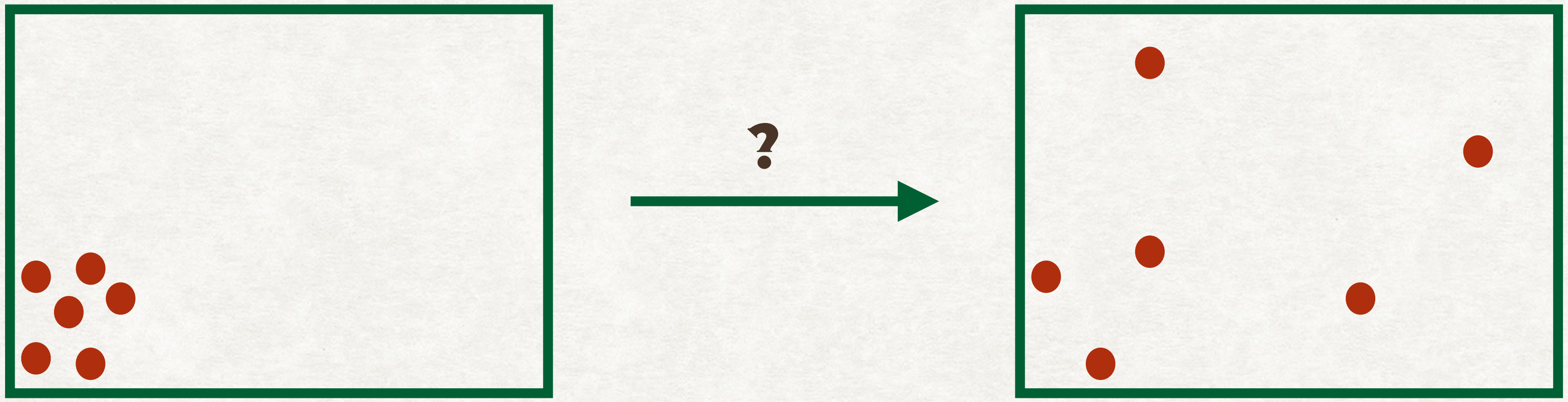
  - Setting: equilibrium, large-system limit, implicit averaging



In thermodynamic resource theory



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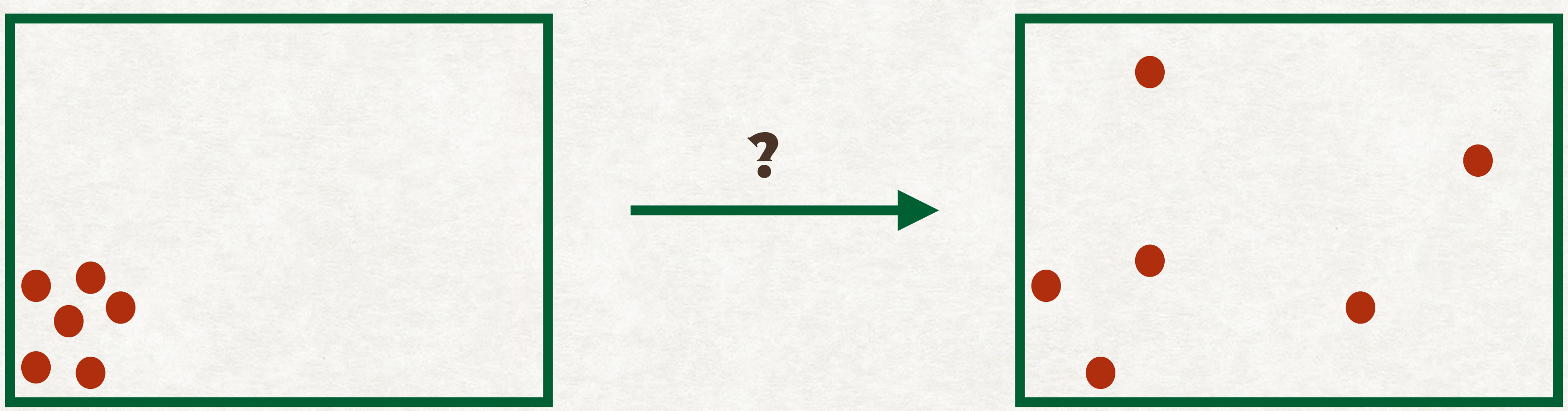
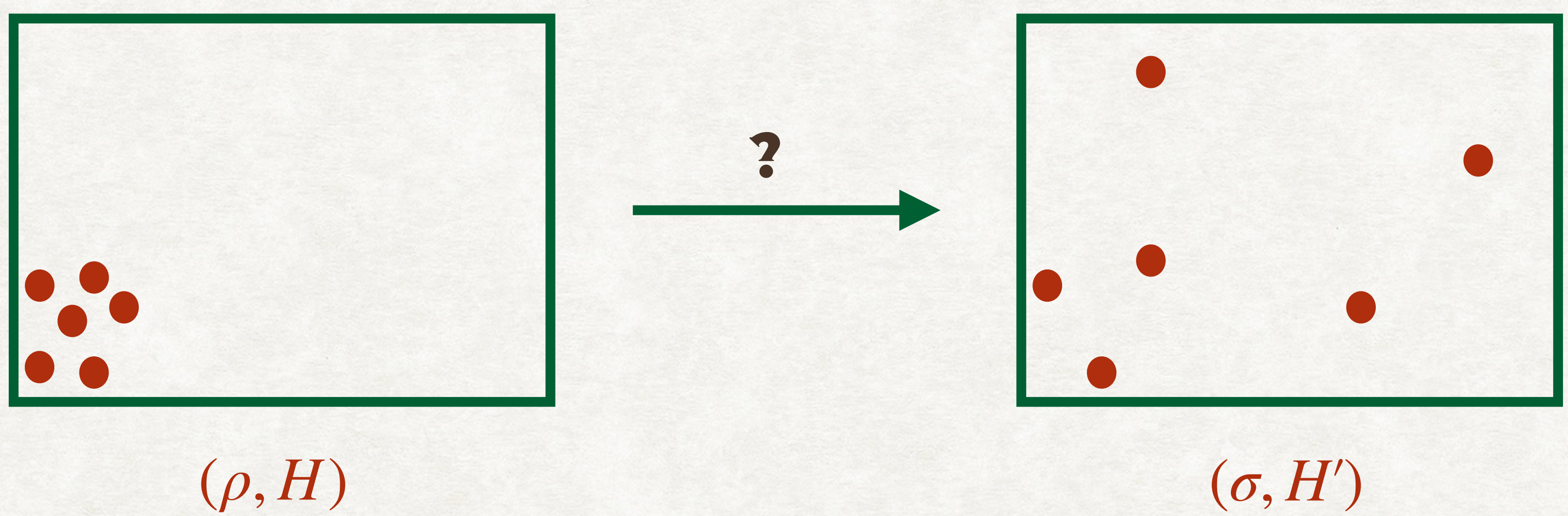


(ρ, H) (σ, H')

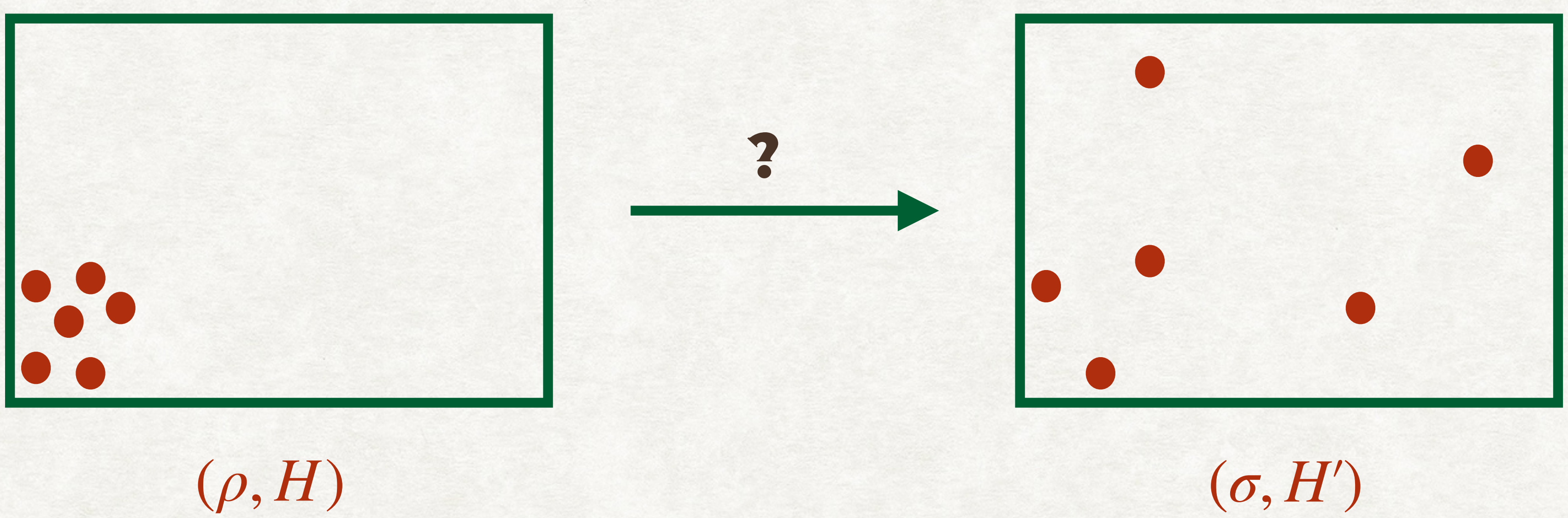
In thermodynamic resource theory

- 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 $\longrightarrow$ **"second laws"**



Second laws of thermodynamics

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$$\Big\downarrow H$$

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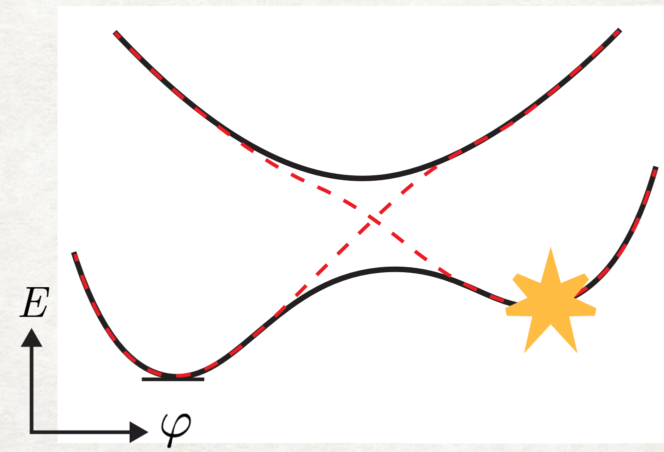
- Another subfamily governs the coherences.

- We want to bound a diagonal element.



Applying the second laws of thermodynamics to the photoisomer

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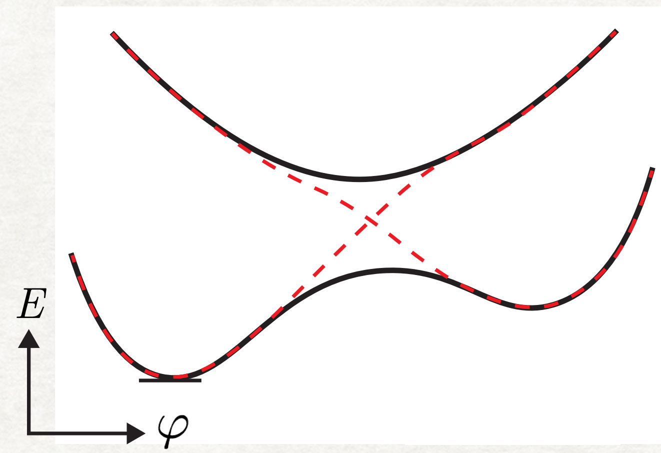

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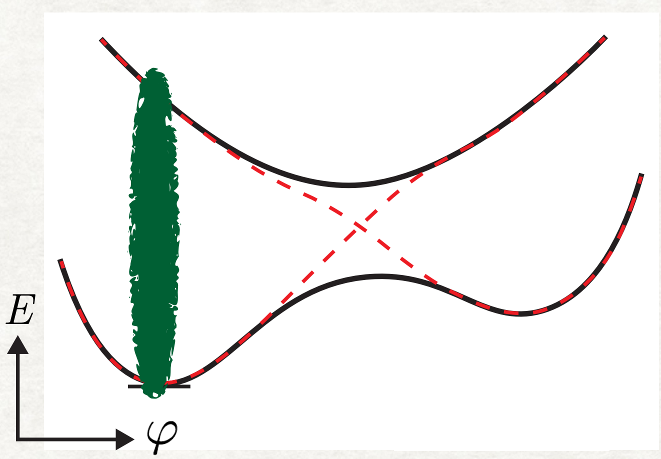

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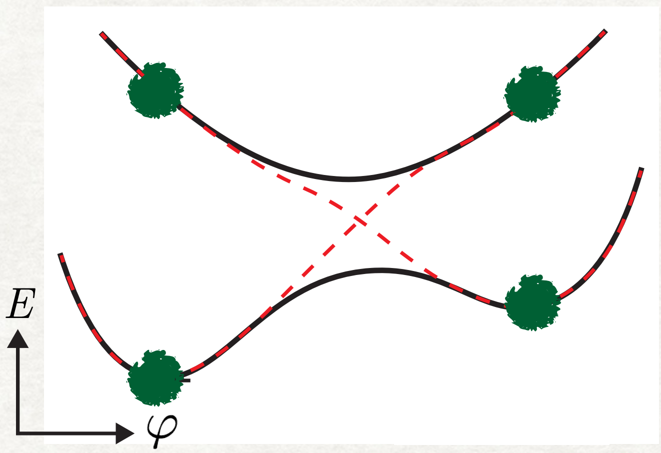

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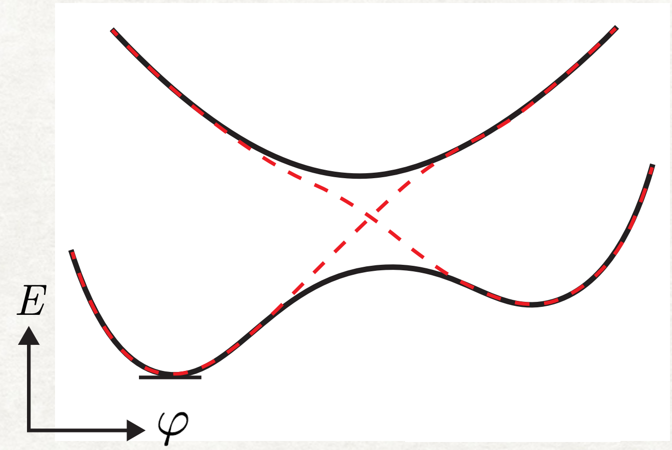

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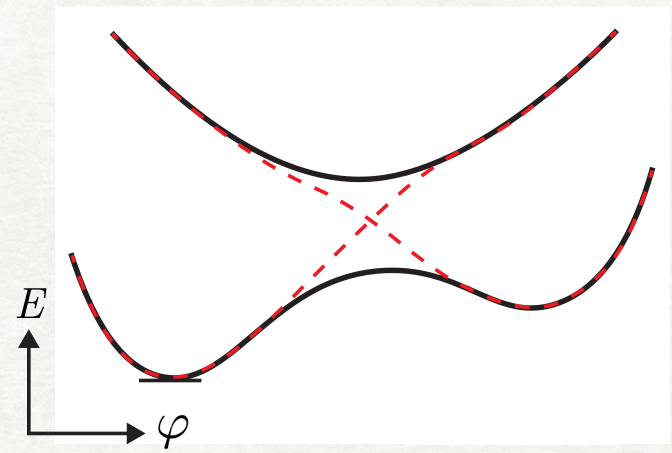
Effective 4-level system:



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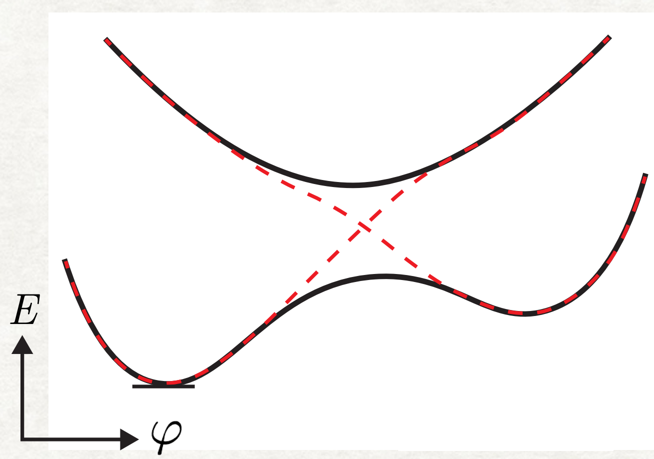
Effective 4-level system:

(2 nuclear states)

$\times$ (2 electronic states)



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Applying the second laws of thermodynamics to the photoisomer

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

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

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Applying the second laws of thermodynamics to the photoisomer

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The modes transform independently under thermal operations.

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Applying the second laws of thermodynamics to the photoisomer

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Applying the second laws of thermodynamics to the photoisomer

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Applying the second laws of thermodynamics to the photoisomer

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Applying the second laws of thermodynamics to the photoisomer

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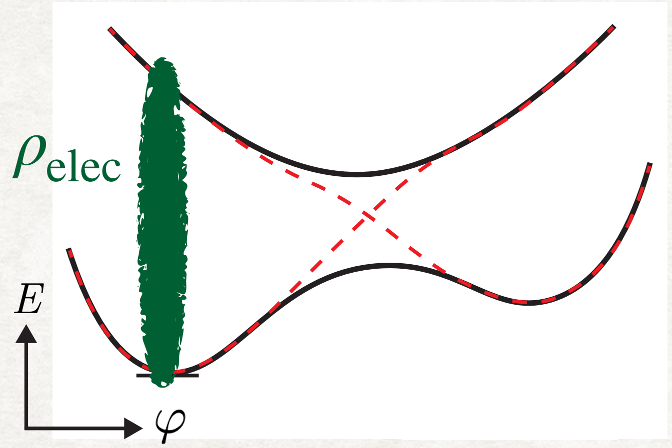

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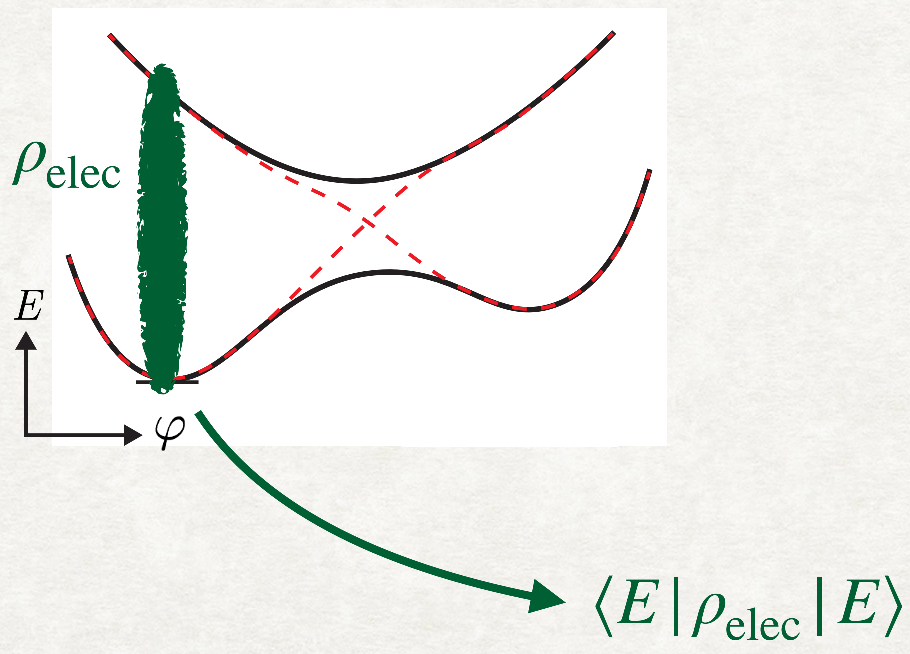

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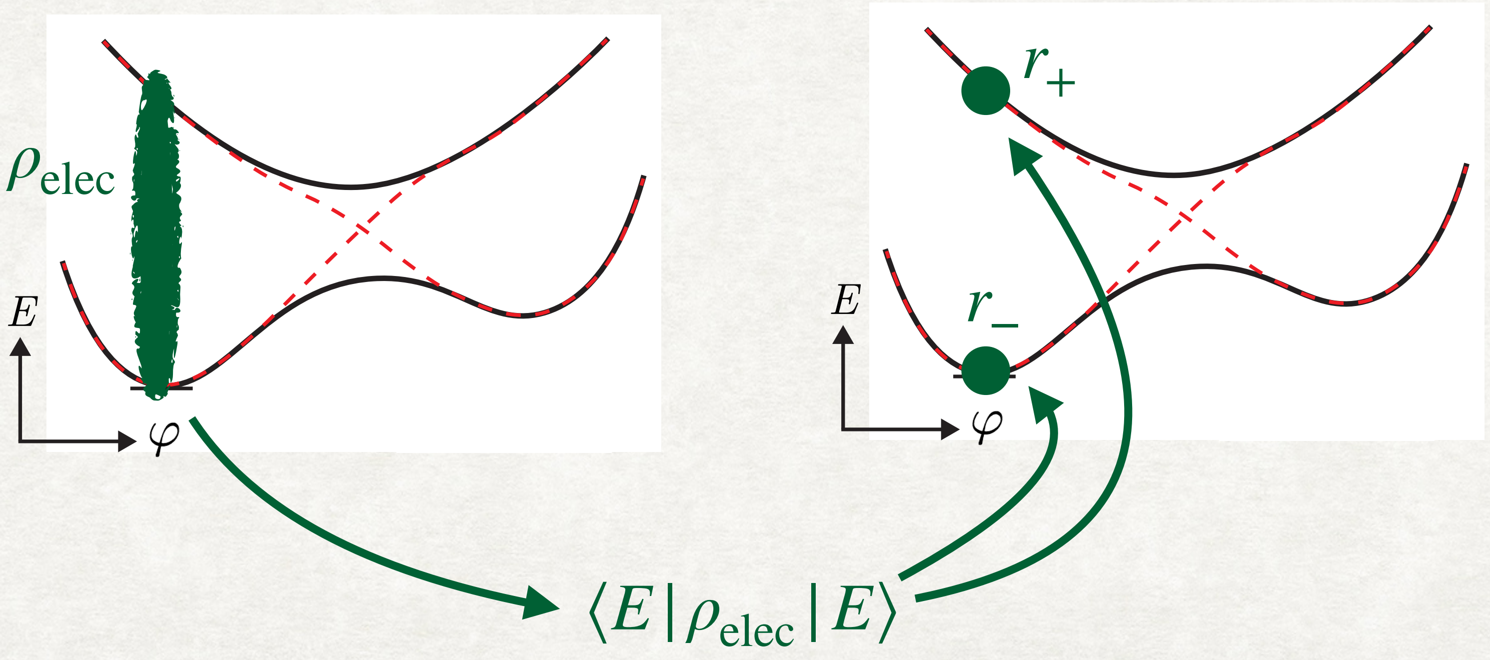

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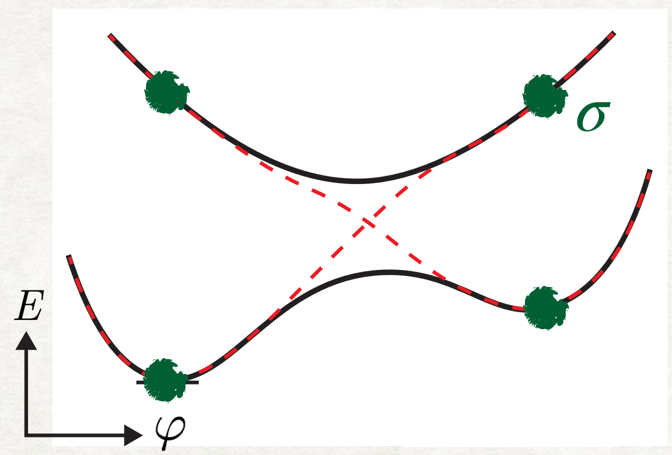

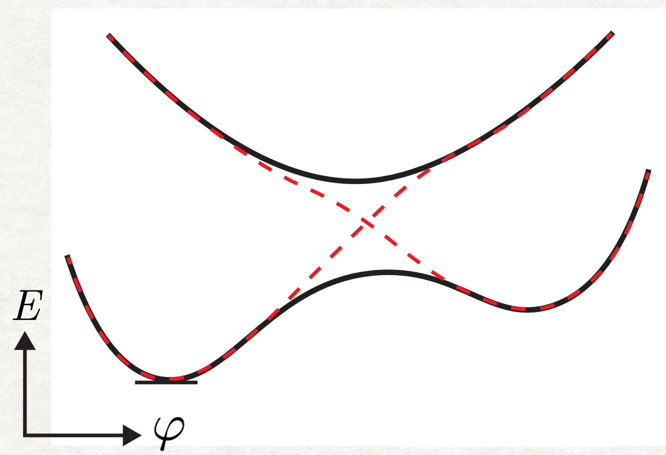

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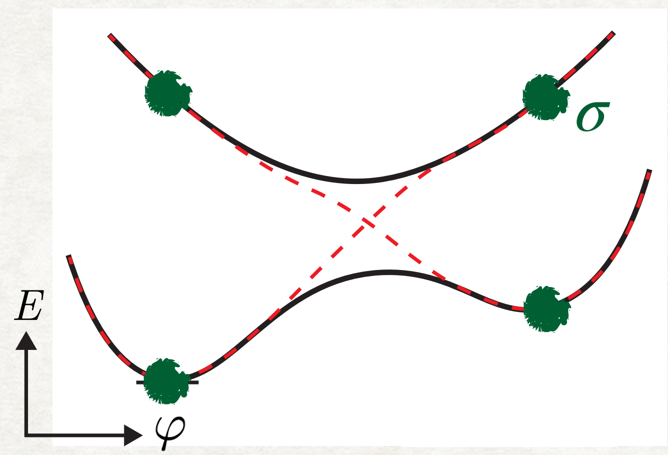
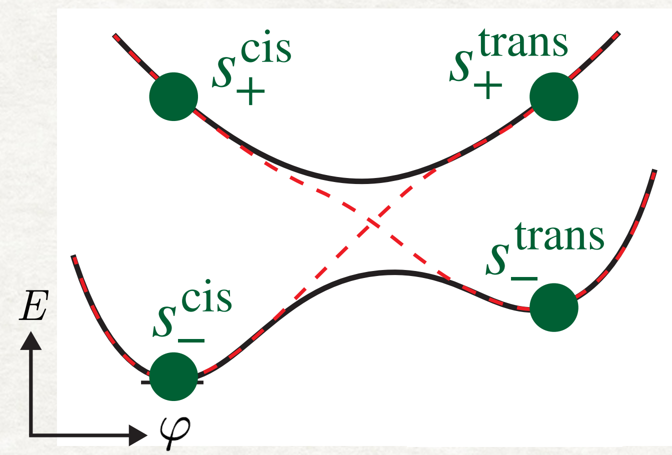
- So our bound will depend on just the states' diagonal elements.
- So, in our calculations, we can replace the states with decohered states.





Second laws of thermodynamics for the energy diagonal

- Janzing *et al.*, Int. J. Theor. Phys. **39**, 12 (2000).

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- 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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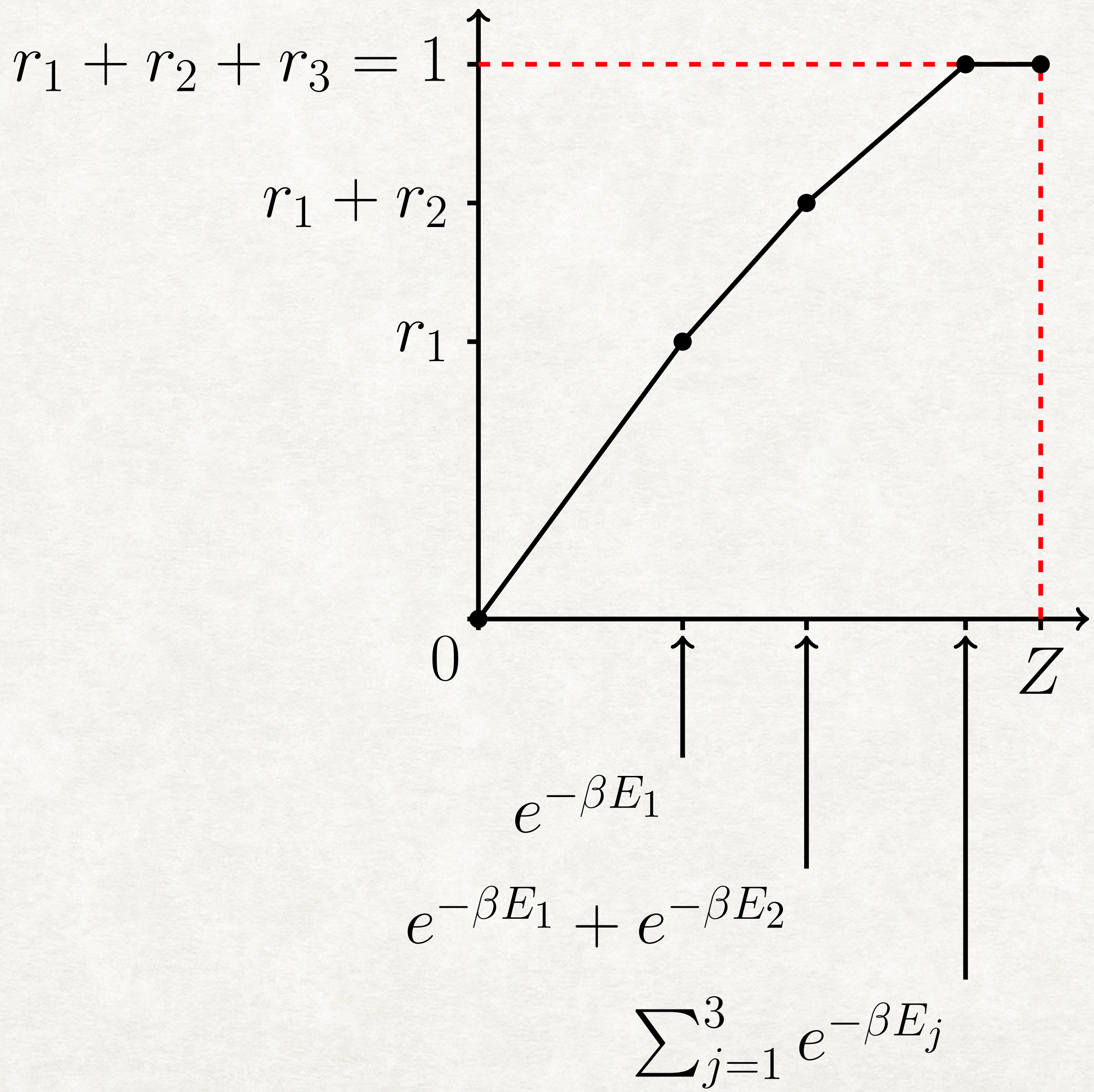
- Plot partial sums.

Second laws of thermodynamics

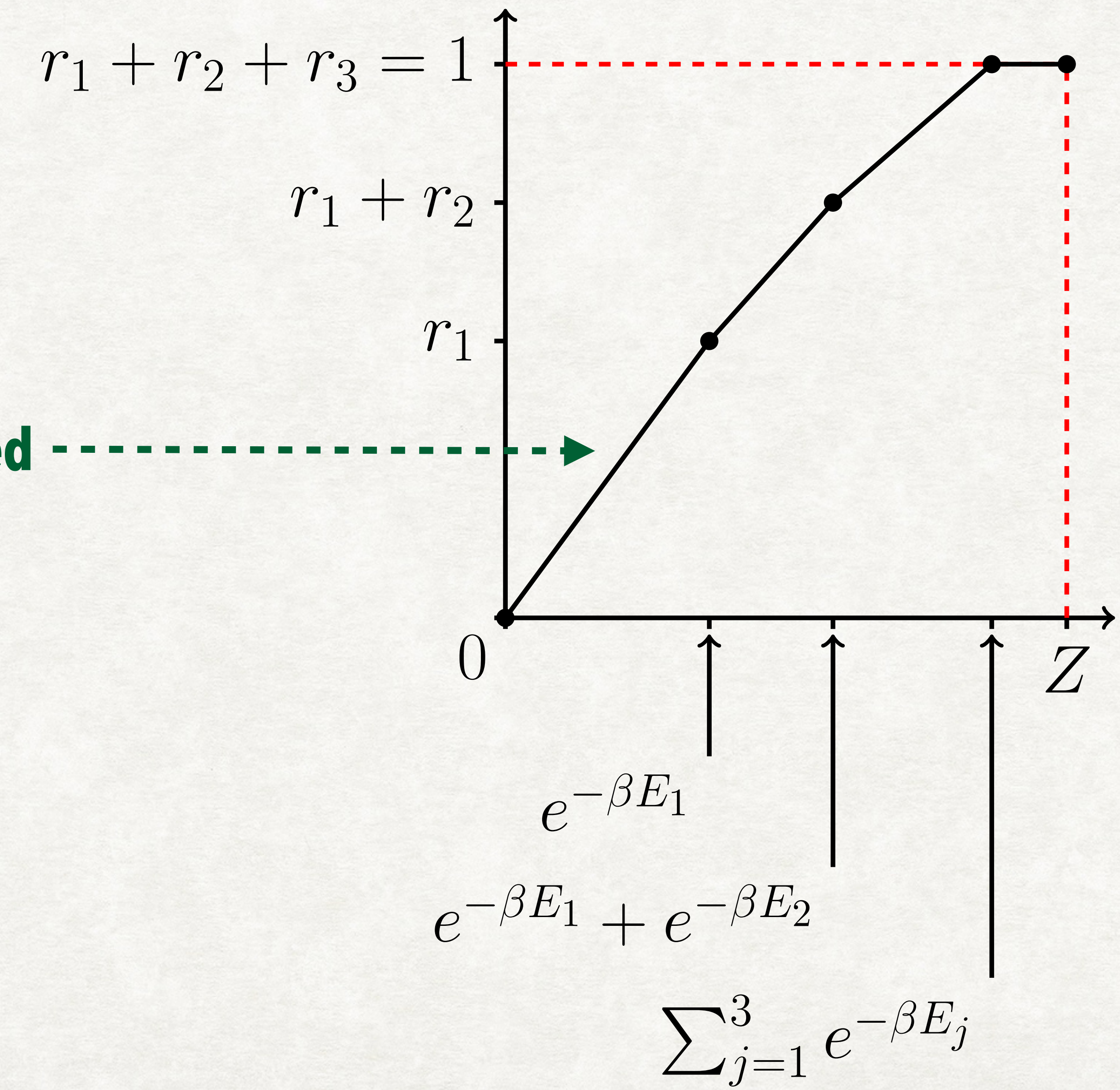
How to check whether $(\rho, H) \mapsto (\sigma, H)$ for free



Second laws of thermodynamics

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

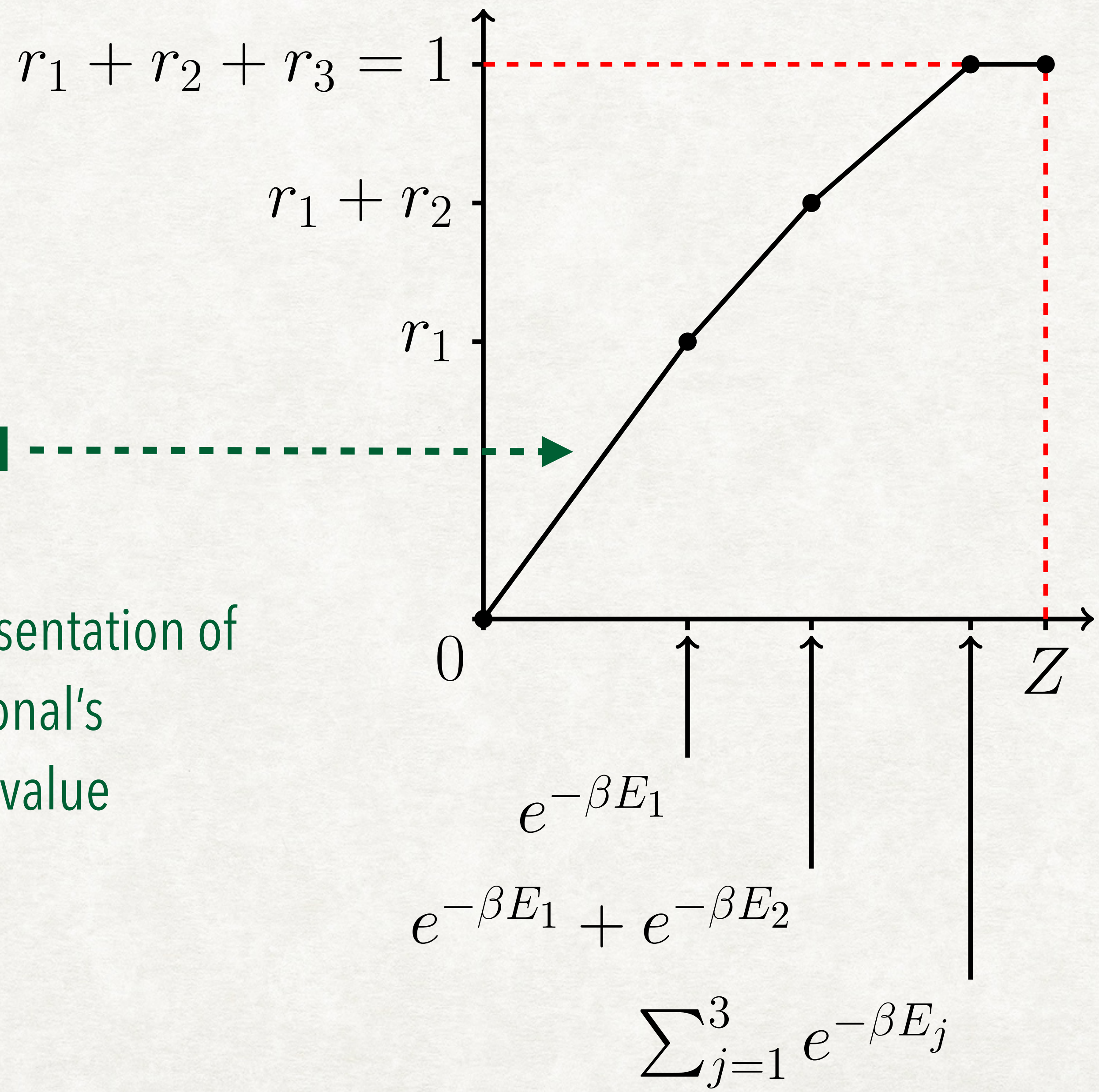
- **Gibbs-rescaled Lorenz curve**



Second laws of thermodynamics

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

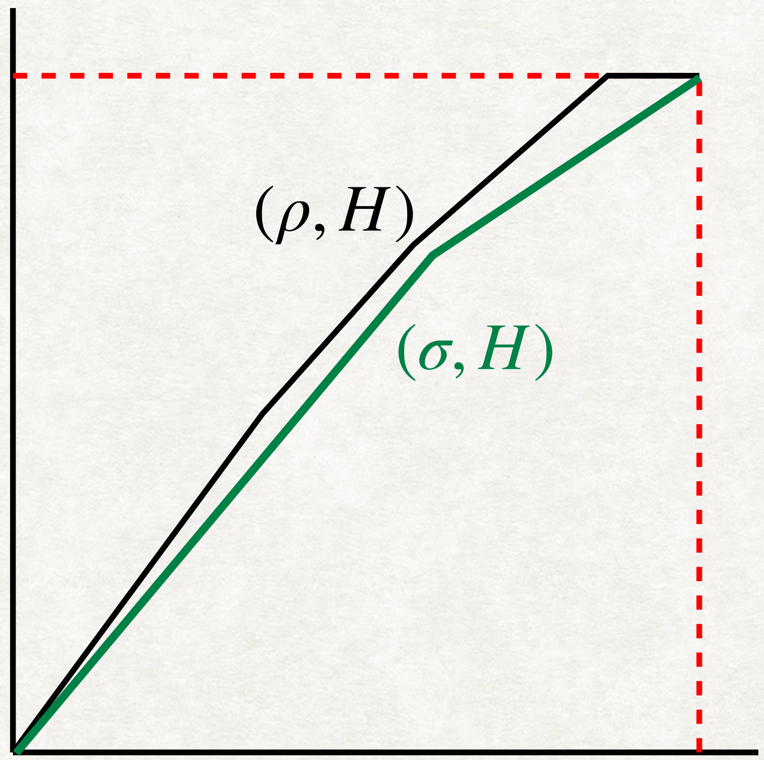
- **Gibbs-rescaled Lorenz curve**
- Geometric representation of the energy diagonal's thermodynamic value



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

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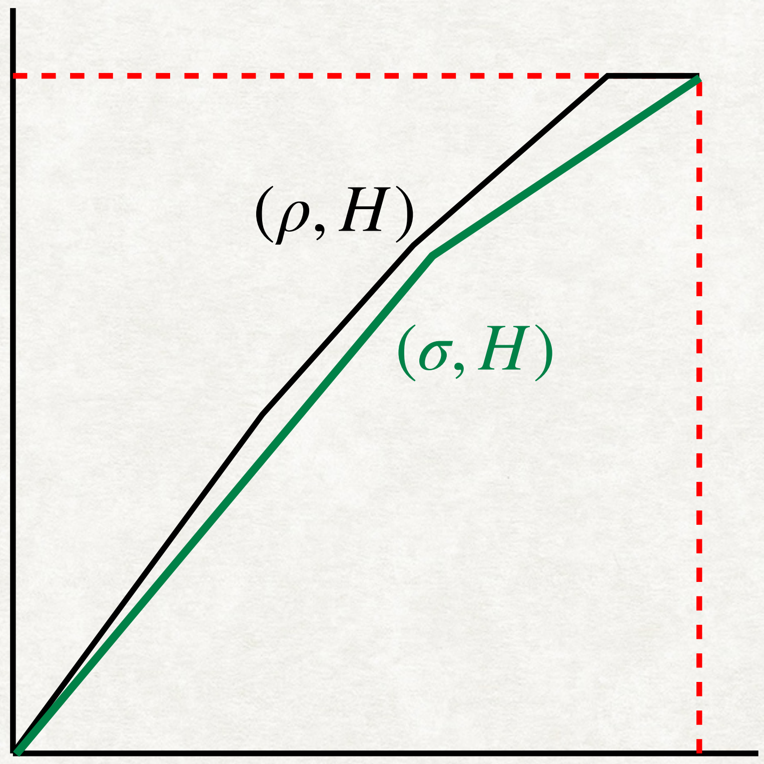
- Plot the (ρ, H) and (σ, H) curves on the same plot.

- <u>Theorem</u>: $(\rho, H) \mapsto (\sigma, H)$ if and only if the (ρ, H) curve lies, everywhere, above or on the (σ, H) curve.



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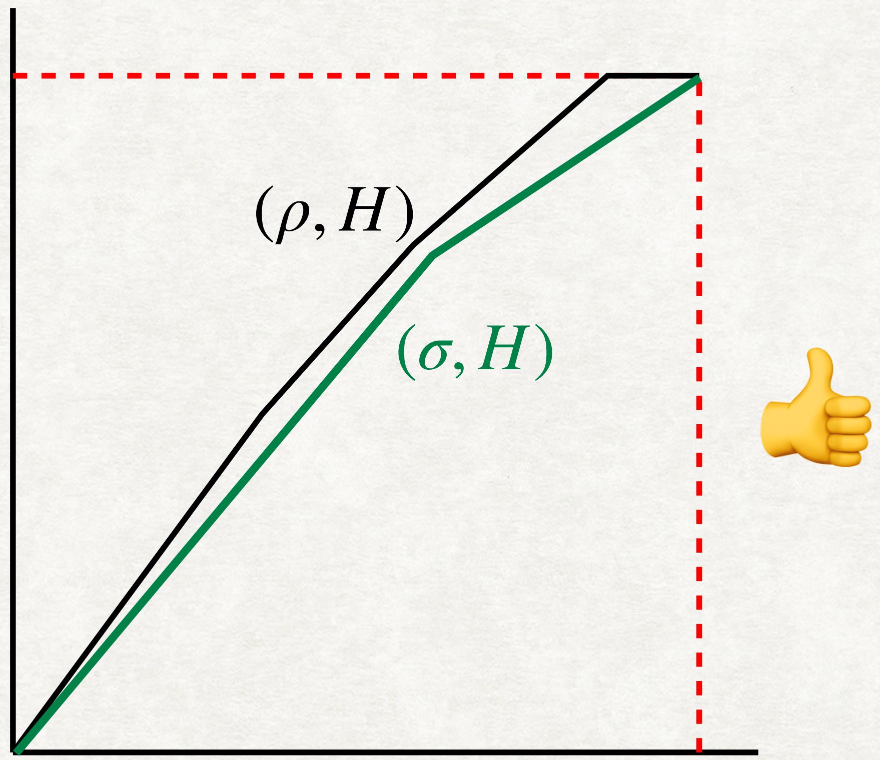

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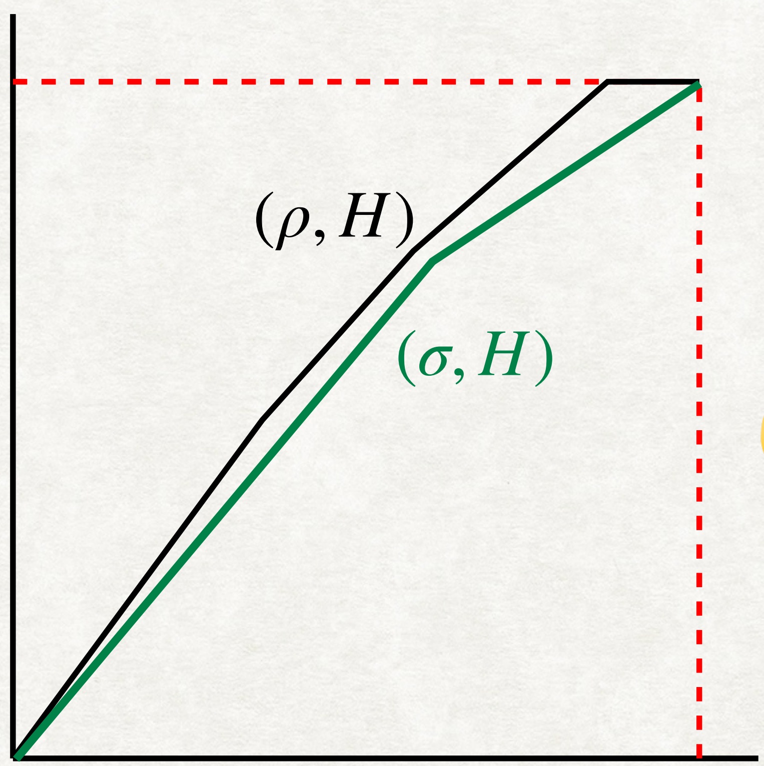
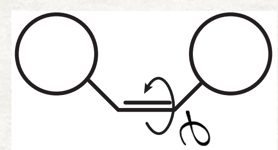
Encodes a bunch of inequalities



Apply the second laws of thermodynamics
to the photoisomer.



NYH and Limmer, arXiv:1811.06551 (2018).

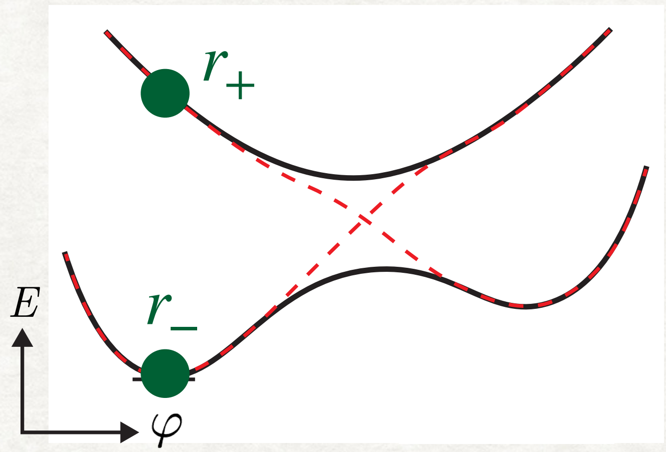
Applying the second laws to the photoisomer

Strategy

Applying the second laws to the photoisomer

Strategy

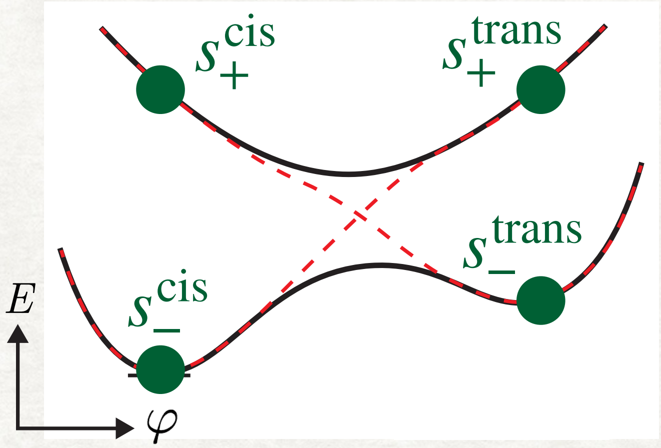
- For any state ρ to which the laser can excite the molecule,



Applying the second laws to the photoisomer

<u>Strategy</u>

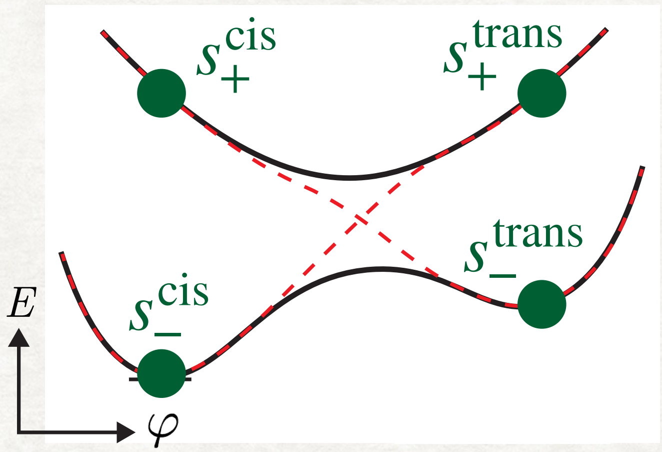
- For any state ρ to which the laser can excite the molecule, four parameters specify the final state.



Applying the second laws to the photoisomer

Strategy

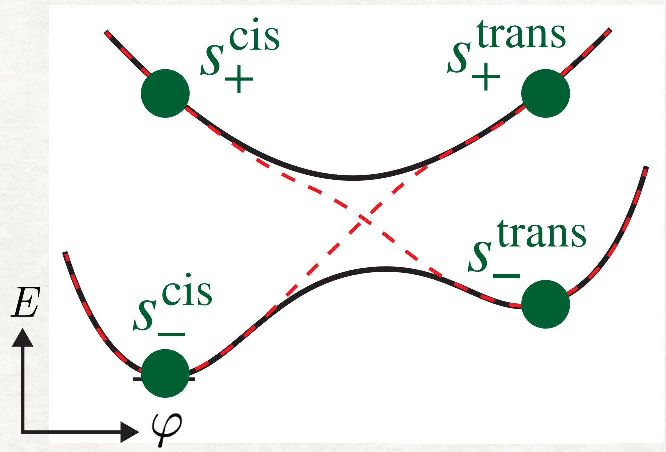
- For any state ρ to which the laser can excite the molecule, four parameters specify the final state.
- Plug into the second laws for the energy diagonal.



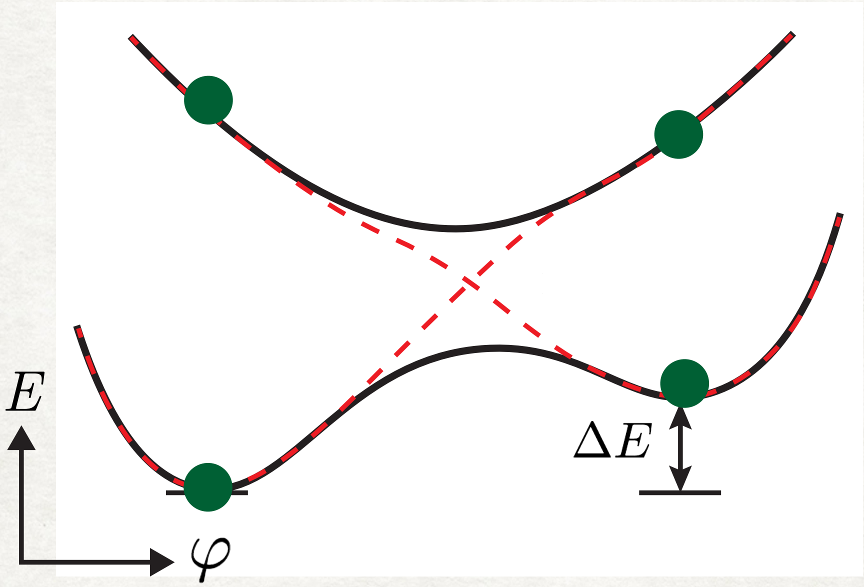
Applying the second laws to the photoisomer

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



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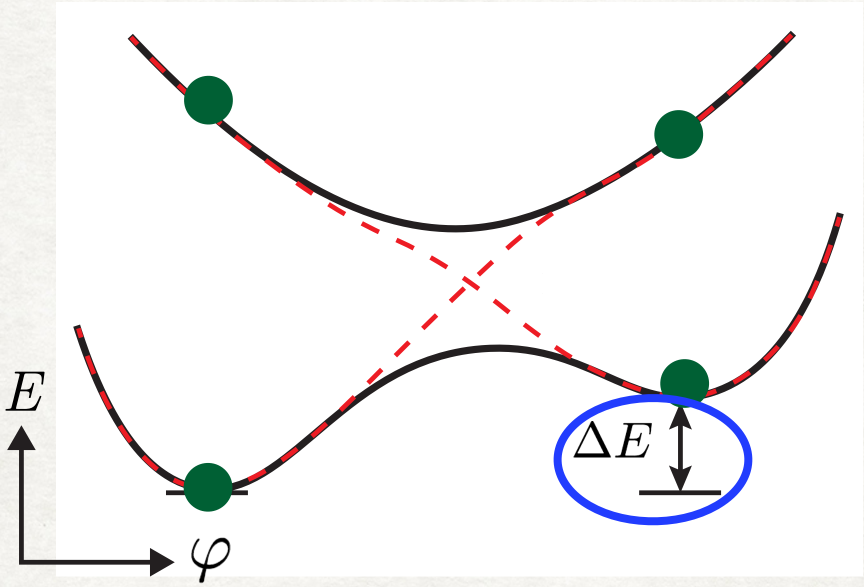

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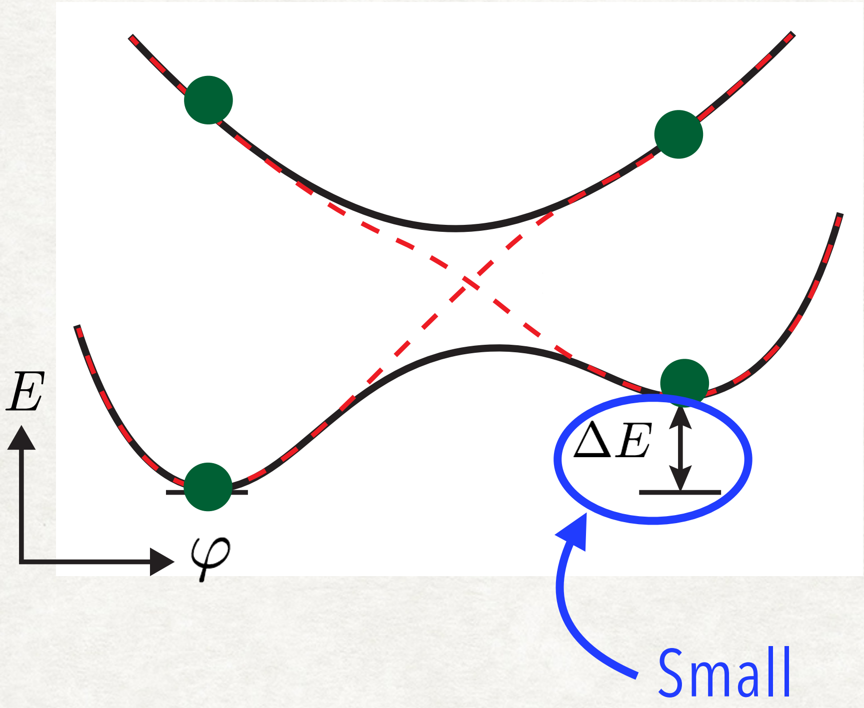

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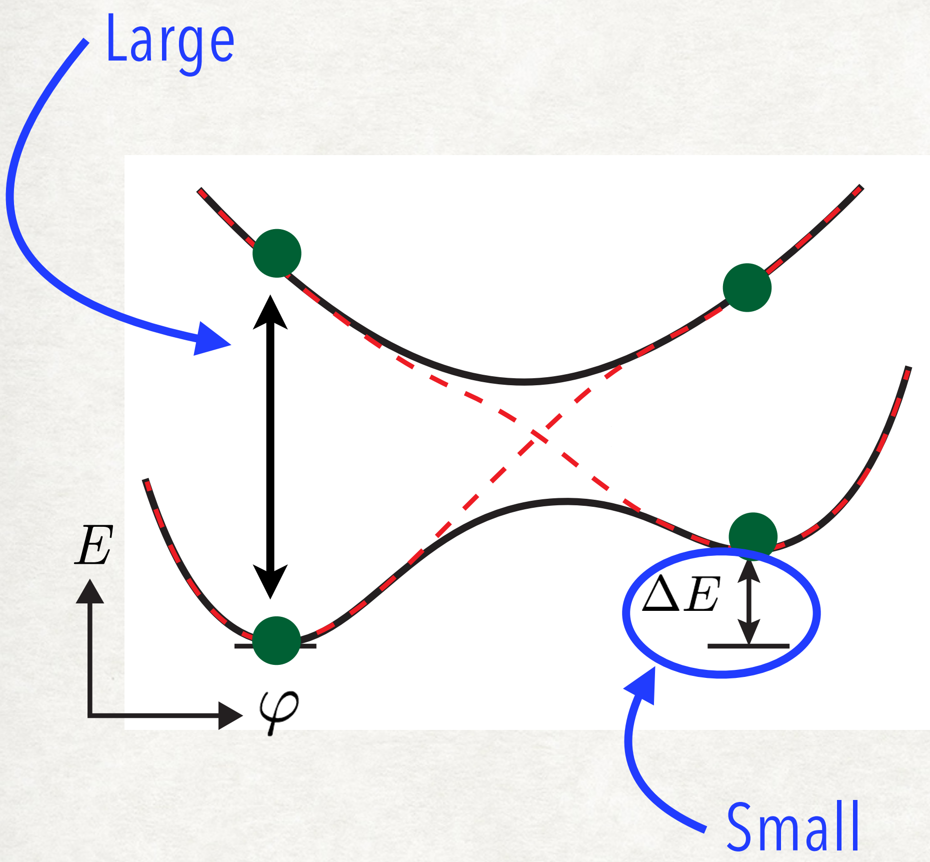

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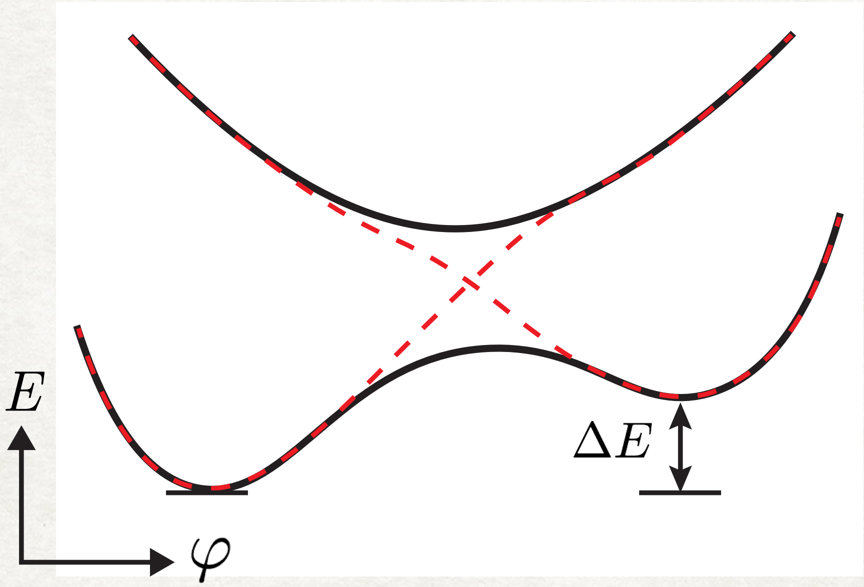

$\beta \Delta E$

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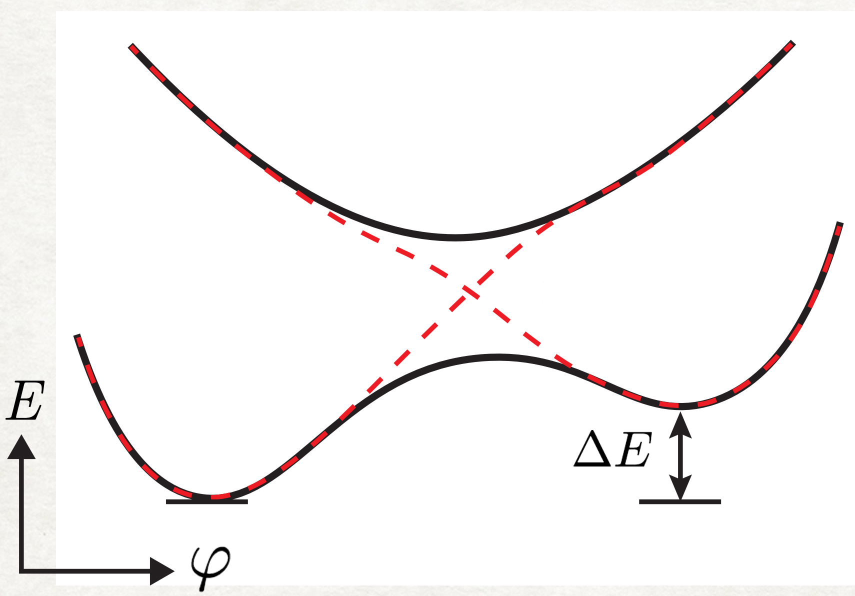

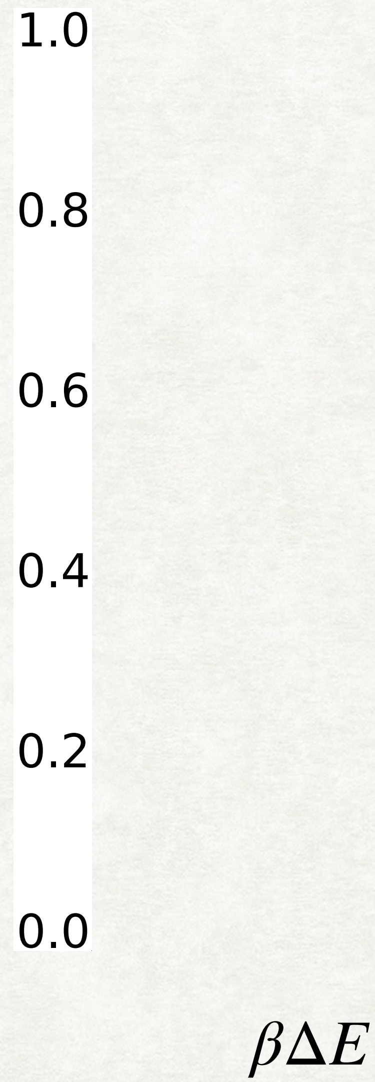

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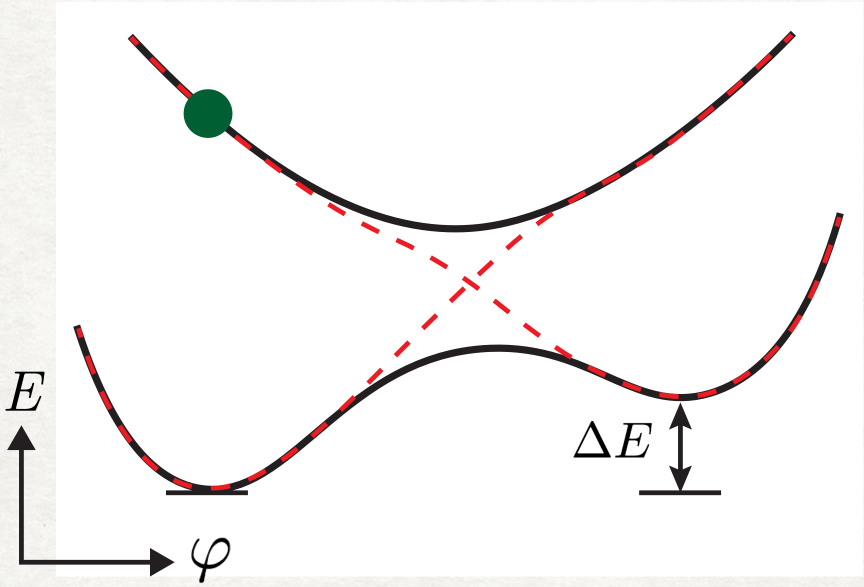
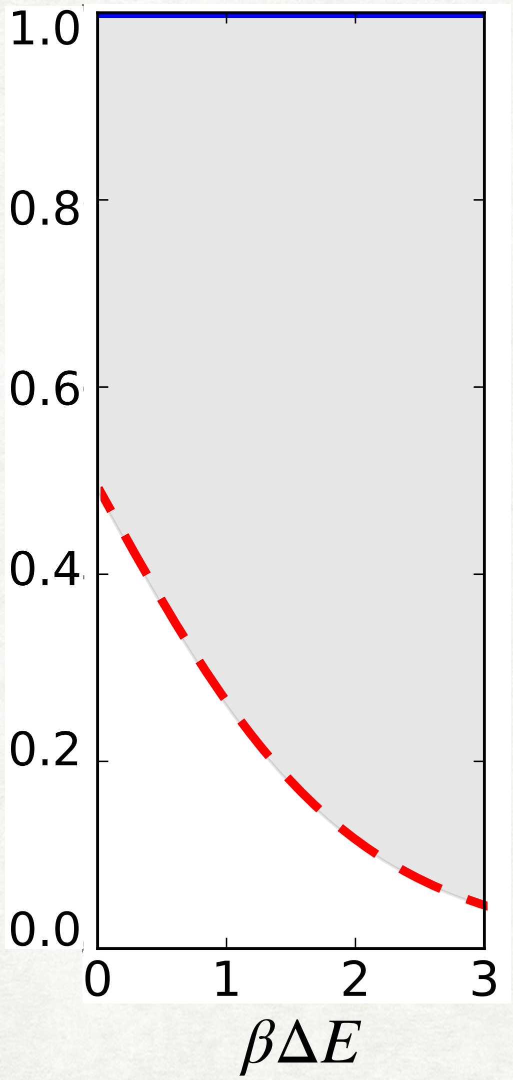


Good-laser regime



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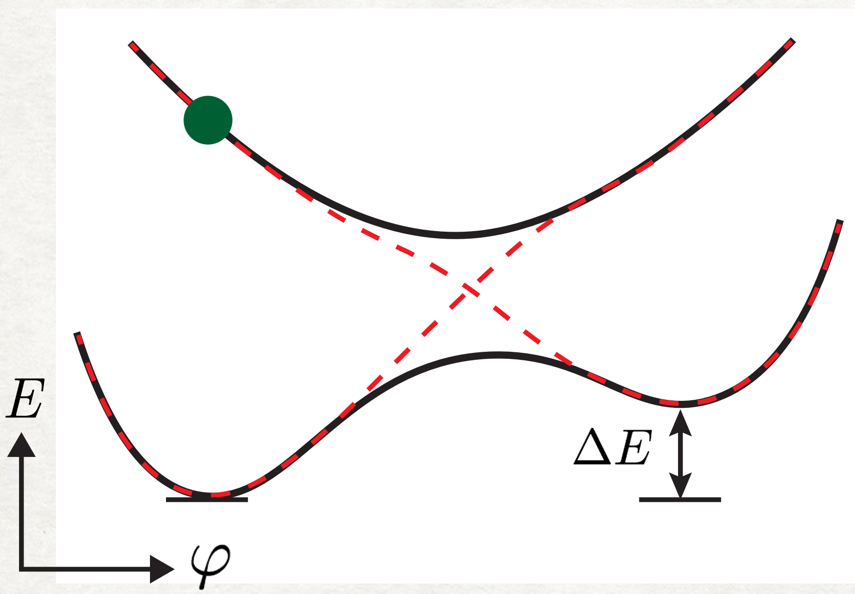

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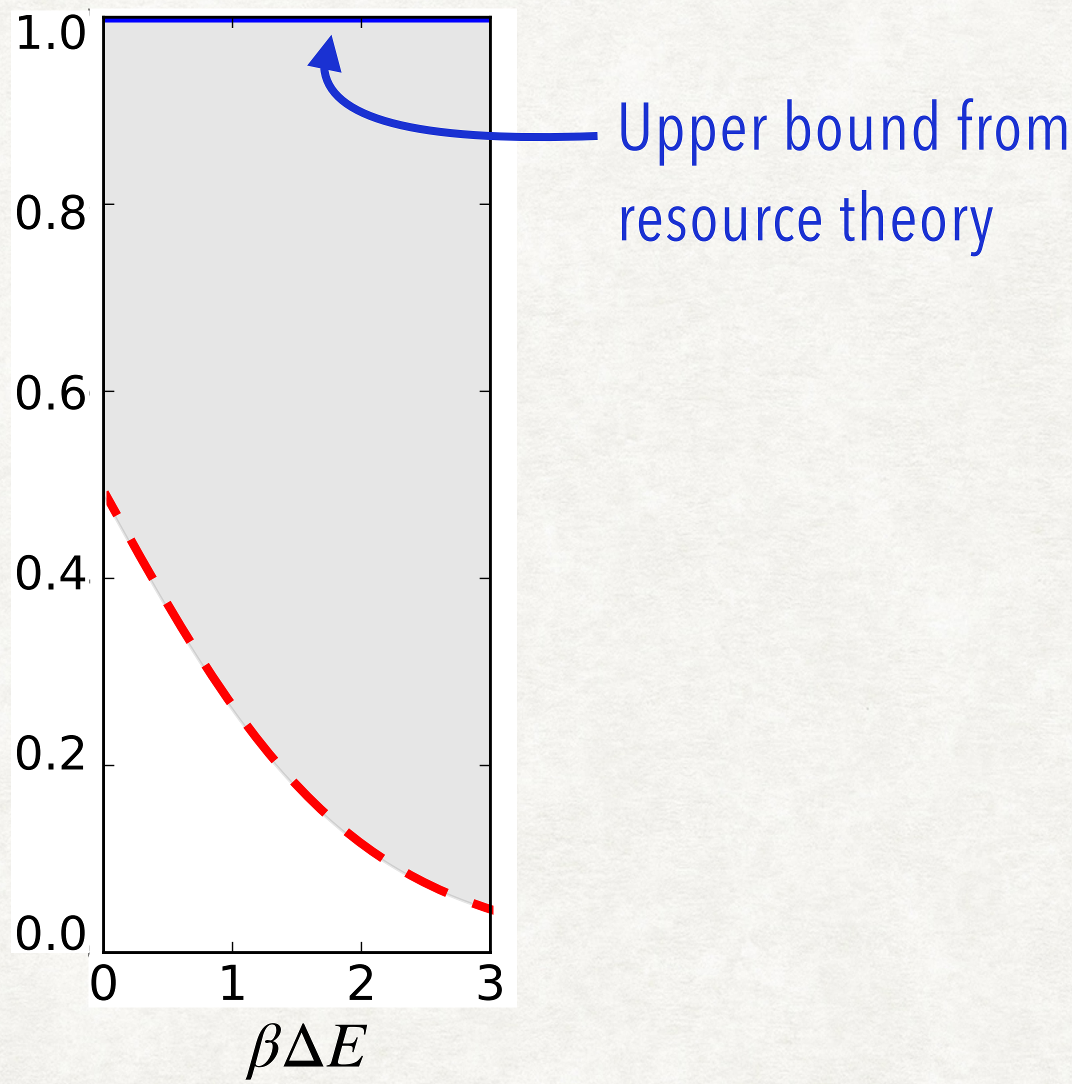

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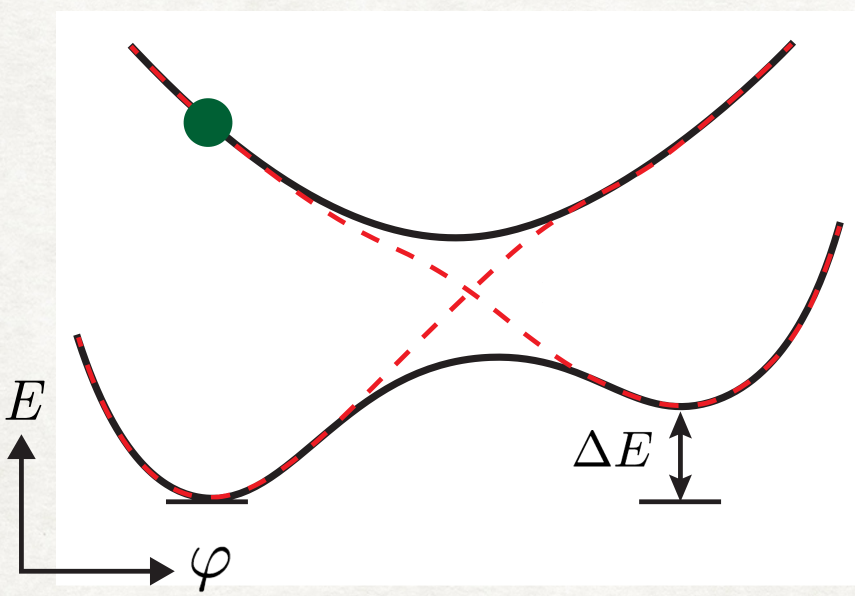

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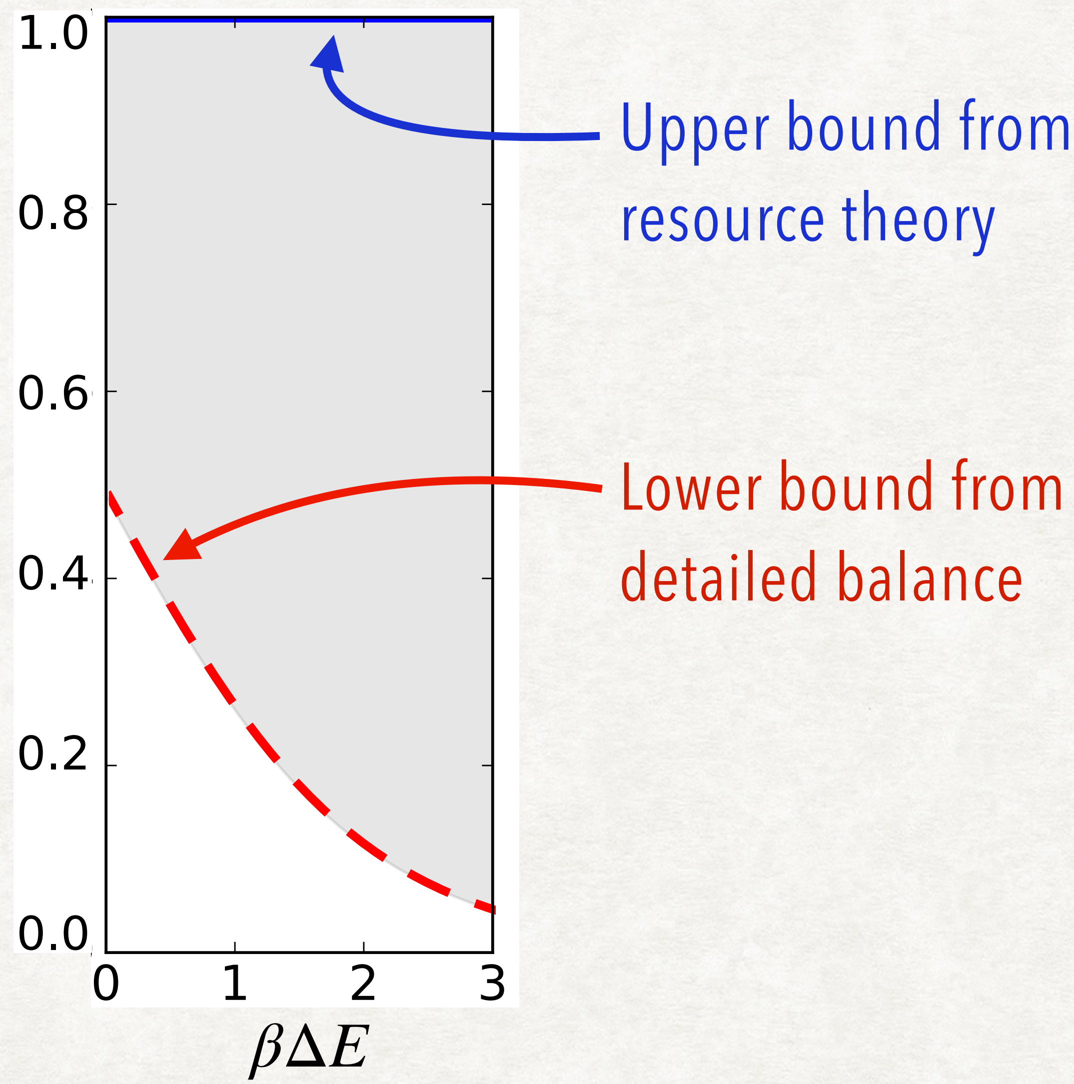

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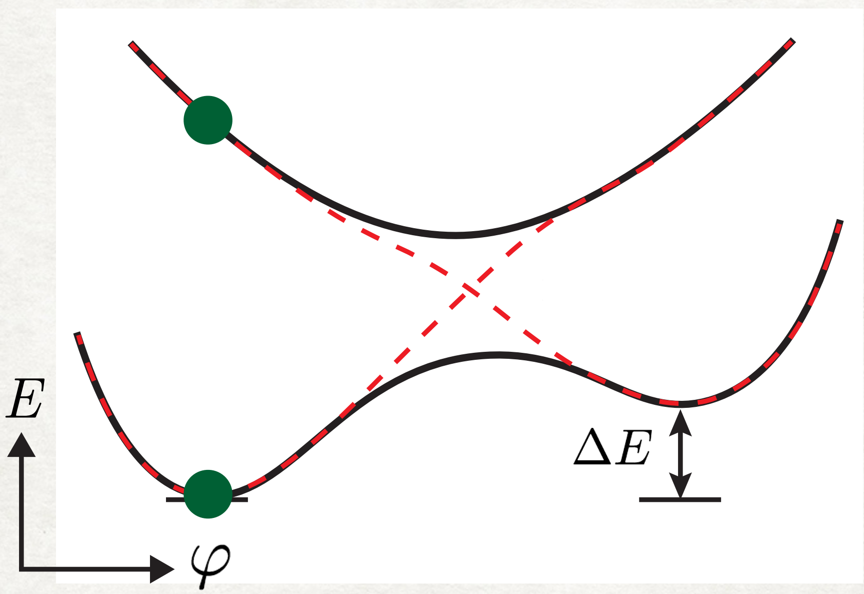
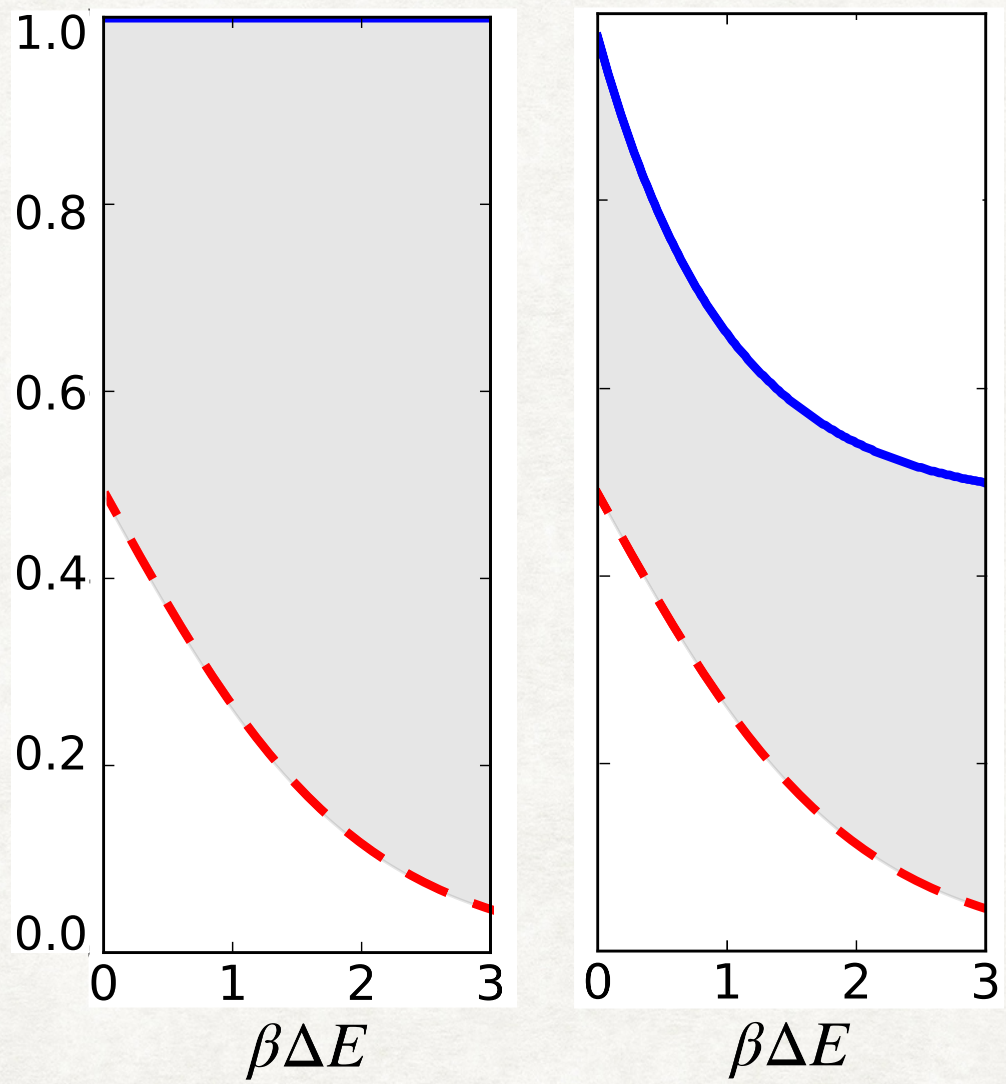


Good-laser regime

So-so laser



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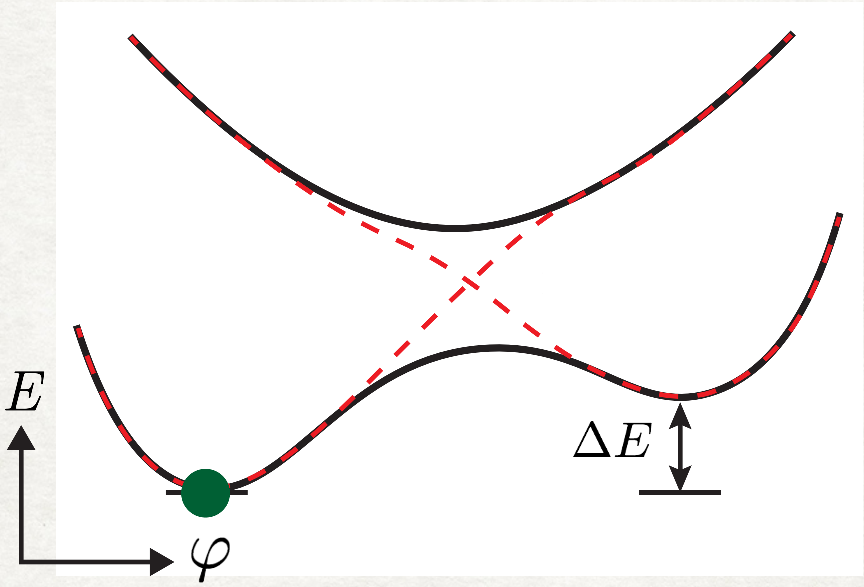

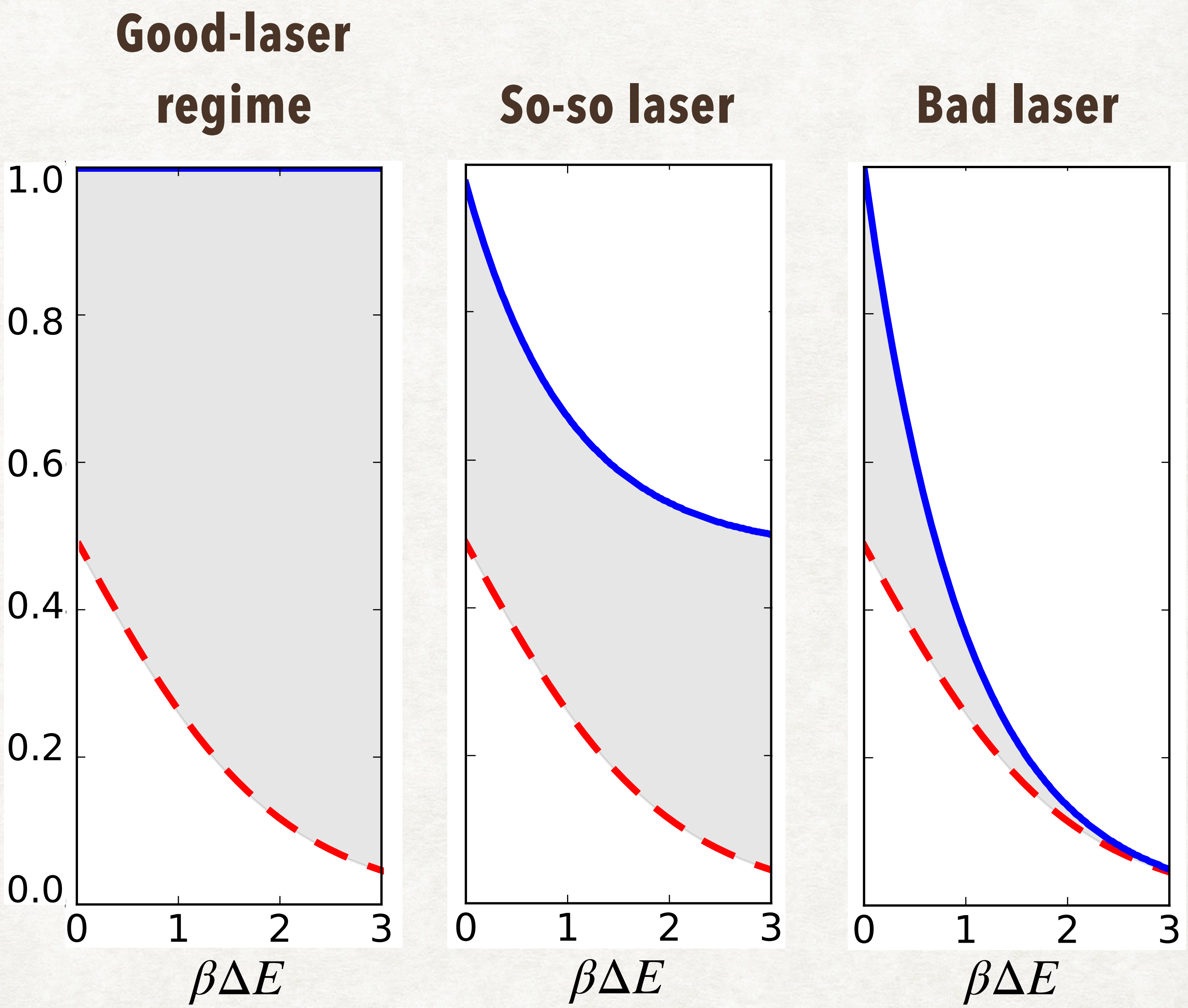

Takeaways

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- Electronic energy coherences can't help.

More applications of resource-theory results to the photoisomer

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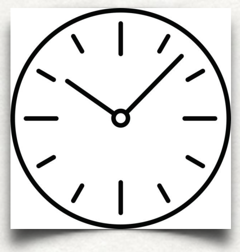
(1) Model of the molecule's rotational degree of freedom as a quantum clock



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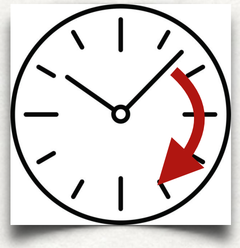

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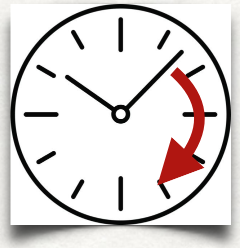

5 AM:

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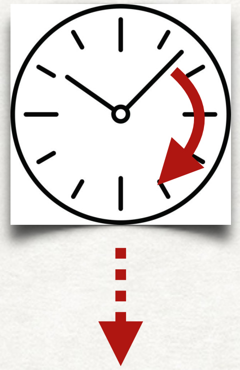

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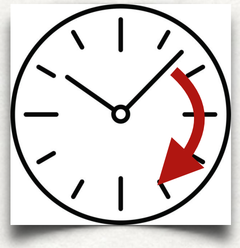

5 AM:

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Hopefully not now:

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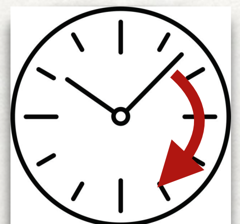

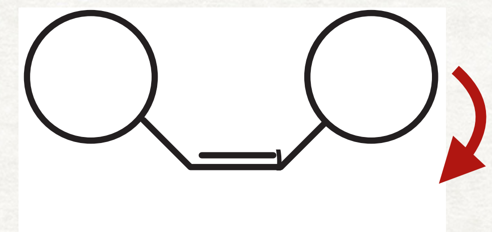

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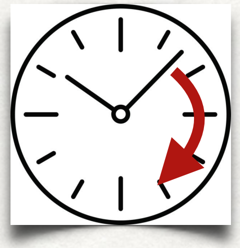

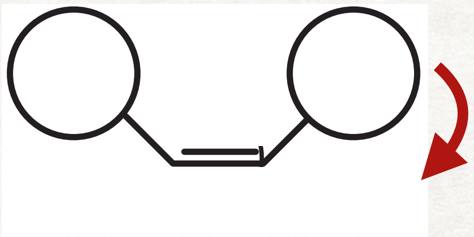

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$$H_{\text{mol}} = \int_0^\pi d\varphi \left[H_{\text{elec}}(\varphi) \otimes |\varphi\rangle\langle\varphi| + 1_{\text{elec}} \otimes \frac{\ell_\varphi^2}{2m} \right]$$

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Loads of papers, including recently, including about thermodynamic resource theories

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About energy → conjugate to time → measured by clocks

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  (A) Natural realization of a quantum clock

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(1) Model of the molecule's rotational degree of freedom as a <u>quantum clock</u>

↑

Loads of papers, including recently, including about <u>thermodynamic</u> resource theories

↑

About energy →
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- <u>Upshots</u>

  (A) Natural realization of a quantum clock

  (B) Resource-theoretic model for a (dissipative Landau-Zener) transition prevalent in chemistry and condensed matter

More applications of resource-theory results to the photoisomer

(2) Extraction of work from coherences

More applications of resource-theory results to the photoisomer

(2) Extraction of work from coherences

(3) Quantification of the post-isomerization electronic energy coherences

More applications of resource-theory results to the photoisomer

(2) Extraction of work from coherences

(3) Quantification of the post-isomerization electronic energy coherences

(4) Etc.

Opportunity 

Opportunity

- We've accrued many abstract resource-theory results. →

⋮
Theorem
Corollary
Theorem
Theorem
Lemma

Opportunity

⋮

Theorem

Corollary

Theorem

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Lemma

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- Let's apply them to answer preexisting questions about chemistry, condensed matter, high-energy physics, …

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⋮
Theorem
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Lemma

- Let's apply them to answer preexisting questions about chemistry, condensed matter, high-energy physics, …
  - Why should anyone outside the resource-theory community care about resource theories?

Opportunity

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Opportunity

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  - Holmes, Weidt, Jennings, Anders, and Mintert, Quantum **3**, 124 (2019).

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- See also
  - Alhambra, Lostaglio, and Perry, arXiv:1807.07974 (2018).
  - 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

Opportunity

<u>Goals</u>

- Contribute value to the broader scientific community.

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Potential settings

- Exciton transport in films made from quantum dots

Opportunity

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- Apply our abstract theorems to real physical systems.

Potential settings

- Exciton transport in films made from quantum dots
  - Photovoltaics

Opportunity

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Potential settings

- Exciton transport in films made from quantum dots
  - Photovoltaics
- Proton transport in molecular systems

Opportunity

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- Exciton transport in films made from quantum dots
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Recap

NYH and Limmer, arXiv:1811.06551 (2018).

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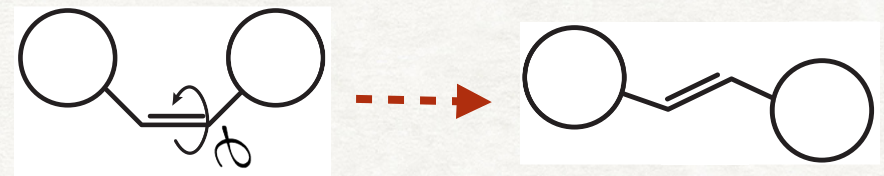
-  **The photoisomer** 

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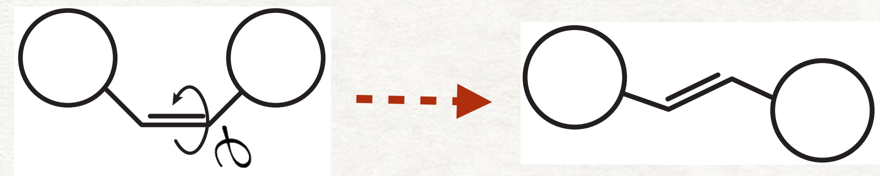
-  **The photoisomer** 

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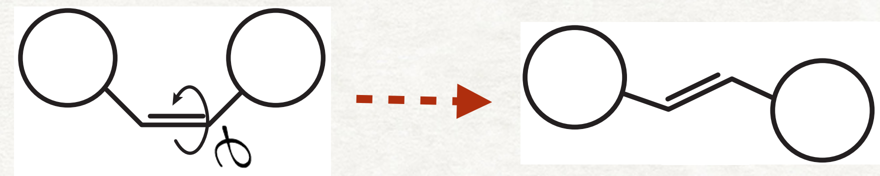
-  **The photoisomer** 

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    - How to model your favorite system

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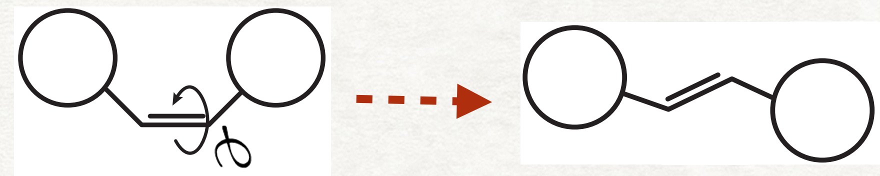
-  **The photoisomer** 

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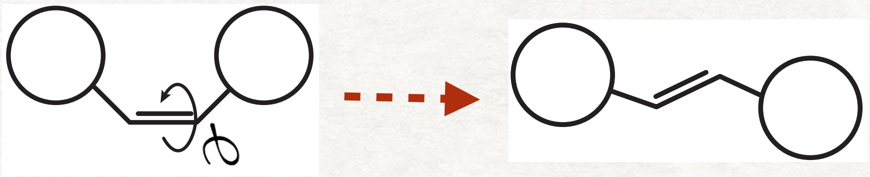
-  **The photoisomer** 

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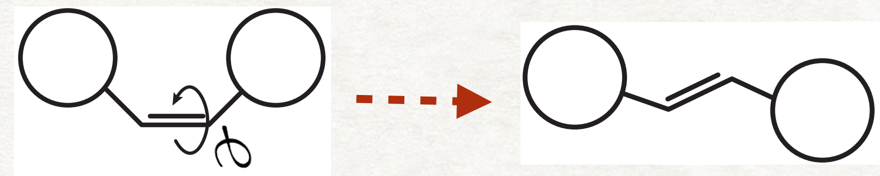
-  **The photoisomer** 

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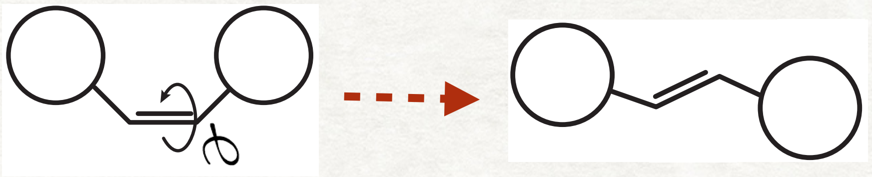
-  **The photoisomer** 

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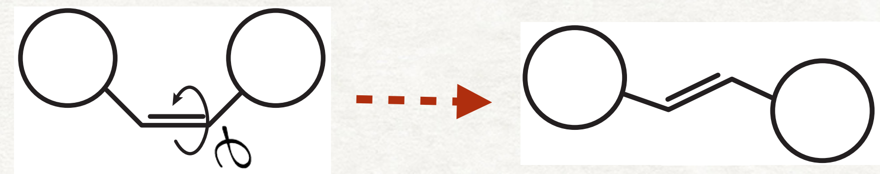
-  **The photoisomer** 

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- **Opportunity** 

Thanks for your time!

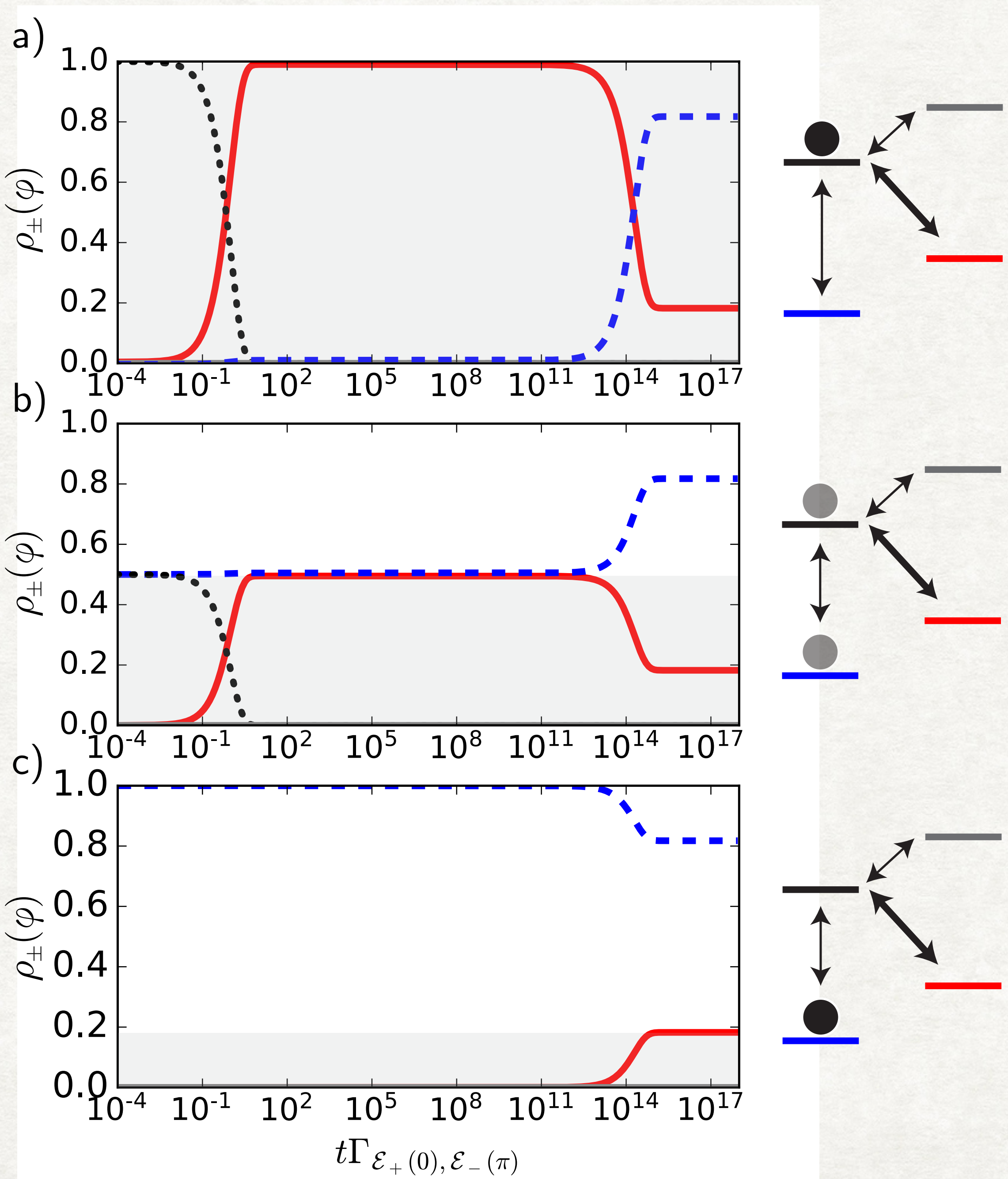
NYH and Limmer, arXiv:1811.06551 (2018).

Comparison of resource-theory bound with time-dependent Lindblad dynamics

Good laser:

So-so laser:

Bad laser:



- Gray shading: region allowed by resource-theory bound

Minimal work required to photoexcite the molecule in a single shot

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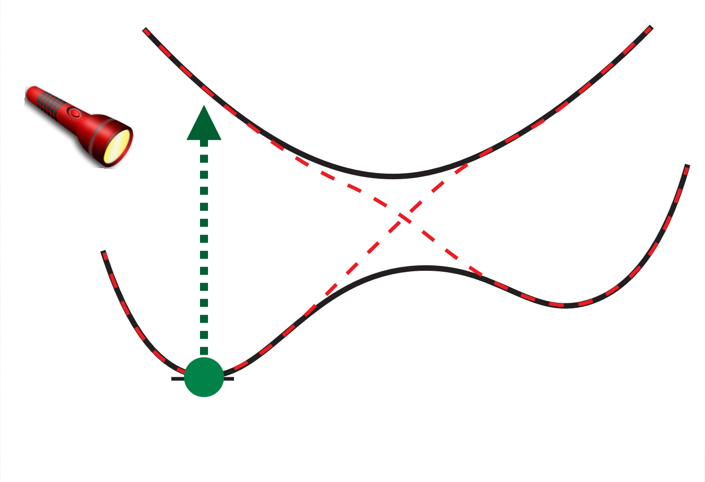

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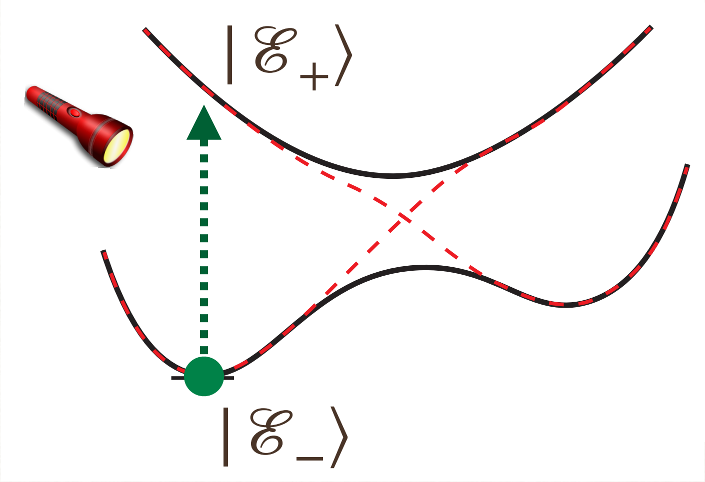

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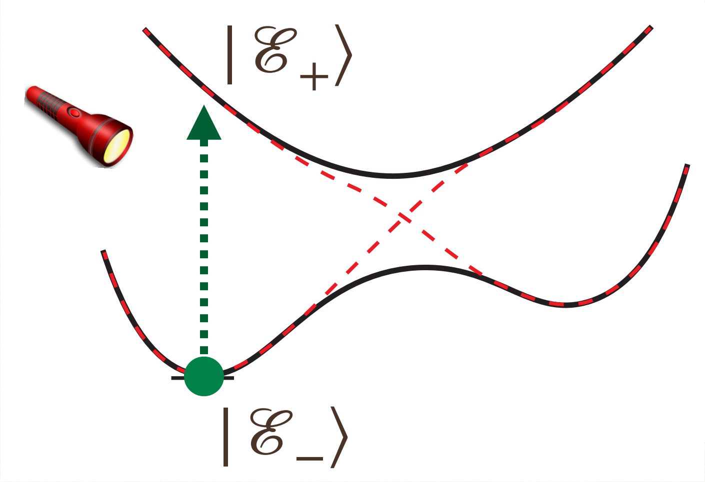

- Not simply $\mathscr{E}_+ - \mathscr{E}_-$

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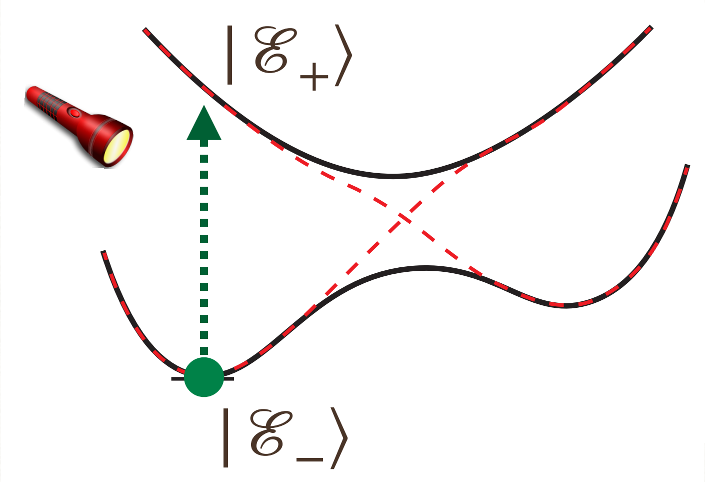

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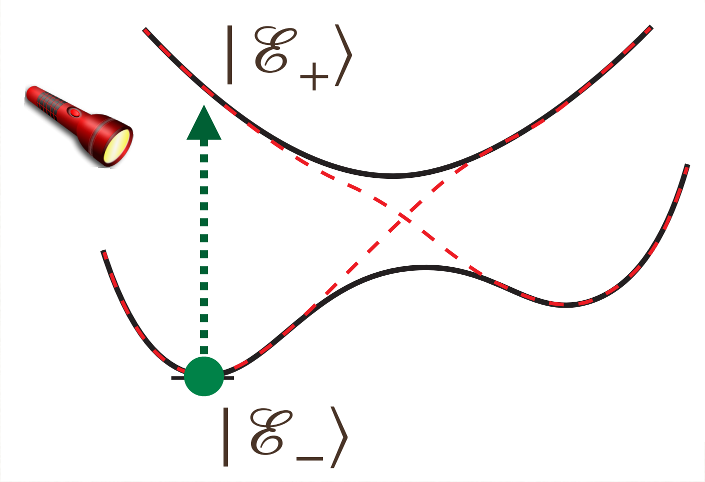

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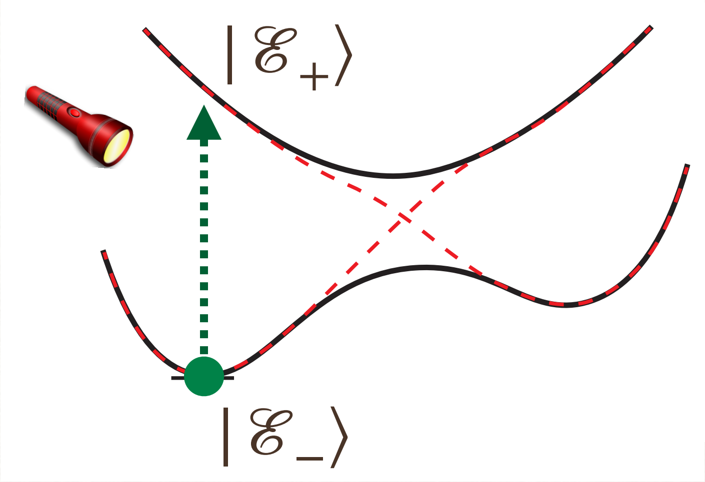

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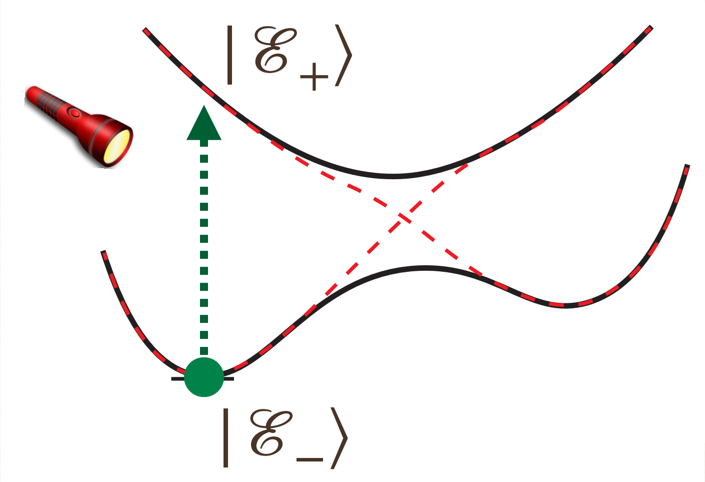

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(State discrimination in the worst case)

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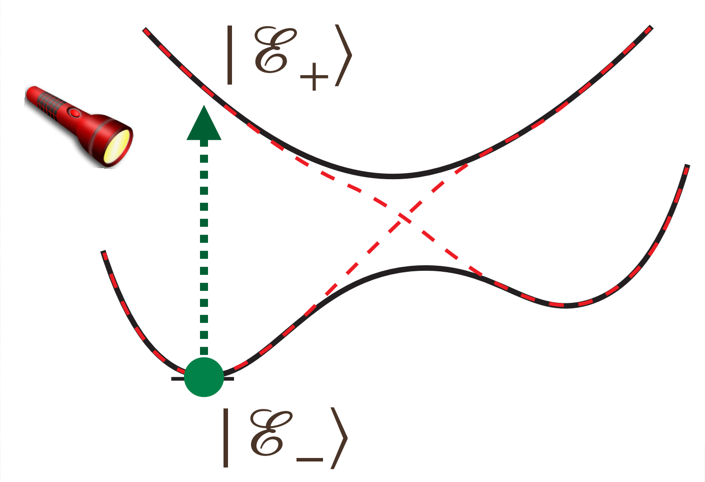

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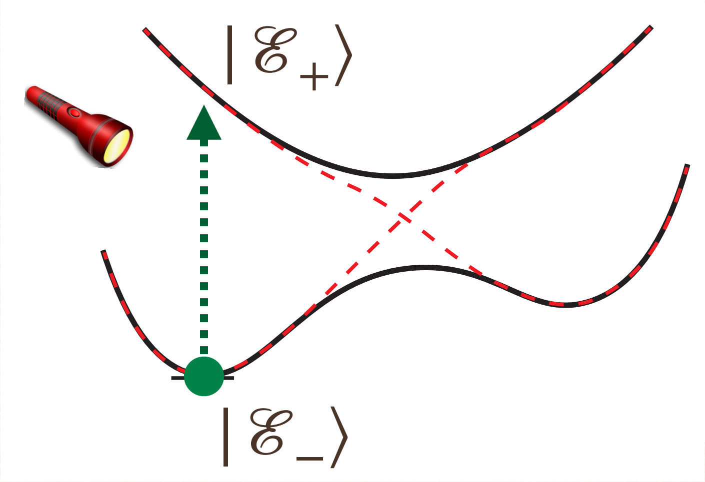

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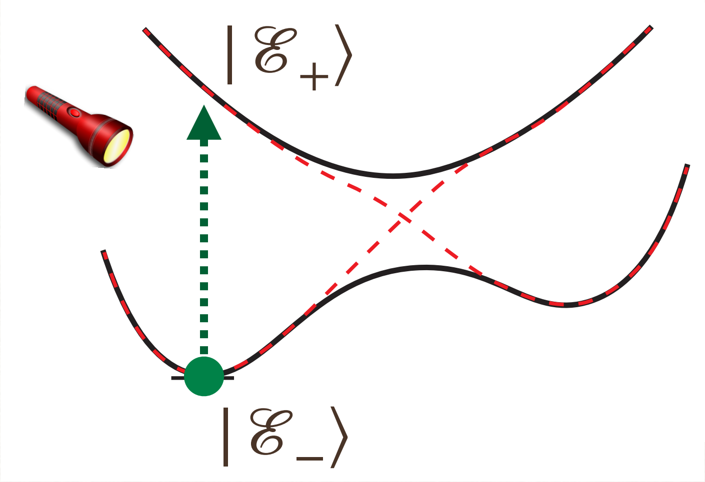

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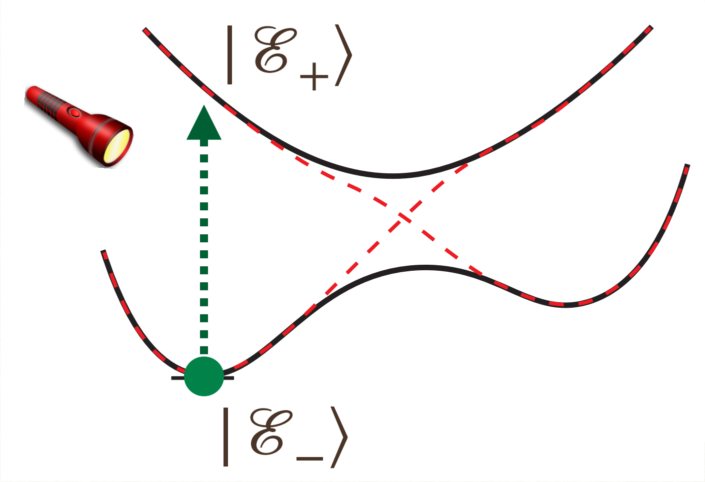

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$\sim F_{\mathrm{noneq}} - F_{\mathrm{eq}}$

Extraction of work from coherence

Extraction of work from coherence 

- Known from resource theory:

- Skrzypczyk, Short, and Popescu, arXiv:1302.2811 (2013).
  Kwon *et al.* PRL **120**, 150602 (2018).
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Extraction of work from coherence

Physical intuition

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- Coherent state has more purity

Extraction of work from coherence 

Physical intuition

- Coherent state has more purity $\longrightarrow$ more predictability

Extraction of work from coherence 

Physical intuition

- Coherent state has more purity → more predictability → more informational resource

Extraction of work from coherence

Physical intuition

- Coherent state has more purity $\rightarrow$ more predictability $\rightarrow$ more informational resource

- *Szilárd's engine*: can use information to turn heat into work

Szilárd, Zeit. F. Phys. **53**, 11-12 (1929).

Extraction of work from coherence

Strategy

- Follow Kwon *et al.* PRL **120**, 150602 (2018).

Extraction of work from coherence 

<u>Strategy</u>

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  Exhibits an example 2-qubit system
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Extraction of work from coherence

<u>Strategy</u>

- Follow Kwon *et al.* PRL **120**, 150602 (2018).
  Exhibits an example 2-qubit system
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- Show that, in principle, such a state can be constructed from photoisomers.

Extraction of work from coherence

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Extraction of work from coherence

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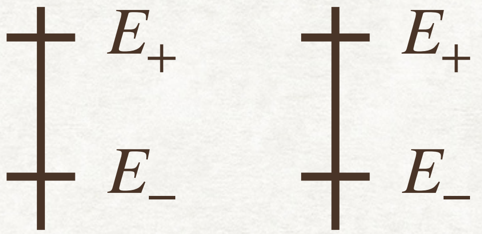
- System of 2 identical qubits:



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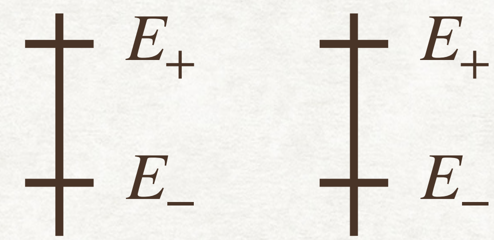

- General form of 2-qubit pure state:

$$\sqrt{p_{--}}\,|E_-,E_-\rangle + \sqrt{p_{-+}}\,|E_-,E_+\rangle + \sqrt{p_{+-}}\,|E_+,E_-\rangle + \sqrt{p_{++}}\,|E_+,E_+\rangle$$

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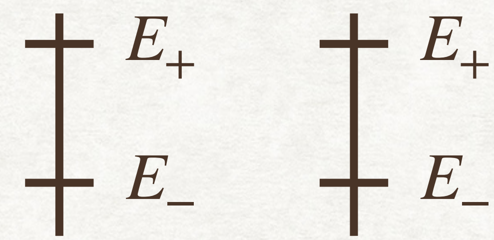

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- <u>Conditions under which work can be extracted from coherence</u>

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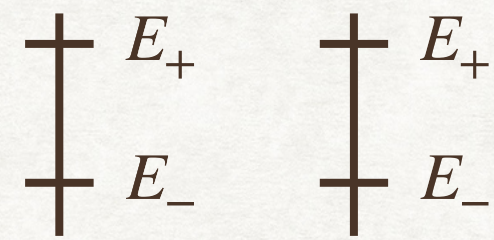

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(i) The equal-energy terms have equal prefactors: $\sqrt{p_{-+}} = \sqrt{p_{+-}}$.

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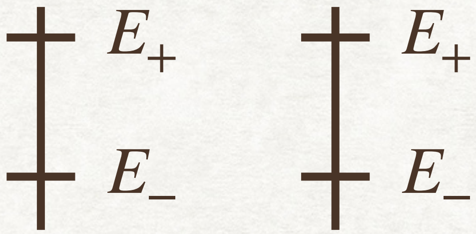

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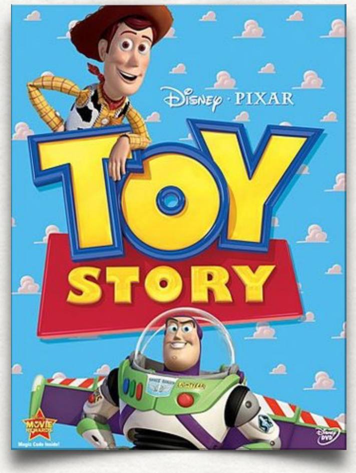
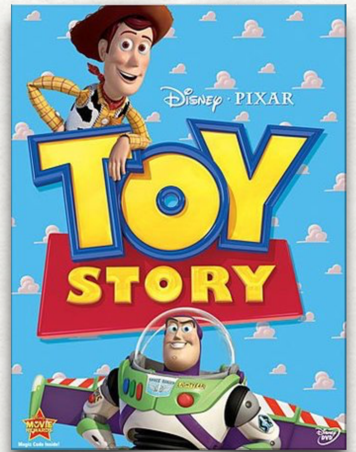
- <u>Conditions under which work can be extracted from coherence</u>

(i) The equal-energy terms have equal prefactors: $\sqrt{p_{-+}} = \sqrt{p_{+-}}$.

(ii) The greatest Gibbs-rescaled probability is p_{+-} .

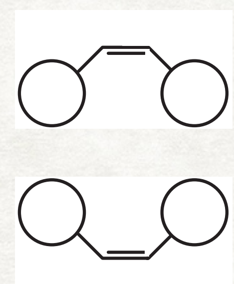


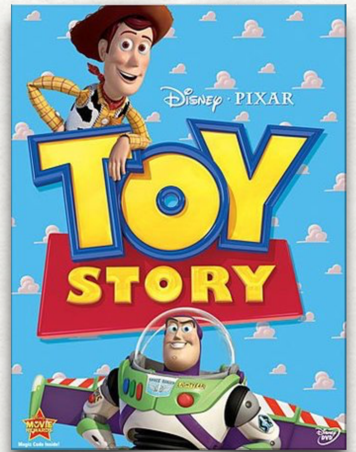
How a photoisomer system could meet the work-from-coherences conditions



How a photoisomer system could meet the work-from-coherences conditions

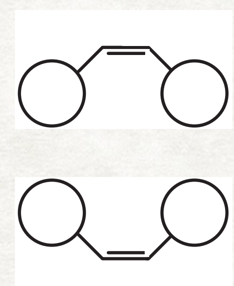
- 2 isomers close together in small, symmetric structure

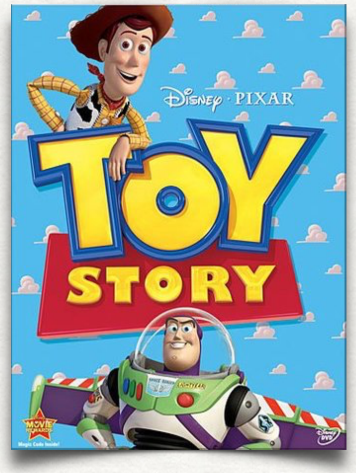




How a photoisomer system could meet the work-from-coherences conditions

- 2 isomers close together in small, symmetric structure
  - Occupy a totally anti/symmetric state





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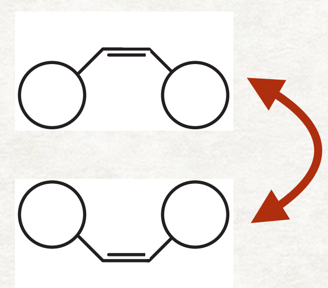
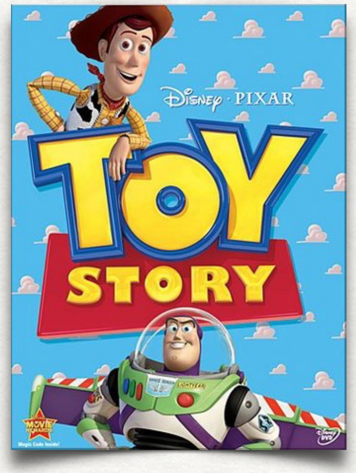


- Interact via Heisenberg coupling, $\vec{\sigma} \cdot \vec{\sigma}$, at very low temperature



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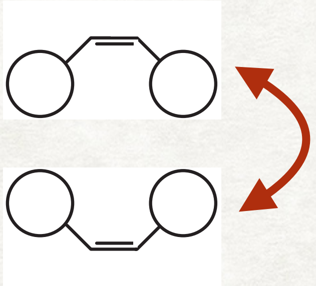
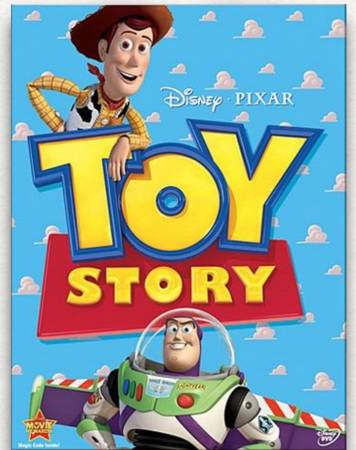


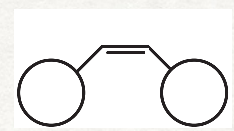
- Interact via Heisenberg coupling, $\vec{\sigma} \cdot \vec{\sigma}$, at very low temperature $\longrightarrow$
- By end of photoisomerization, they drop to the ground, antisymmetric state.

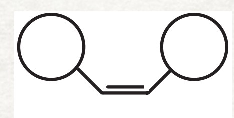
$$\frac{1}{\sqrt{2}}(|\mathscr{E}_+(\pi), \mathscr{E}_-(\pi)\rangle - |\mathscr{E}_-(\pi), \mathscr{E}_+(\pi)\rangle)$$



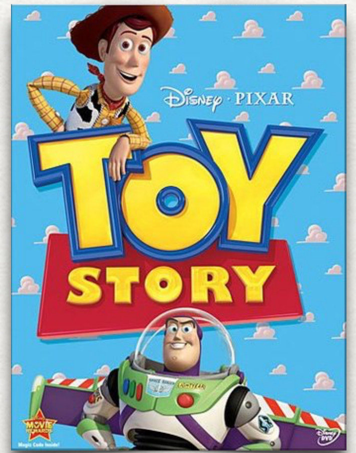
How a photoisomer system could meet the work-from-coherences conditions

- The isomers decouple quickly.





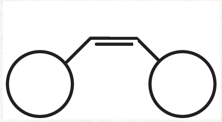
$$\frac{1}{\sqrt{2}}(|\mathscr{E}_+(\pi),\mathscr{E}_-(\pi)\rangle - |\mathscr{E}_-(\pi),\mathscr{E}_+(\pi)\rangle)$$

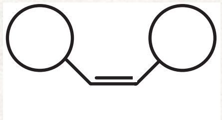


How a photoisomer system could meet the work-from-coherences conditions

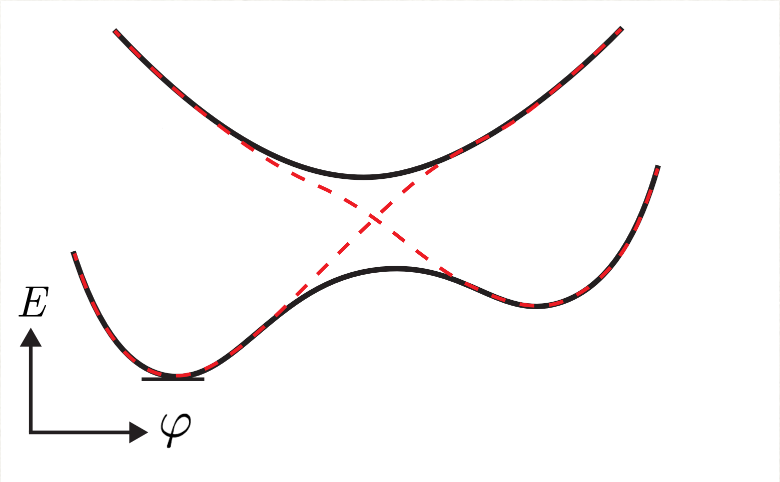
- The isomers decouple quickly.

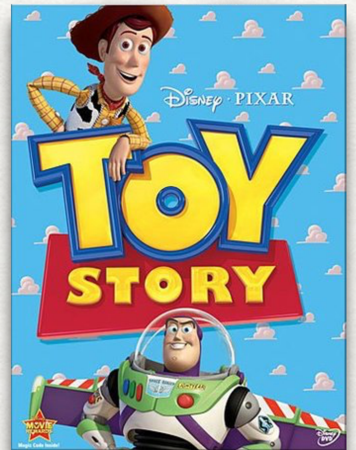
- The Hamiltonian returns to $H_{\text{mol}} + H_{\text{mol}}$.





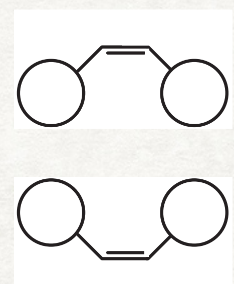
$$\frac{1}{\sqrt{2}}(|\mathscr{E}_+(\pi), \mathscr{E}_-(\pi)\rangle - |\mathscr{E}_-(\pi), \mathscr{E}_+(\pi)\rangle)$$



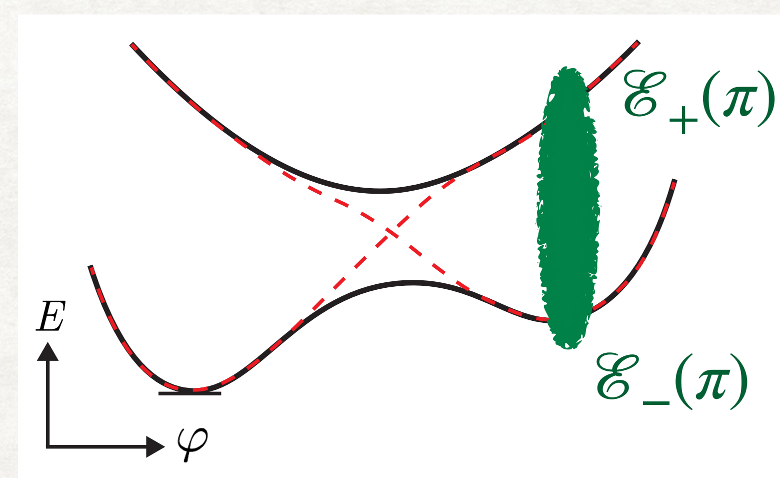


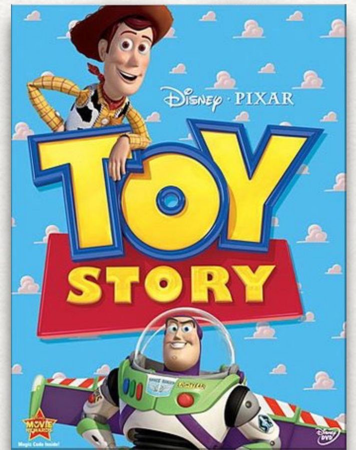
How a photoisomer system could meet the work-from-coherences conditions

- The isomers decouple quickly.
- The Hamiltonian returns to $H_{\text{mol}} + H_{\text{mol}}$. The state remains constant.



$$\frac{1}{\sqrt{2}}\left(|\,\mathscr{E}_+(\pi), \mathscr{E}_-(\pi)\rangle - |\,\mathscr{E}_-(\pi), \mathscr{E}_+(\pi)\rangle\right)$$





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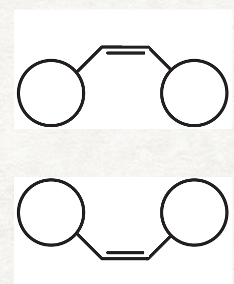

- The state satisfies the Kwon *et al.* conditions.

$$\frac{1}{\sqrt{2}}(|\mathscr{E}_+(\pi), \mathscr{E}_-(\pi)\rangle - |\mathscr{E}_-(\pi), \mathscr{E}_+(\pi)\rangle)$$