

# SA-OO-VQE : a quantum algorithm for an equal footing description of ground and excited states on near term quantum computers

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*Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique*  
*Université de Strasbourg*



# Content

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- I) General introduction
- II) Describing conical intersections on near term quantum computers
- III) SA-OO-VQE: Some results
- IV) Take home messages

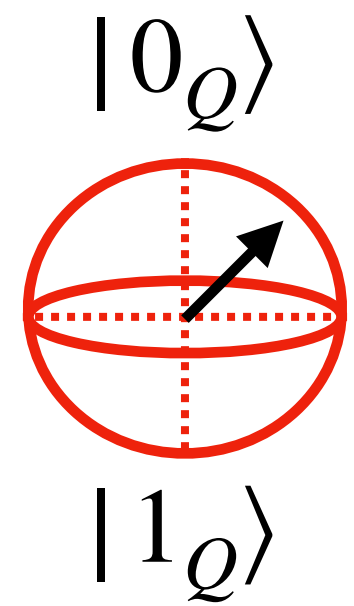
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# I) General introduction

## The Qubit

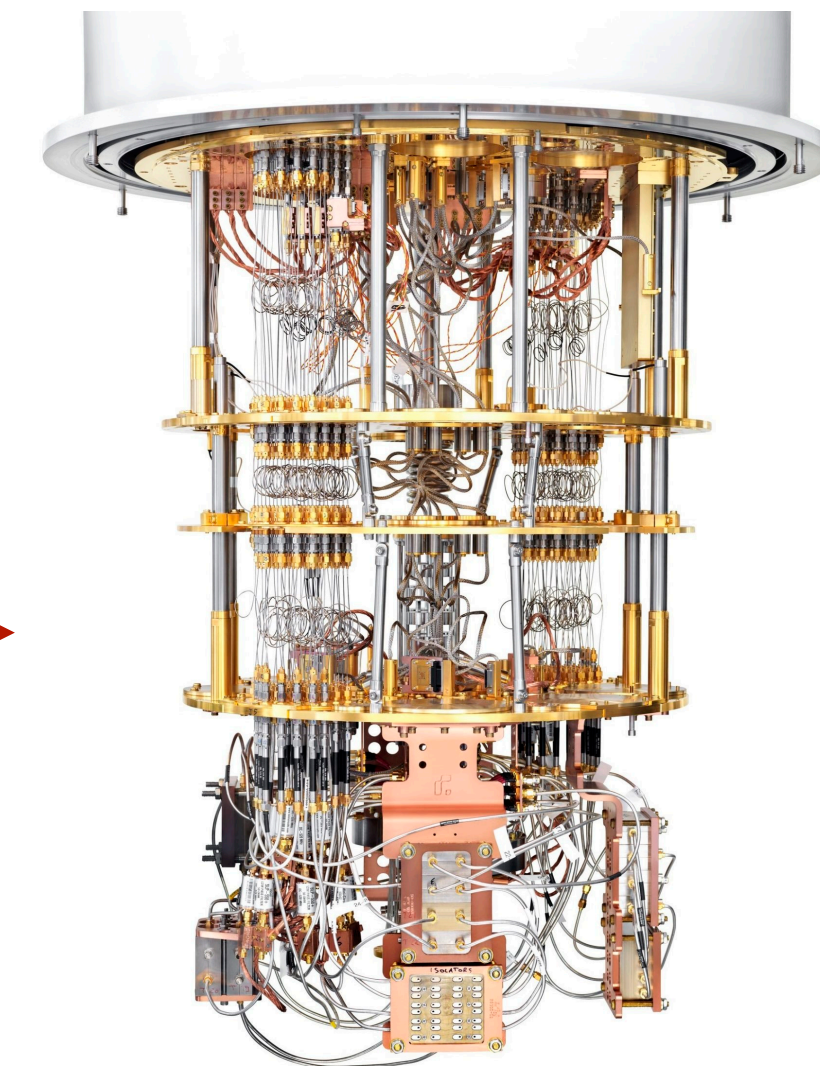
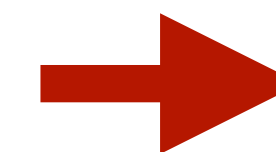
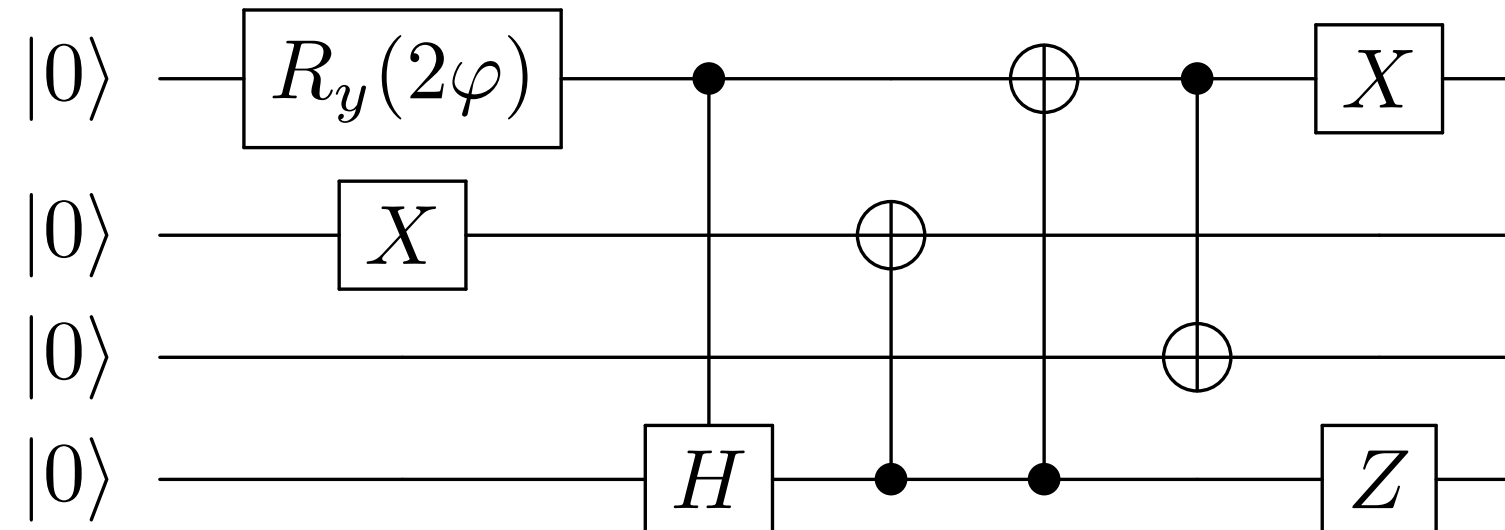


$$|Q\rangle = c_0|0_Q\rangle + c_1|1_Q\rangle$$

Different systems possible :

- Photons
- Excited states
- Electronic Spins

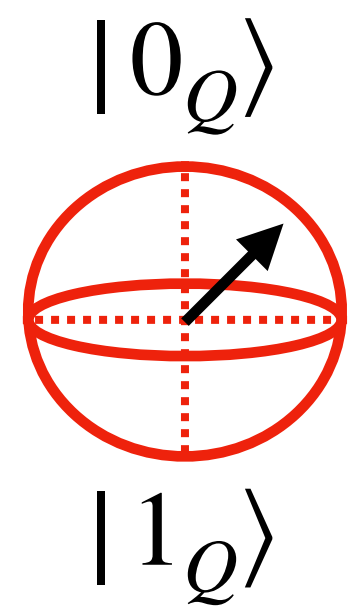
## Quantum circuits



Quantum computer

# I) General introduction

## The Qubit

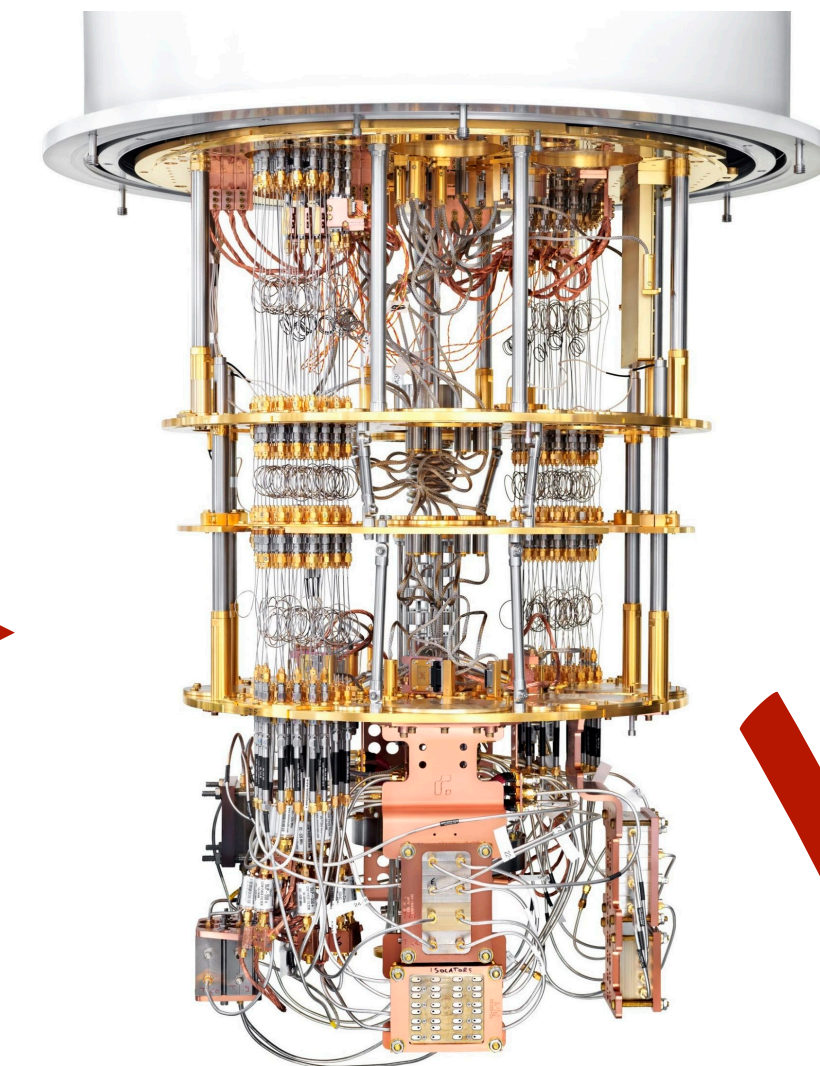
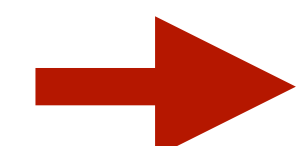
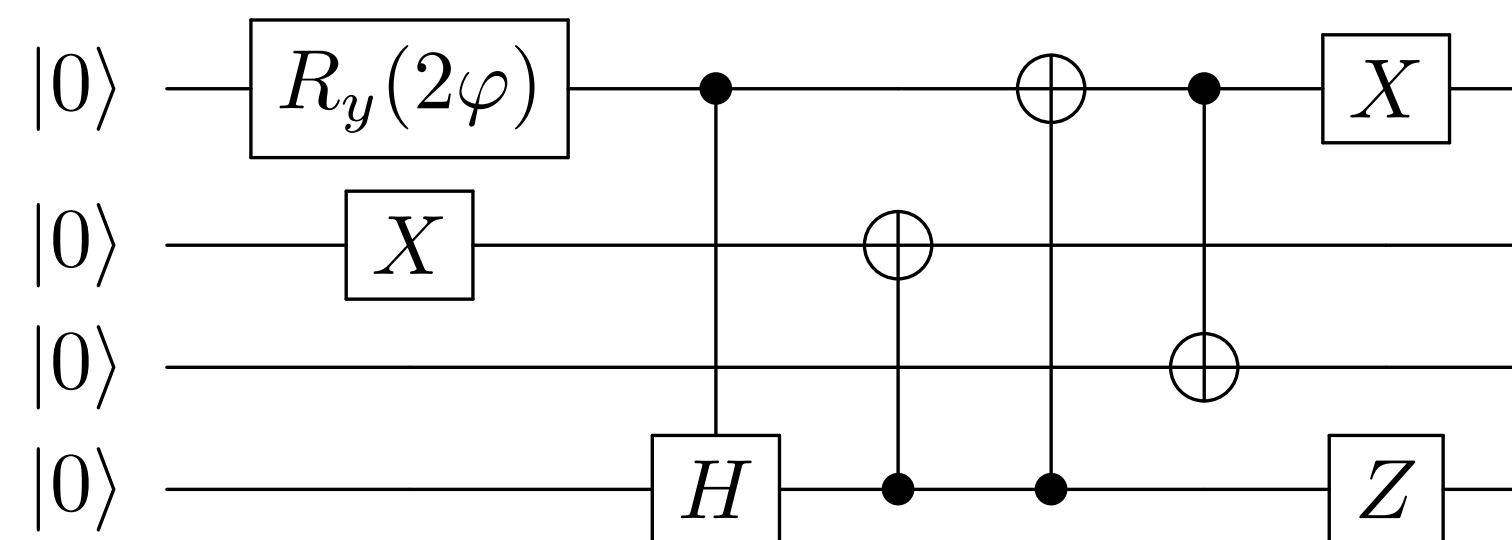


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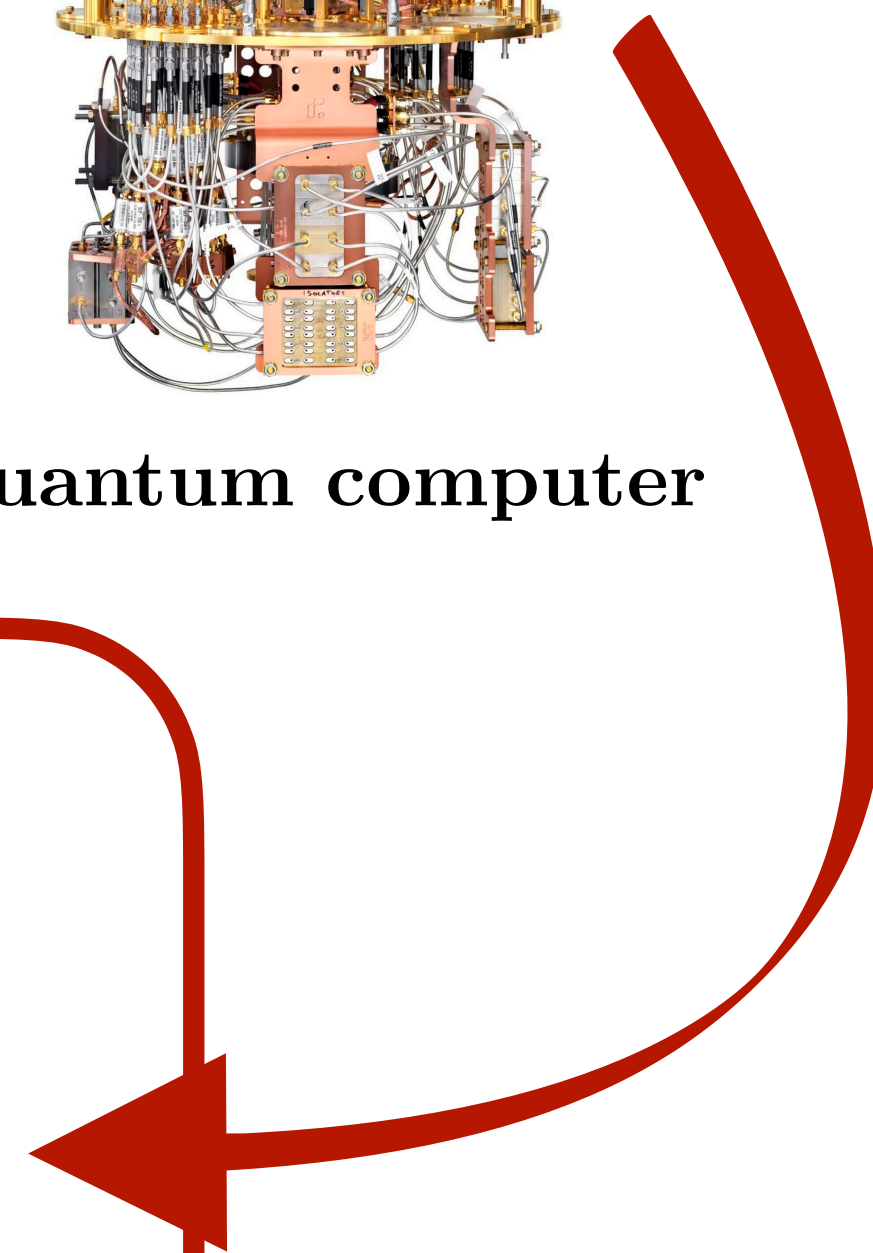
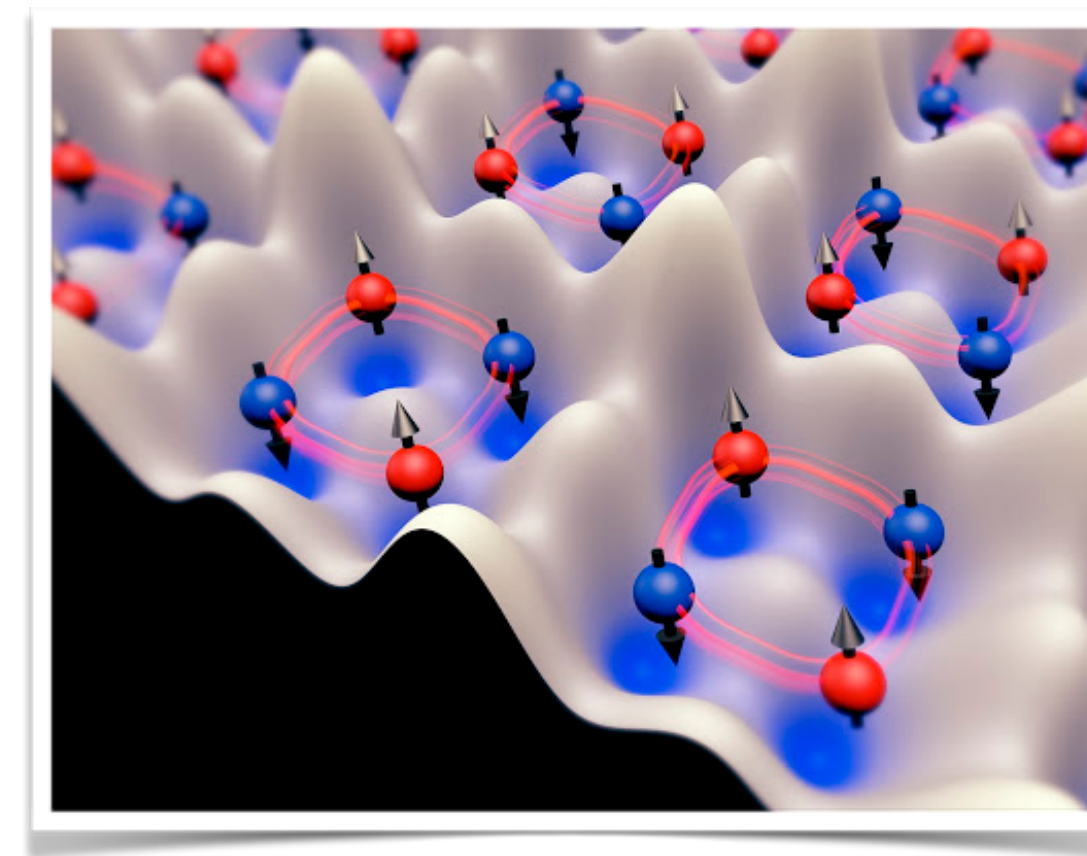
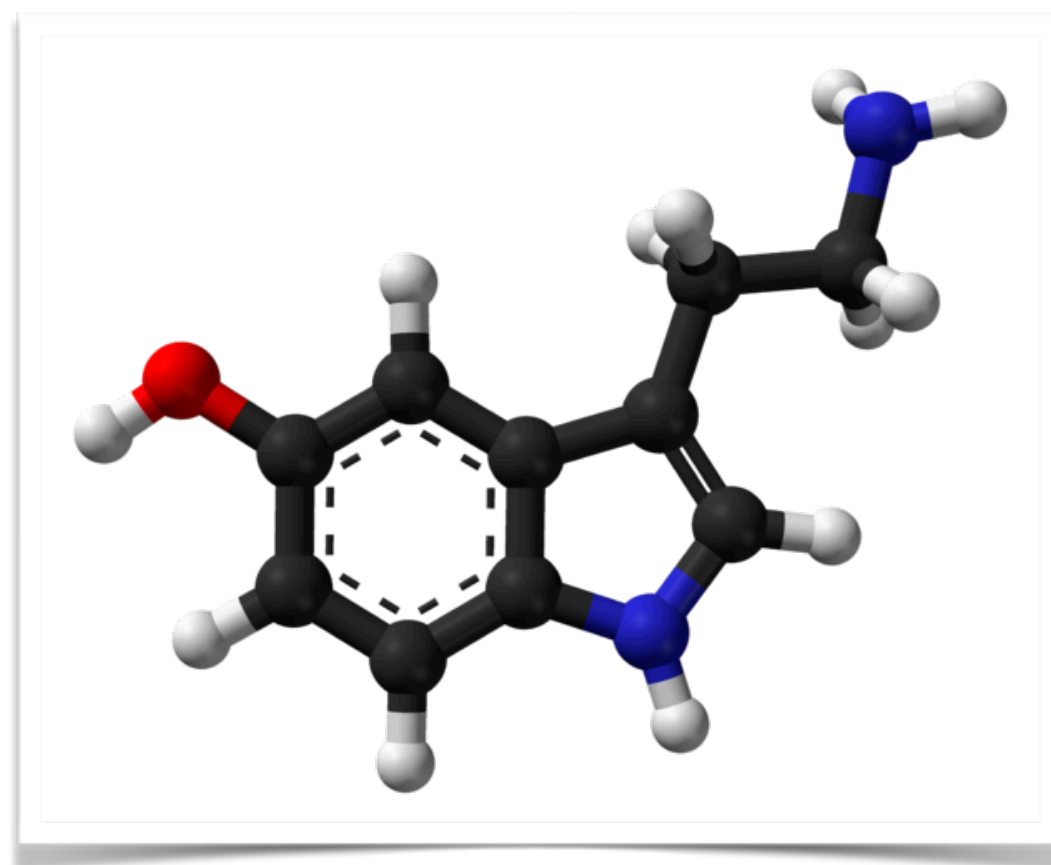
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## Quantum circuits

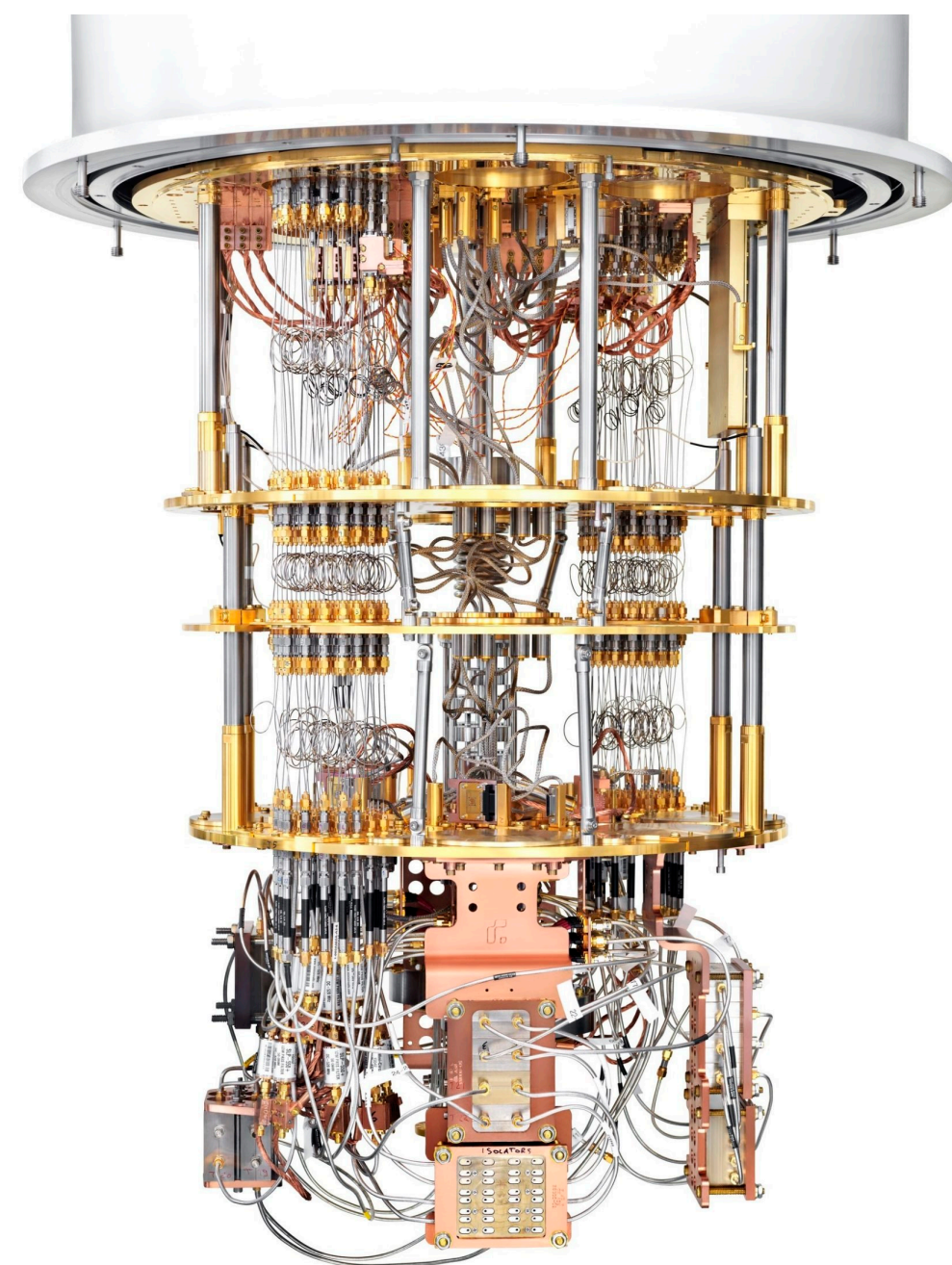


Quantum computer

## Resolution of complex quantum many-body systems

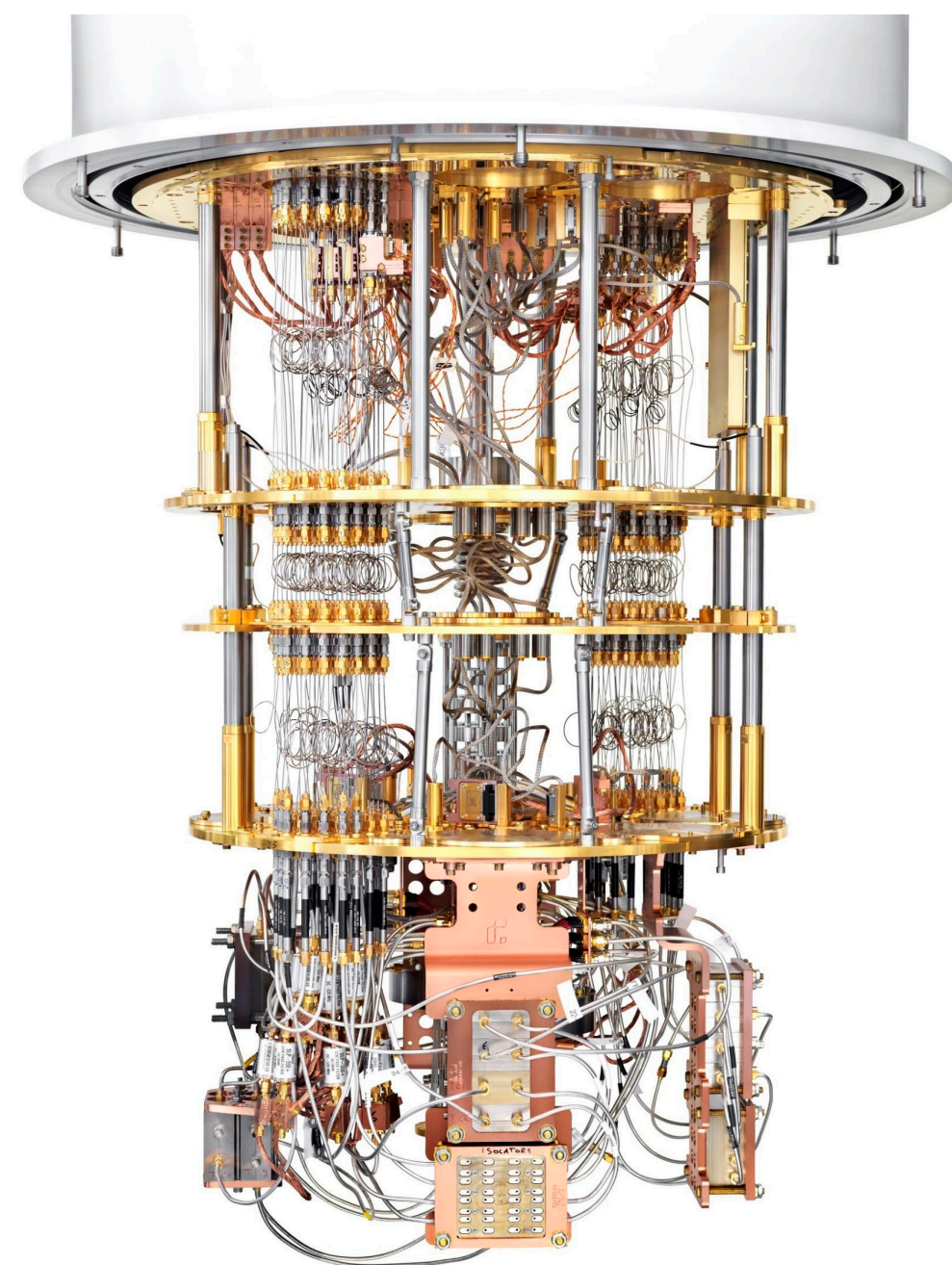


# I) General introduction



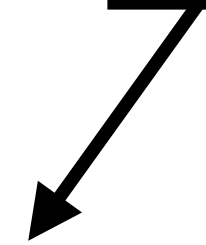
Observation : Current quantum computers are “**NISQ**” devices.  
(**NISQ** : **Noisy Intermediate-Scale Quantum**)

# I) General introduction



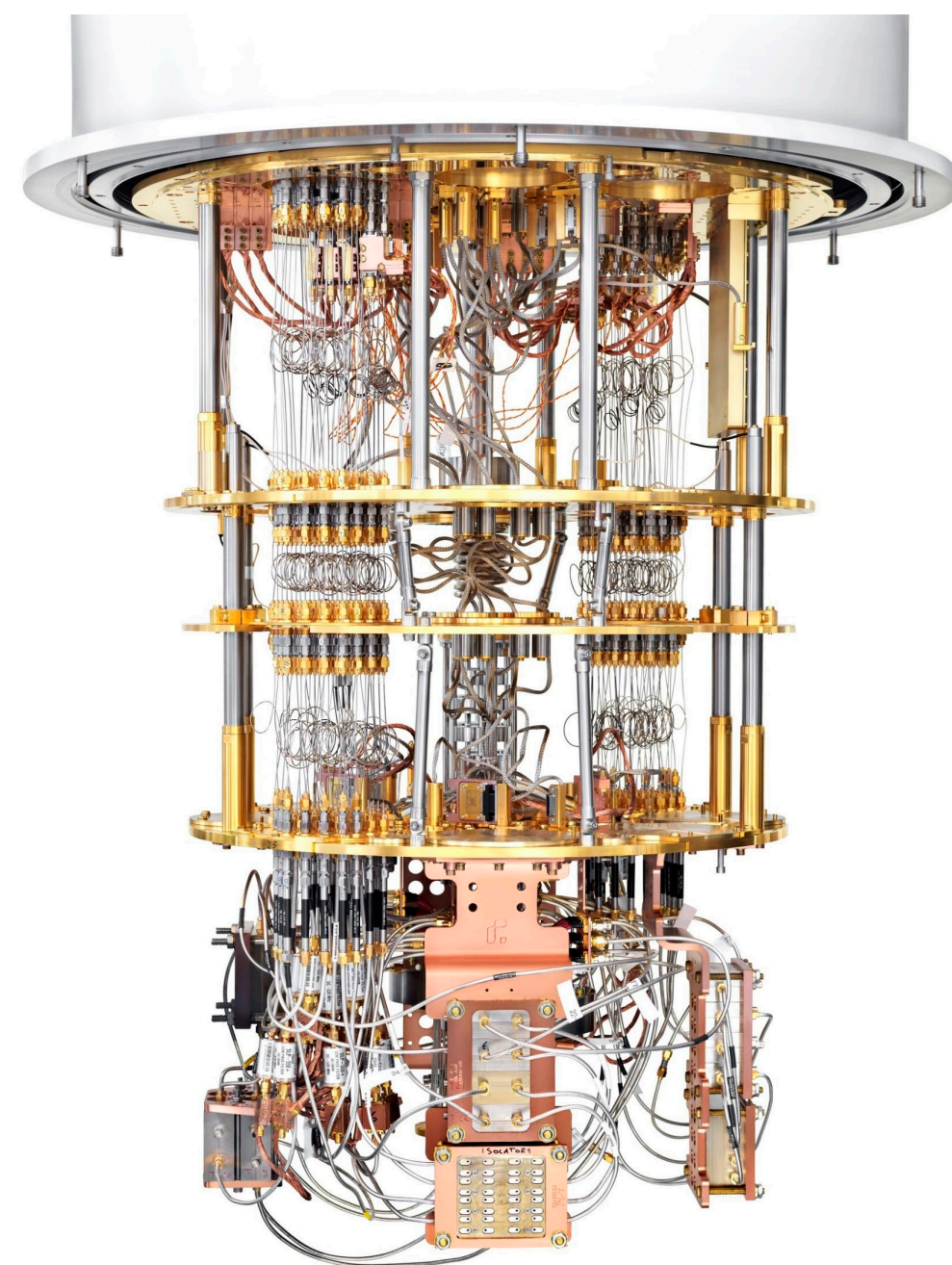
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(qubits = open quantum system).

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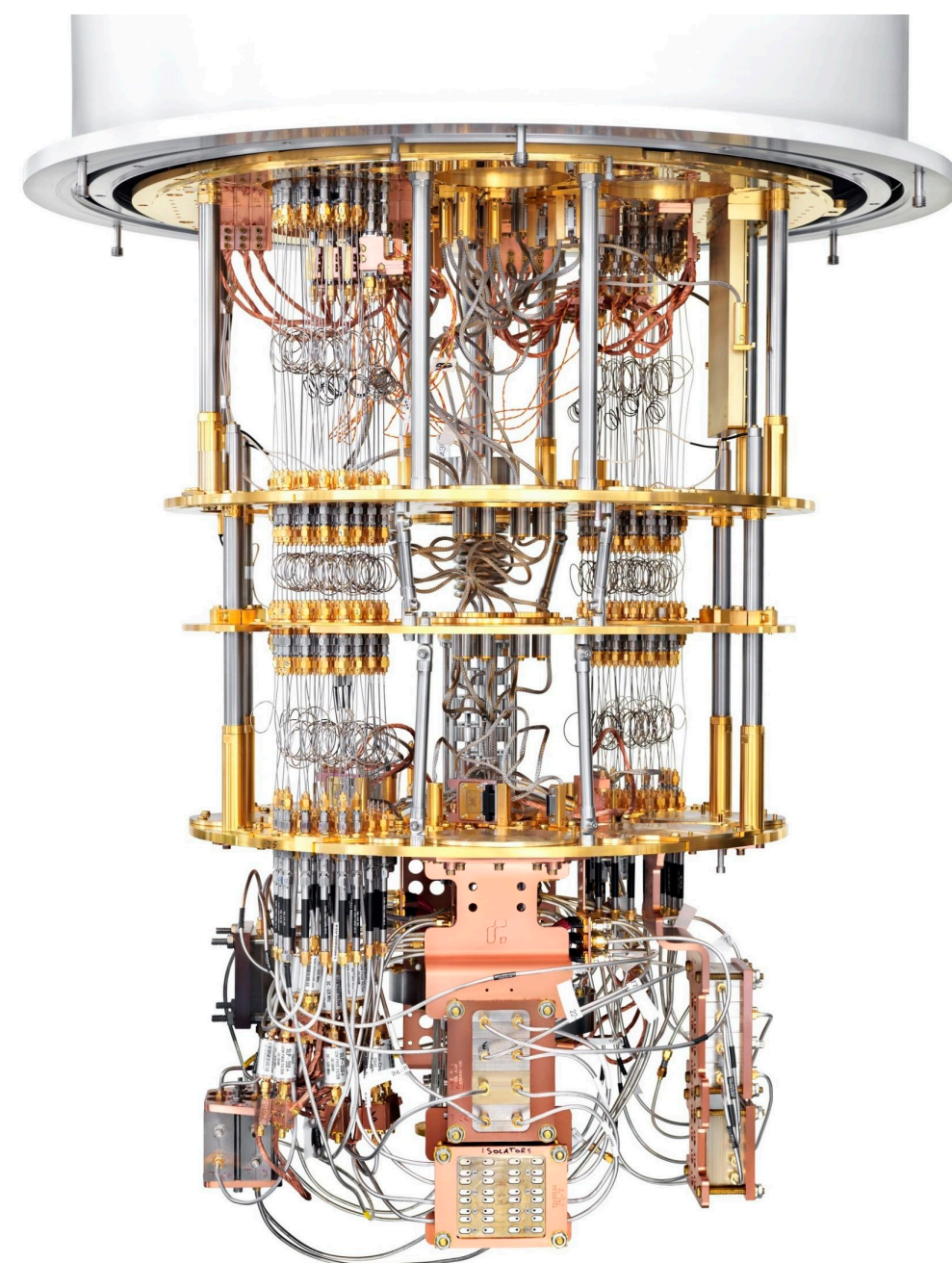
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$$N_{qubits} \sim 10$$



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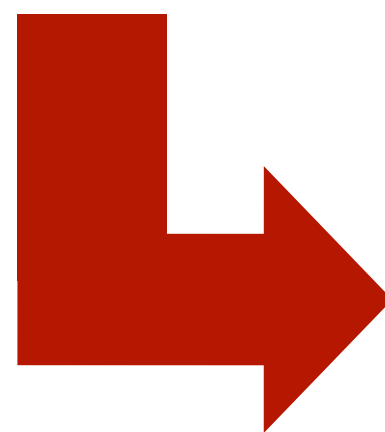
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## Advantages :

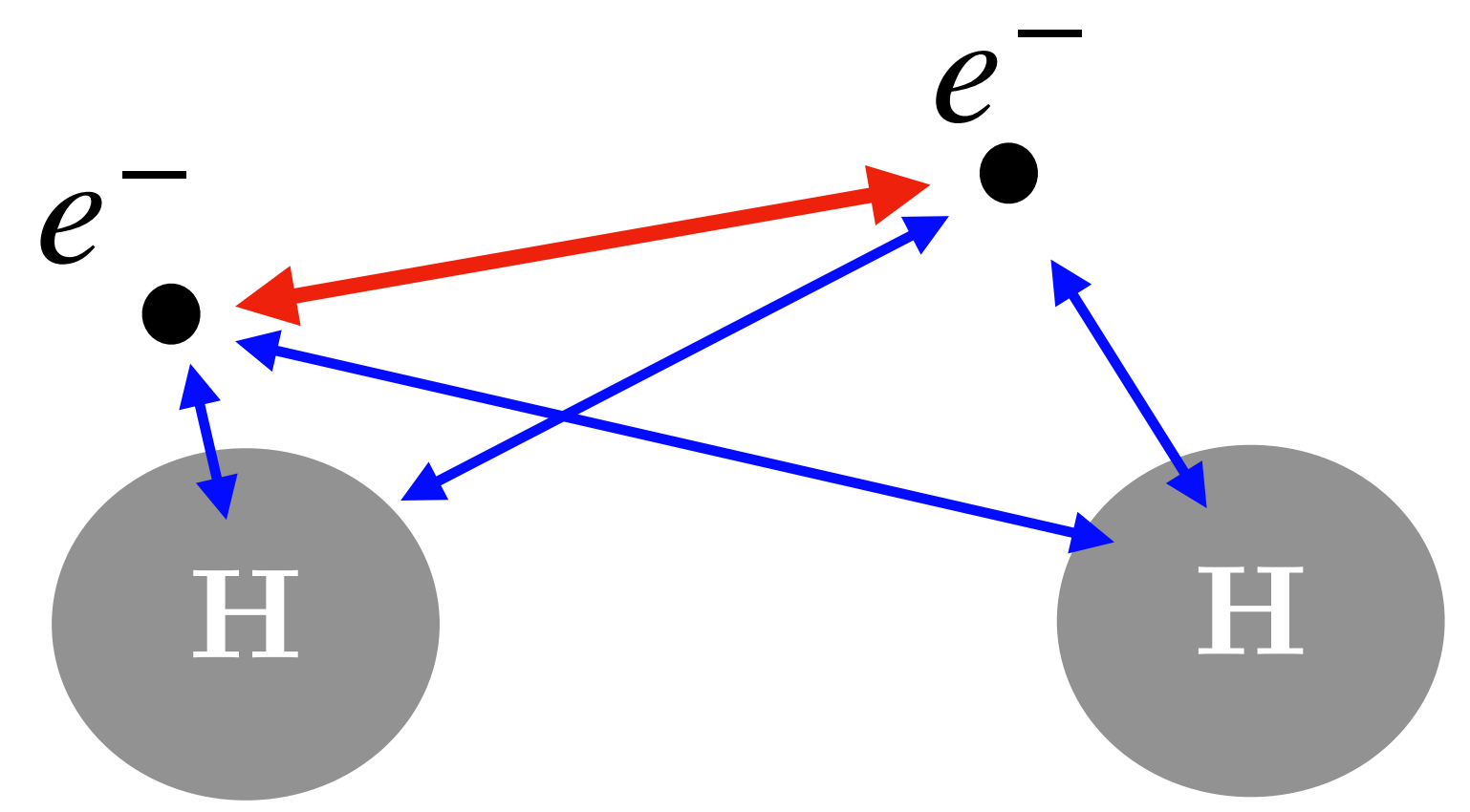
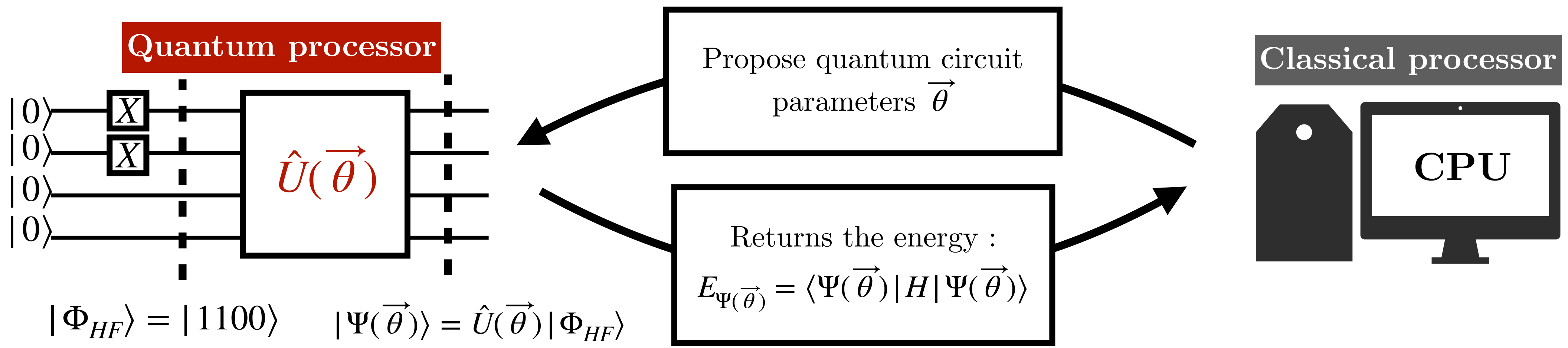
- Exponentially fewer resources to store information (/classical CPU)
- Based on a few qubits.
- Pretty resistant to the noise effects.



NEAR TERM  
QUANTUM ALGORITHMS

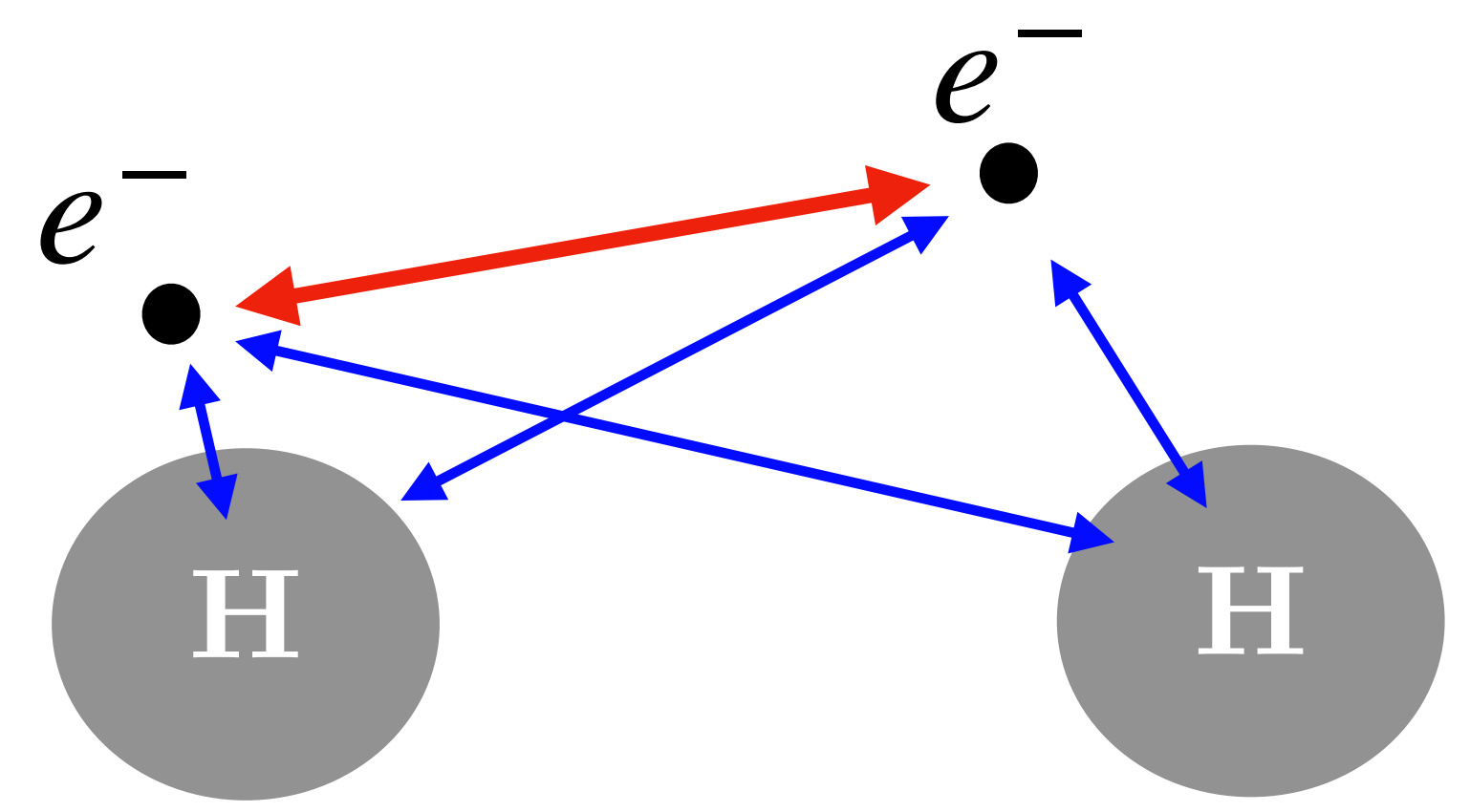
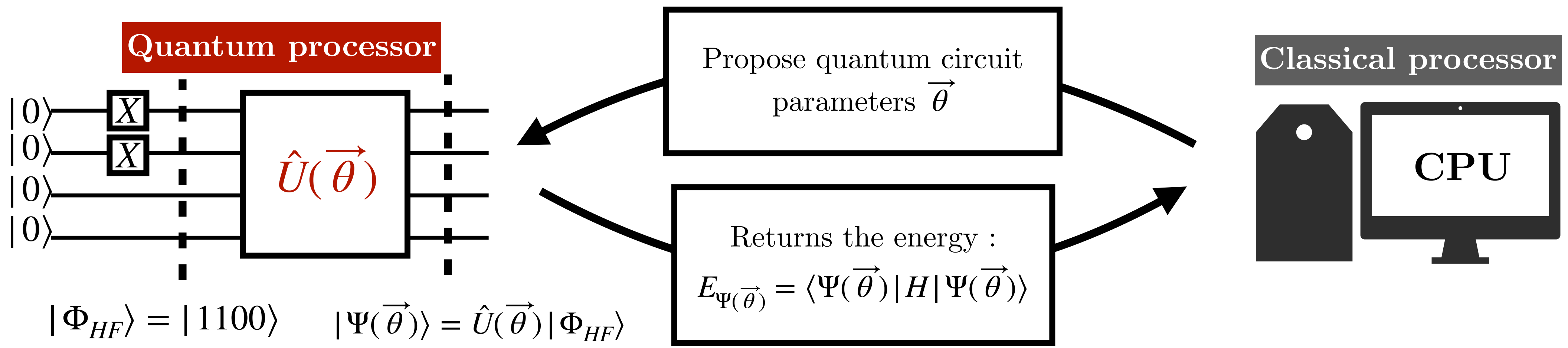
# I) General introduction

## VARIATIONAL QUANTUM EIGENSOLVER (VQE)

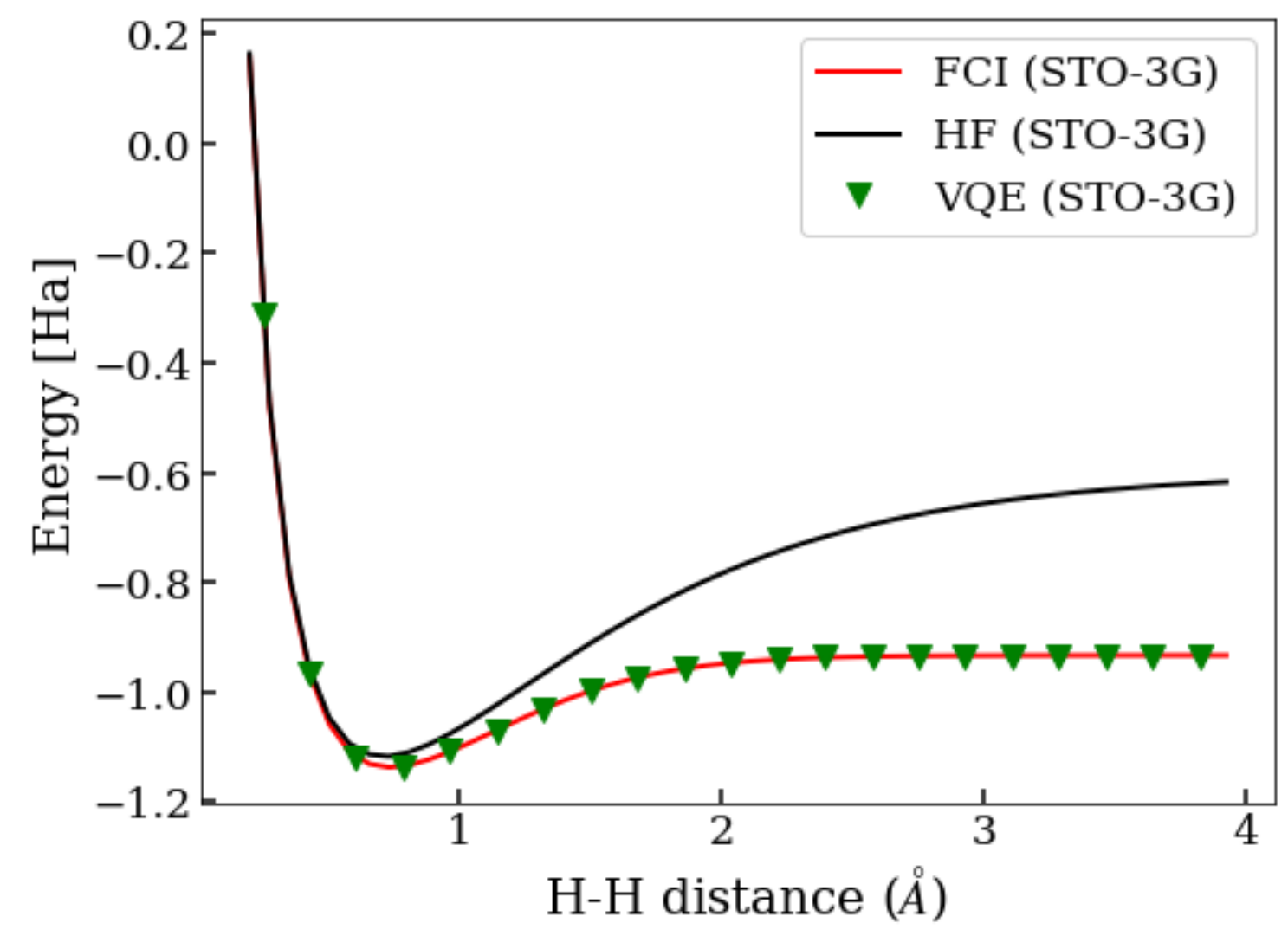


# I) General introduction

## VARIATIONAL QUANTUM EIGENSOLVER (VQE)



Simulation of the VQE algorithm



## I) General introduction

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VQE extensions for the  
computation  
of excited states

## I) General introduction

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### **QSE: Quantum-subspace extension**

J. R. McClean *et al.*, *Phys. Rev. A* **95**, 042308 (2017).



**VQE extensions for the  
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### **SS-VQE: subspace search VQE**

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**VQE extensions for the  
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### **VQD: variational quantum deflation**

O. Higgott *et al.*, *Quantum* **3** (2019): 156.

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### **MC-VQE: multi-contracted states VQE**

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VQE extensions for the  
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VQE extensions for the  
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## SA-OO-VQE: State-averaged orbital-optimised VQE

S. Yalouz, *et al.* *Quantum Science and Technology* 6.2 (2021): 024004.

S. Yalouz, *et al.* *arXiv preprint arXiv:2109.04576* (2021).

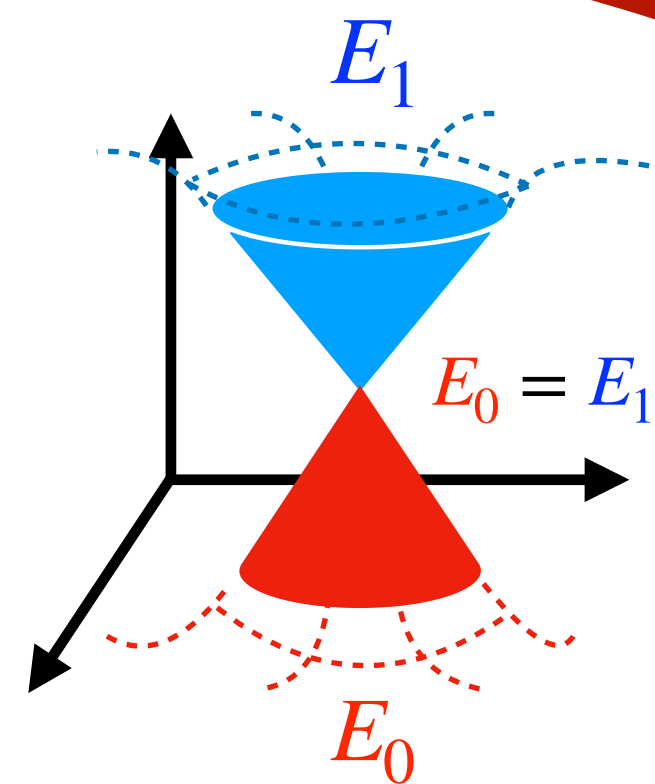
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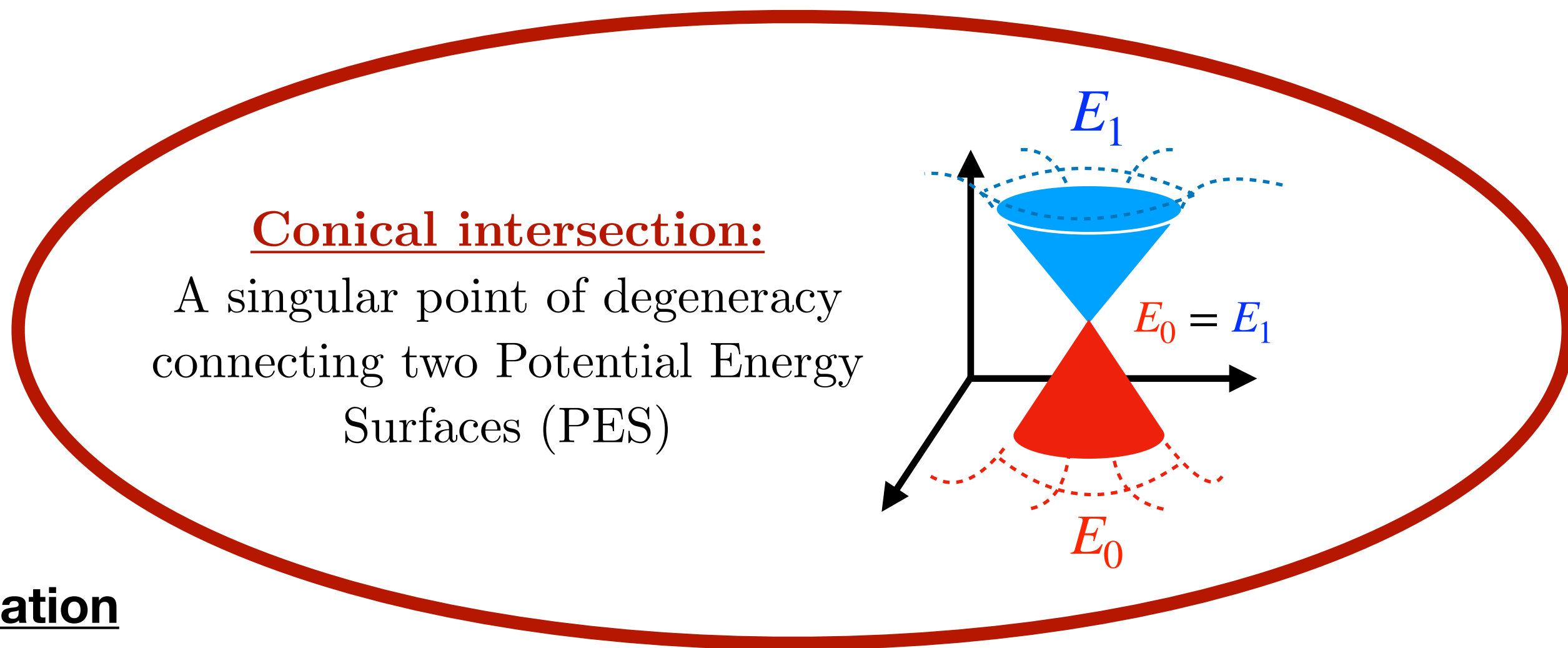
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## II) Describing conical intersections on near term quantum computers

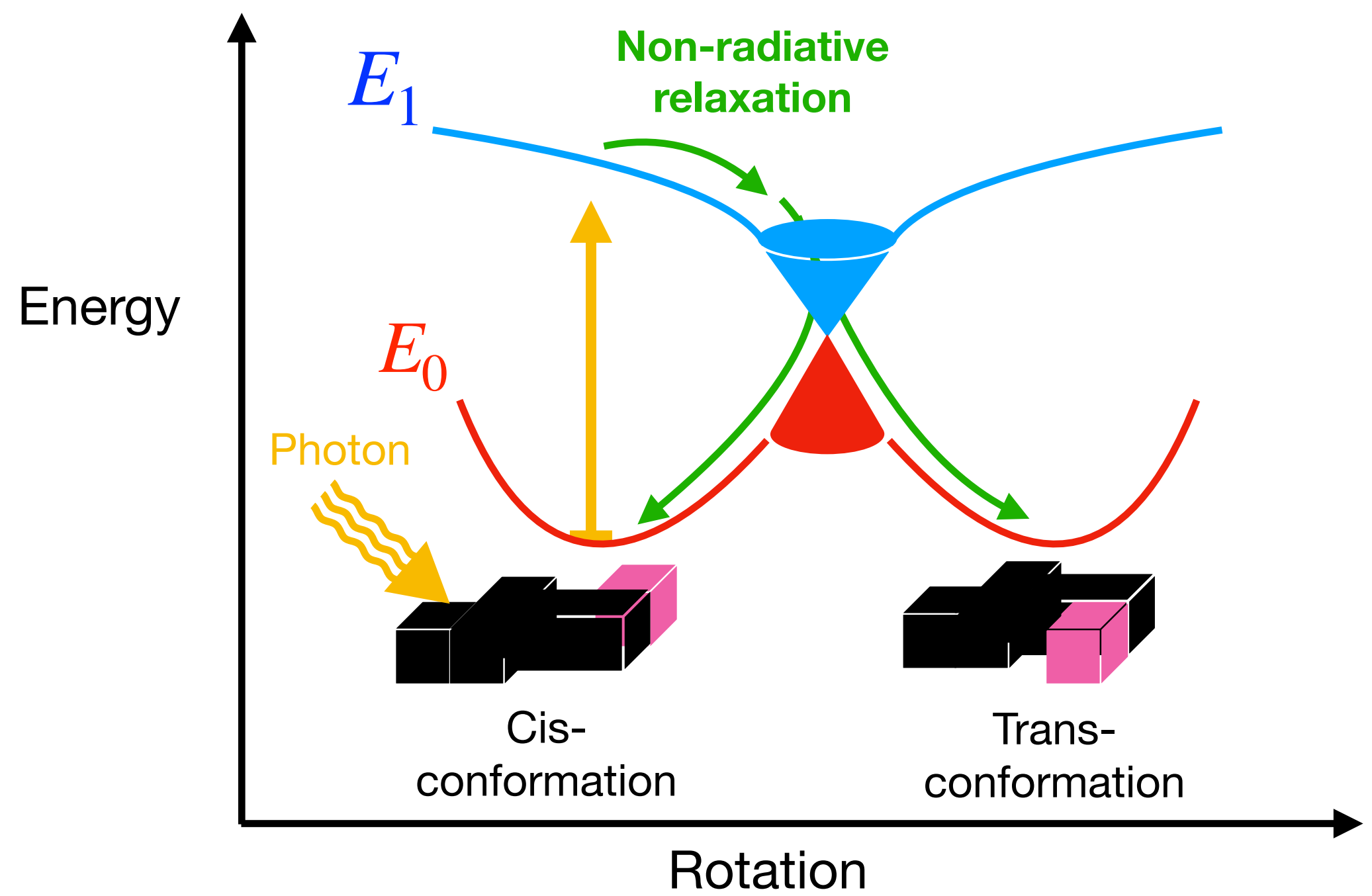
**Conical intersection:**  
A singular point of degeneracy  
connecting two Potential Energy  
Surfaces (PES)



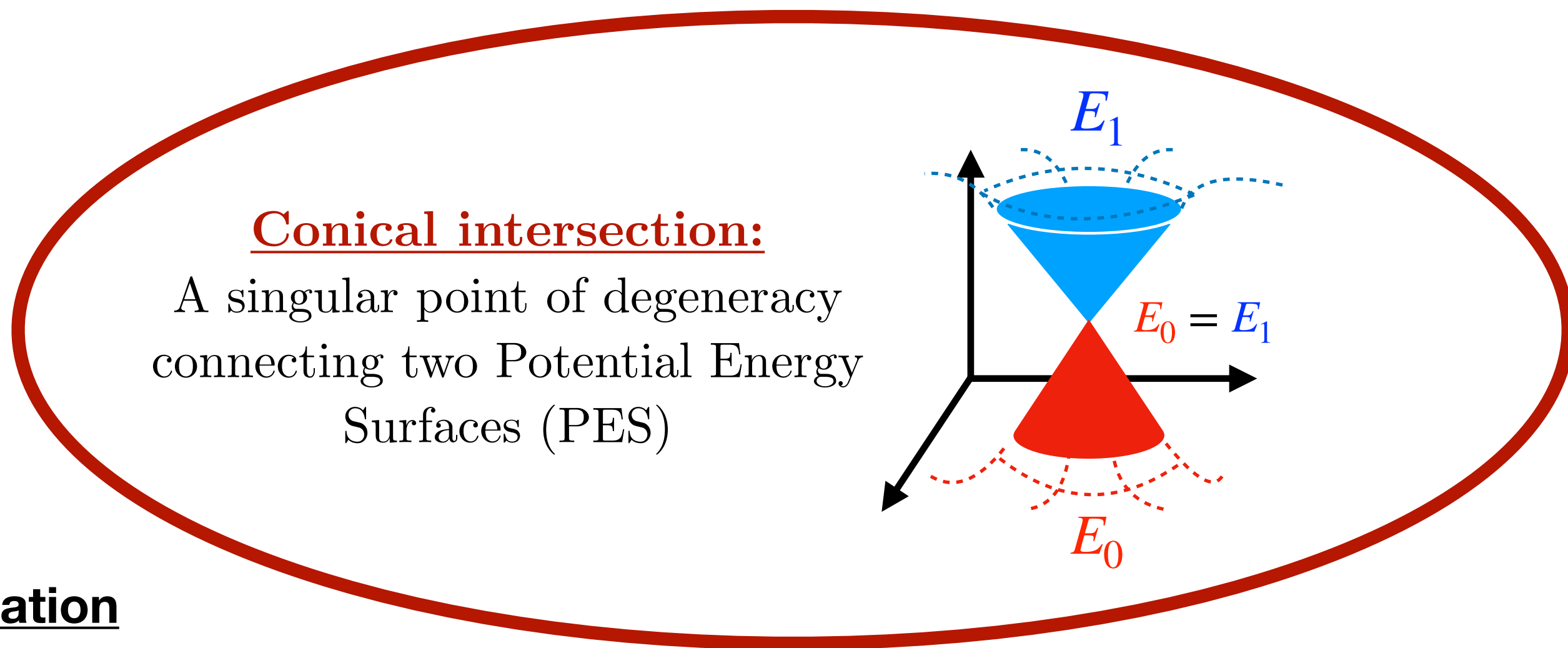
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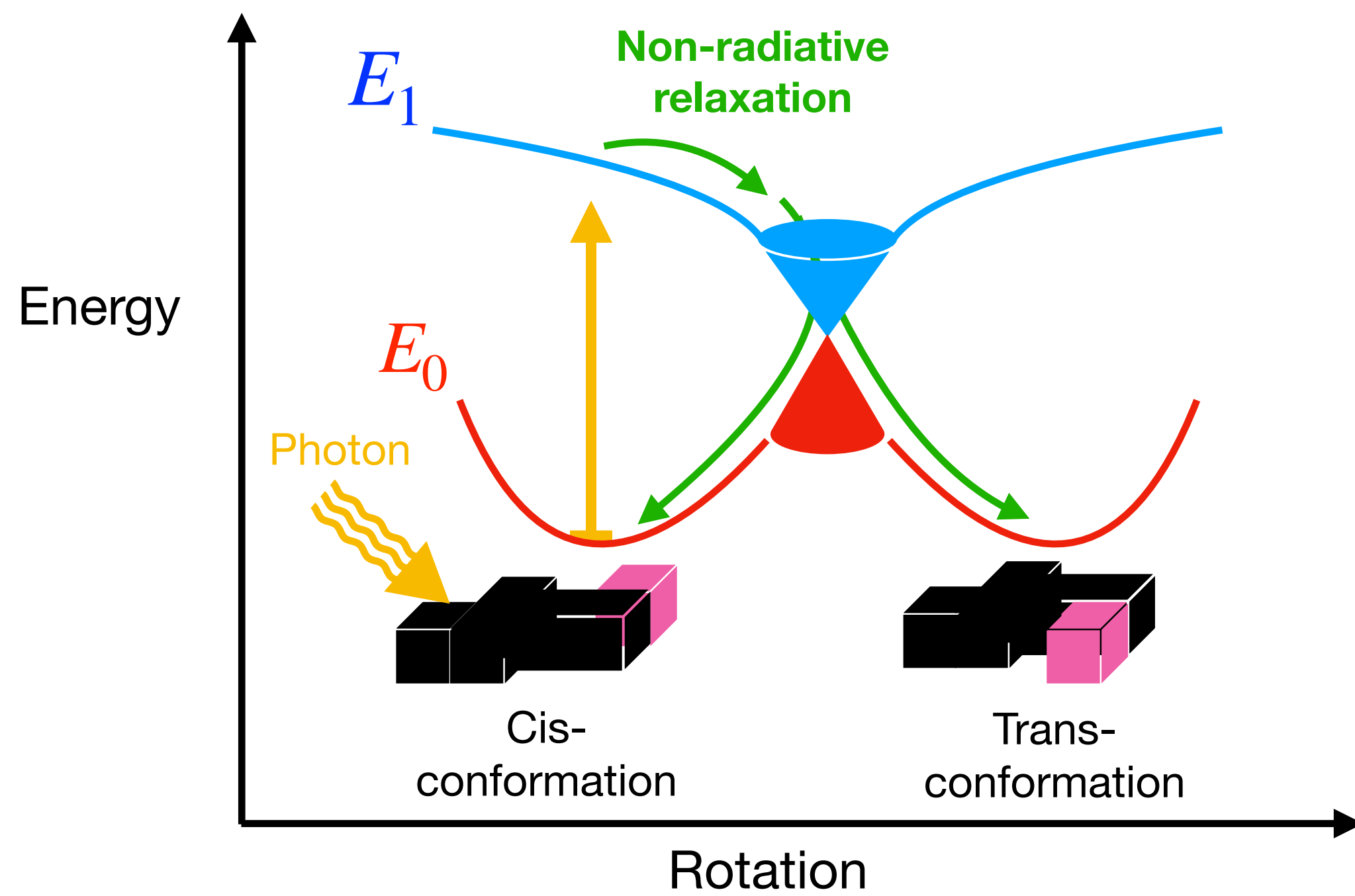
### Photo-isomerization



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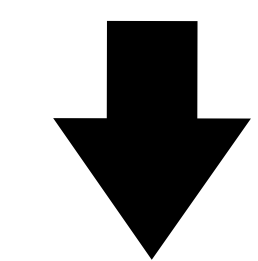
### Photo-isomerization



HARD FOR CLASSICAL COMPUTER

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GOOD TARGET FOR QUANTUM COMPUTERS !



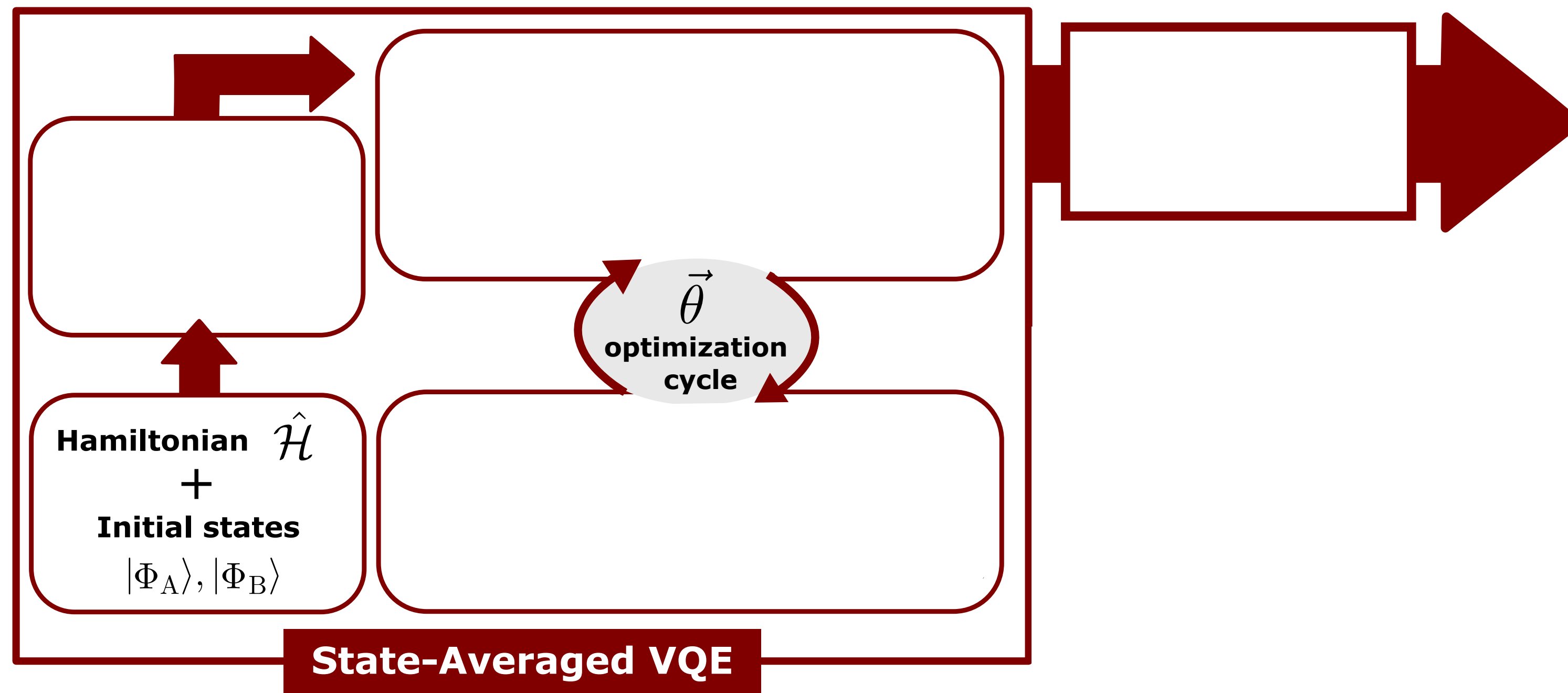
A NISQ algorithm to tackle this problem

**SA-OO-VQE**

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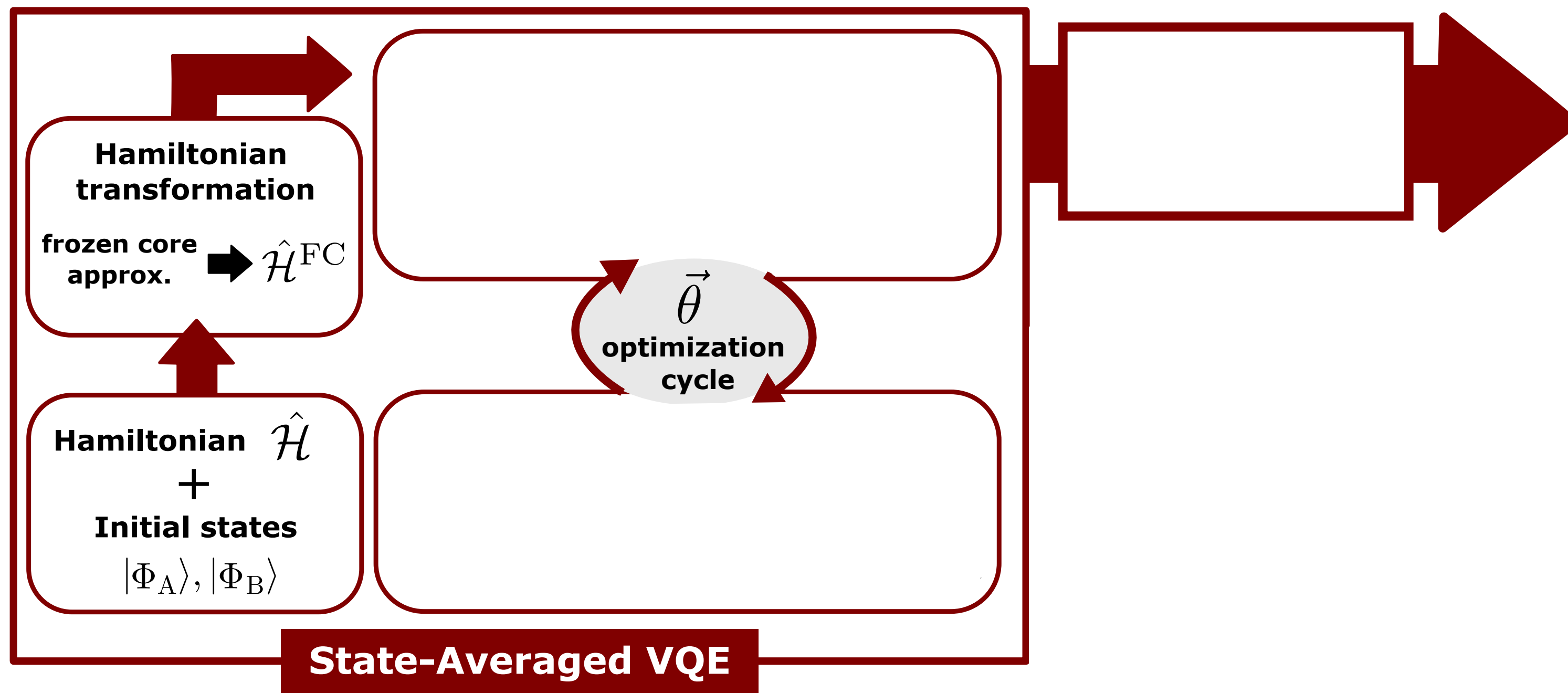
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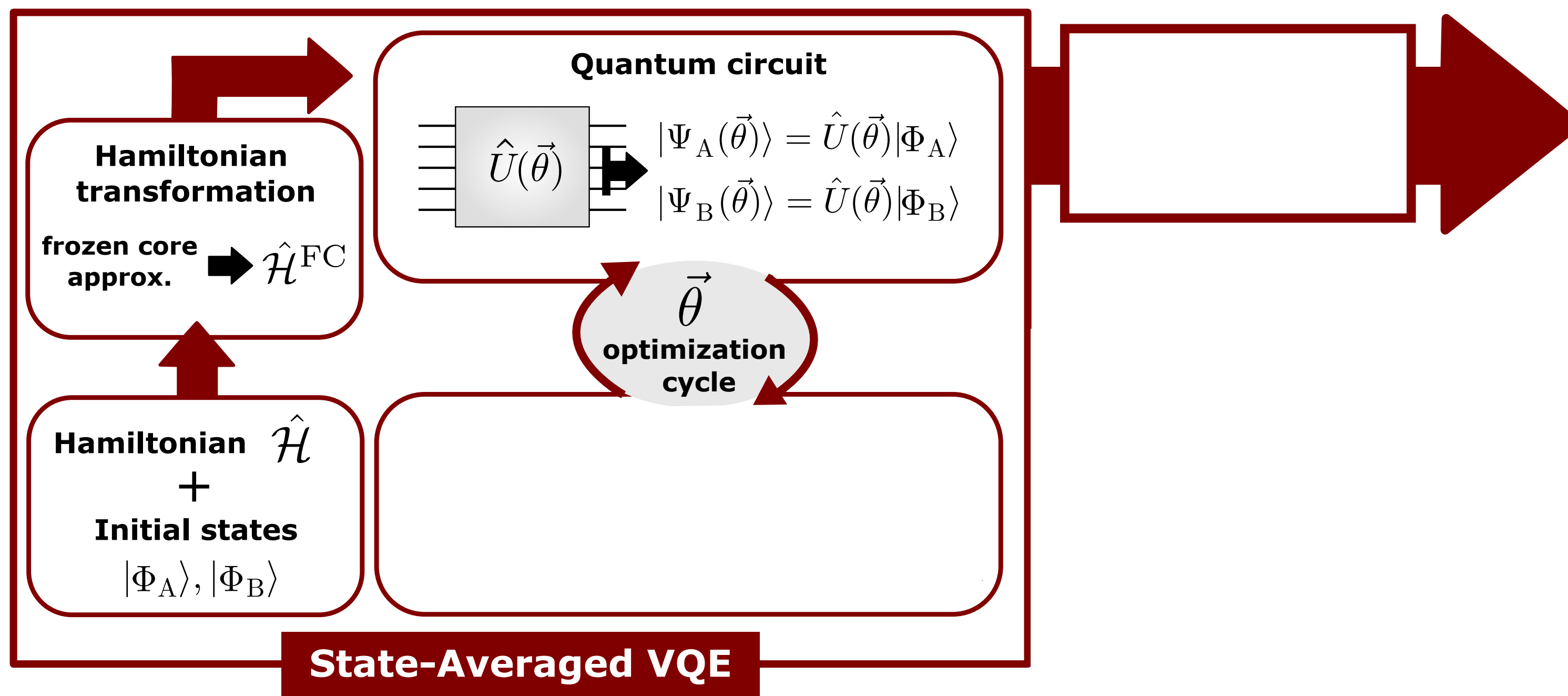
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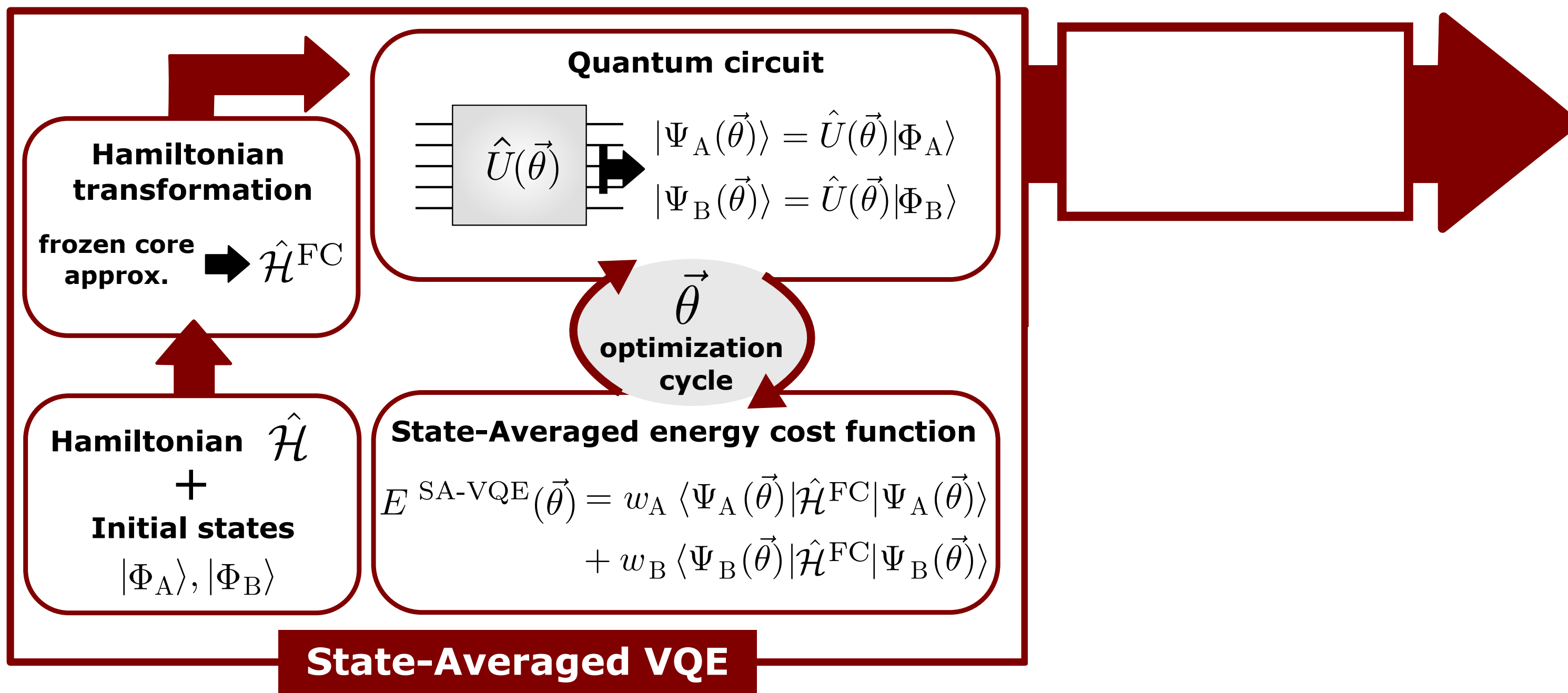




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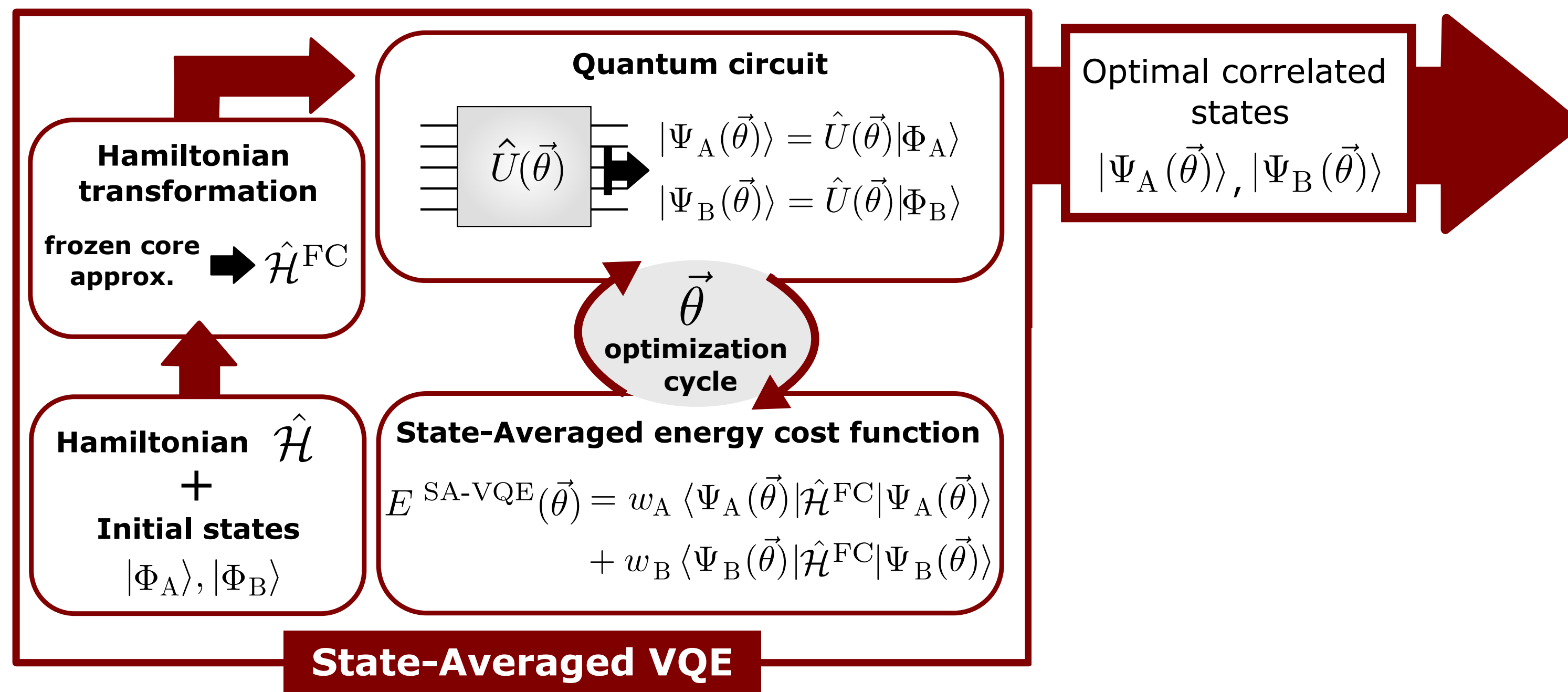
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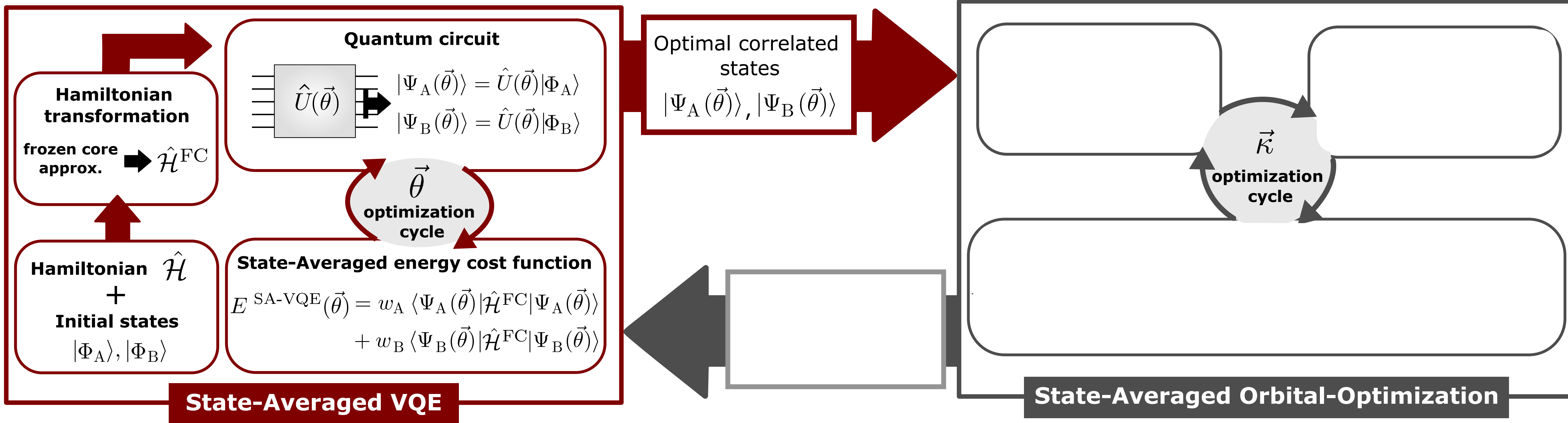
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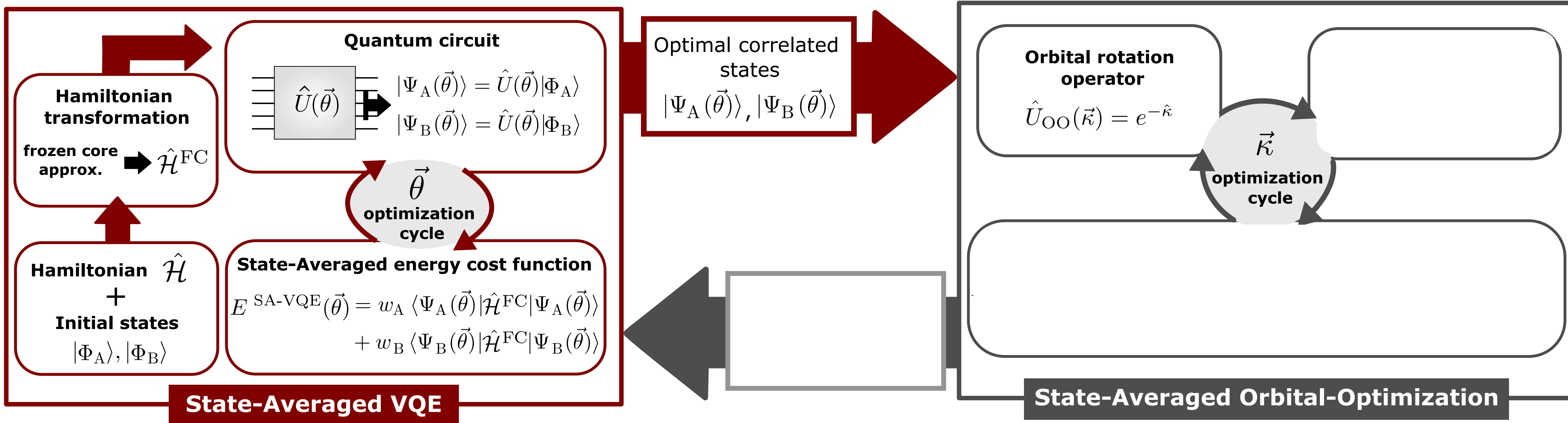
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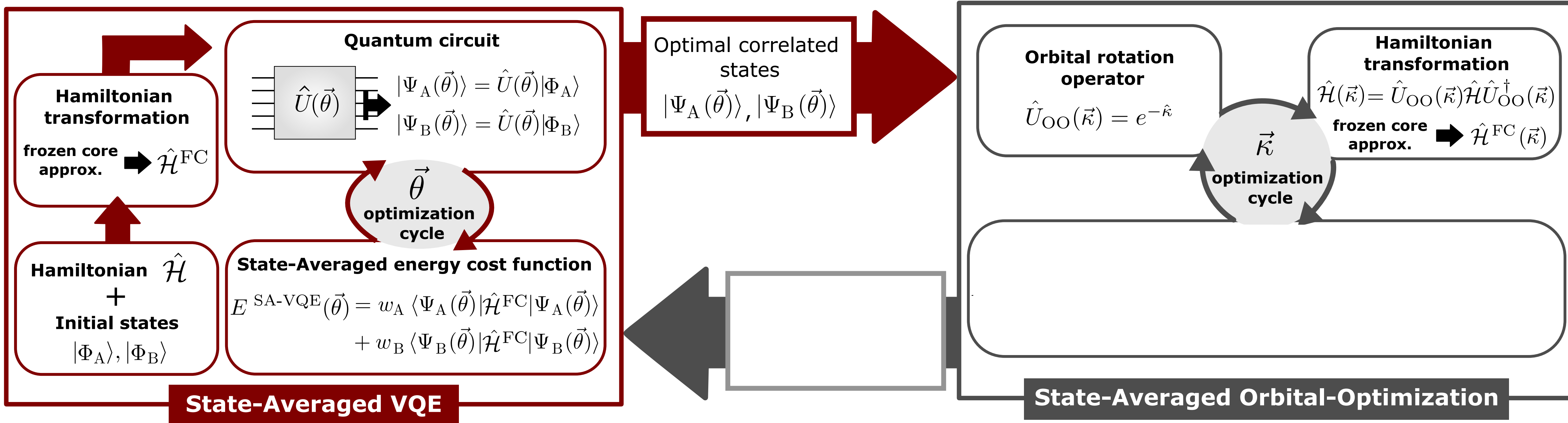
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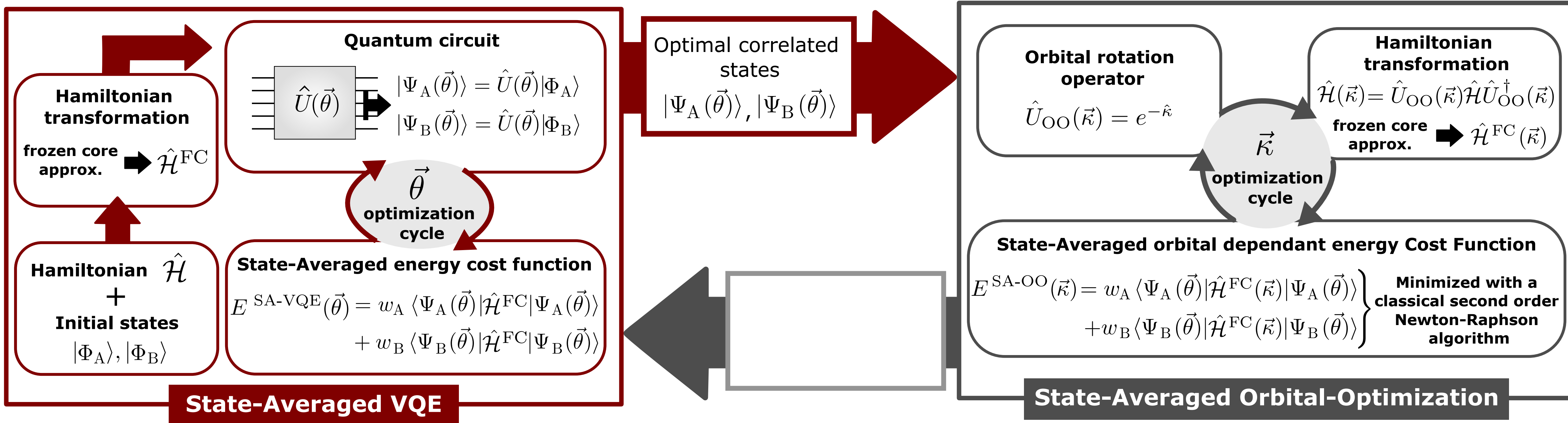
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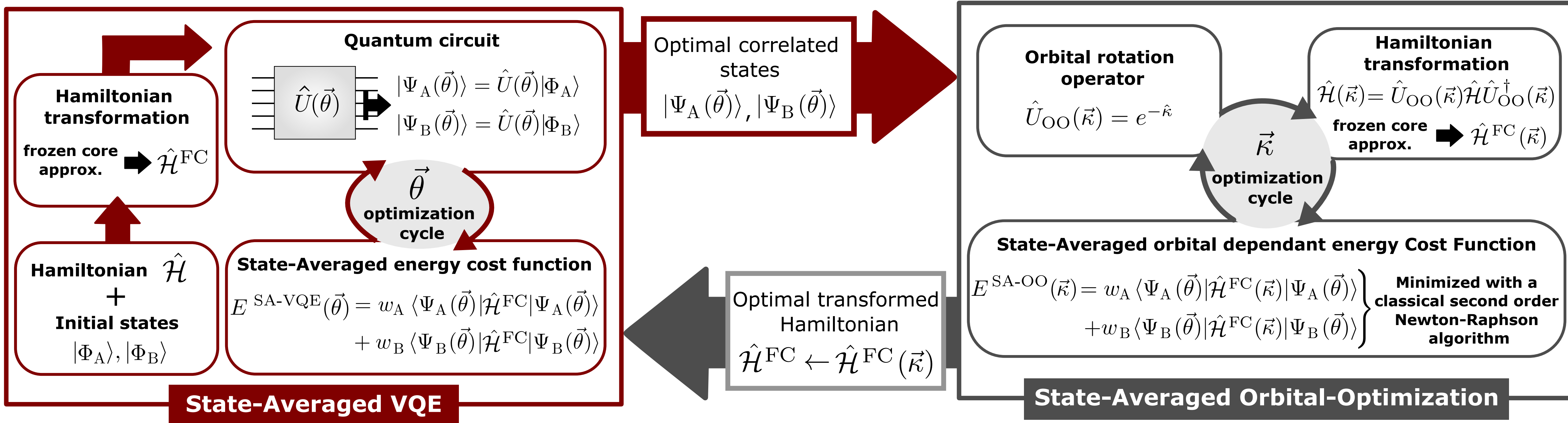
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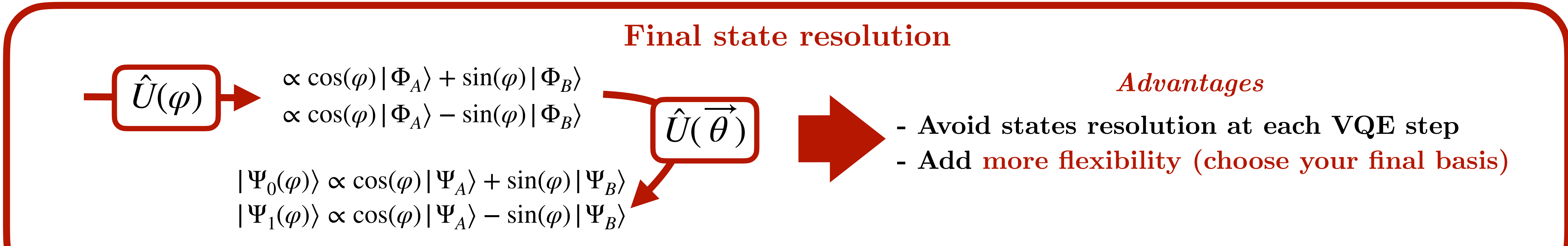
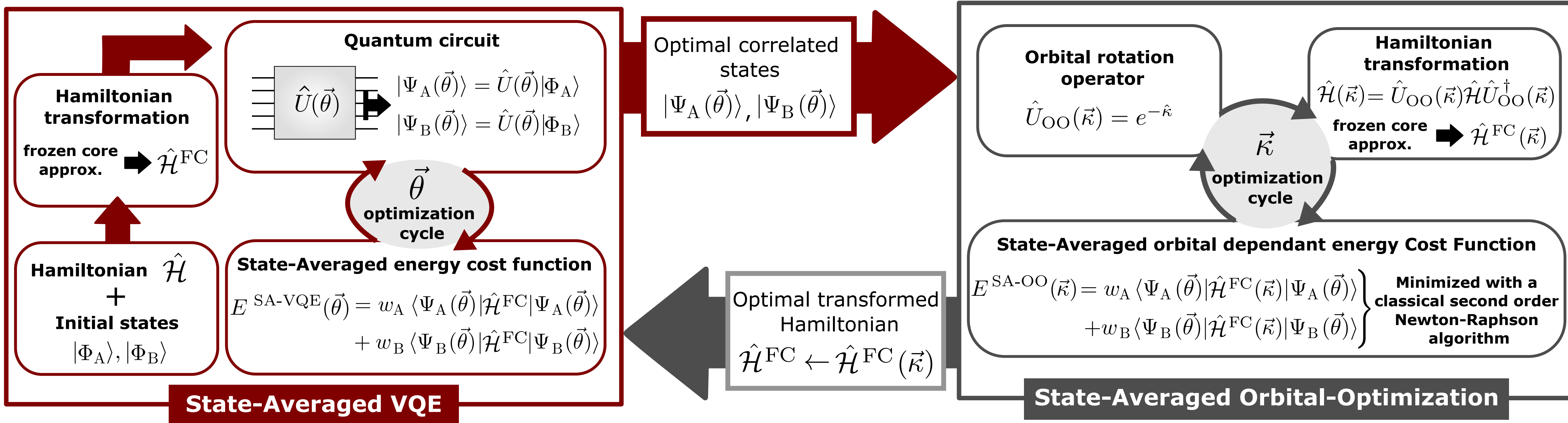
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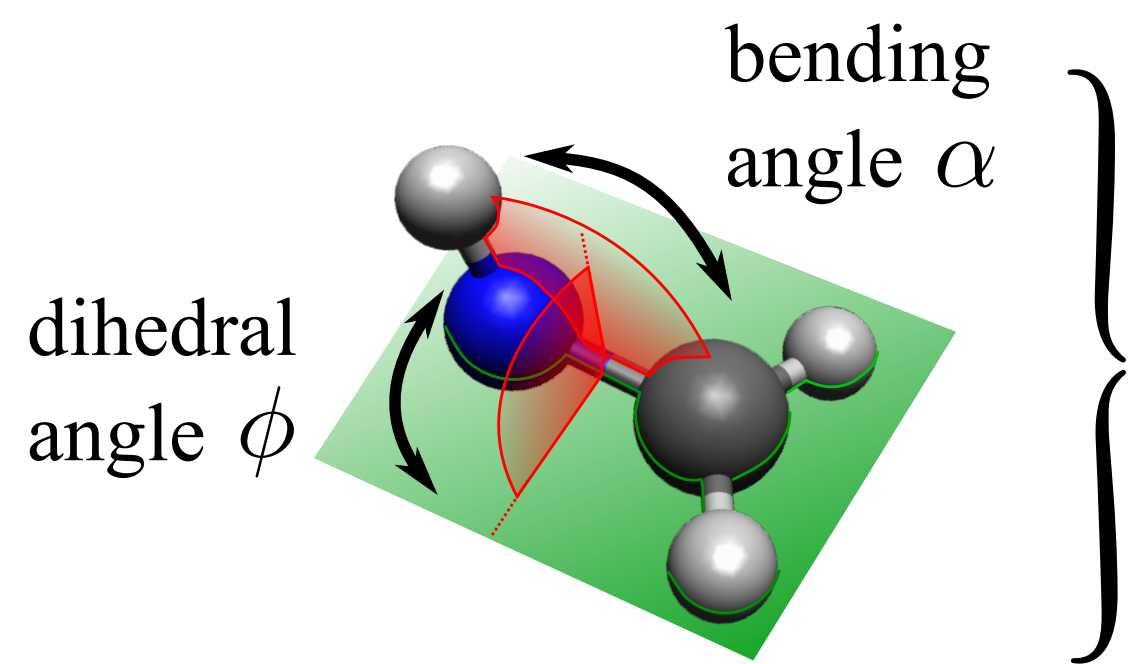


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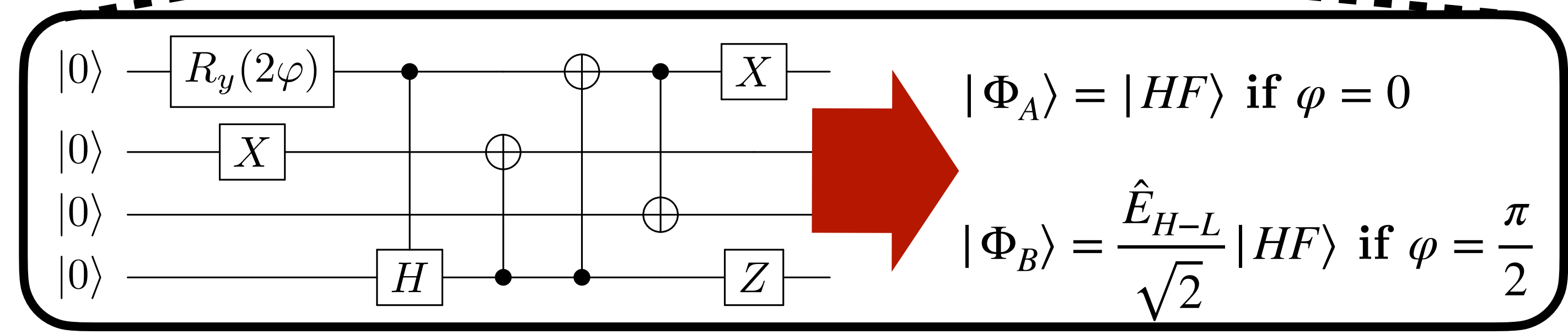
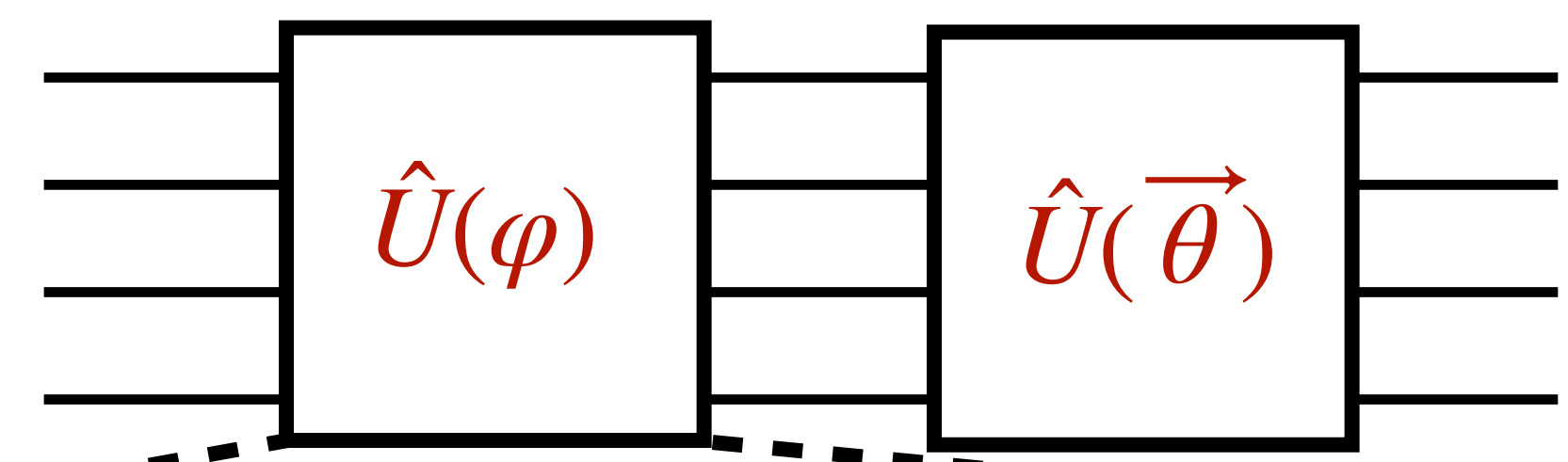
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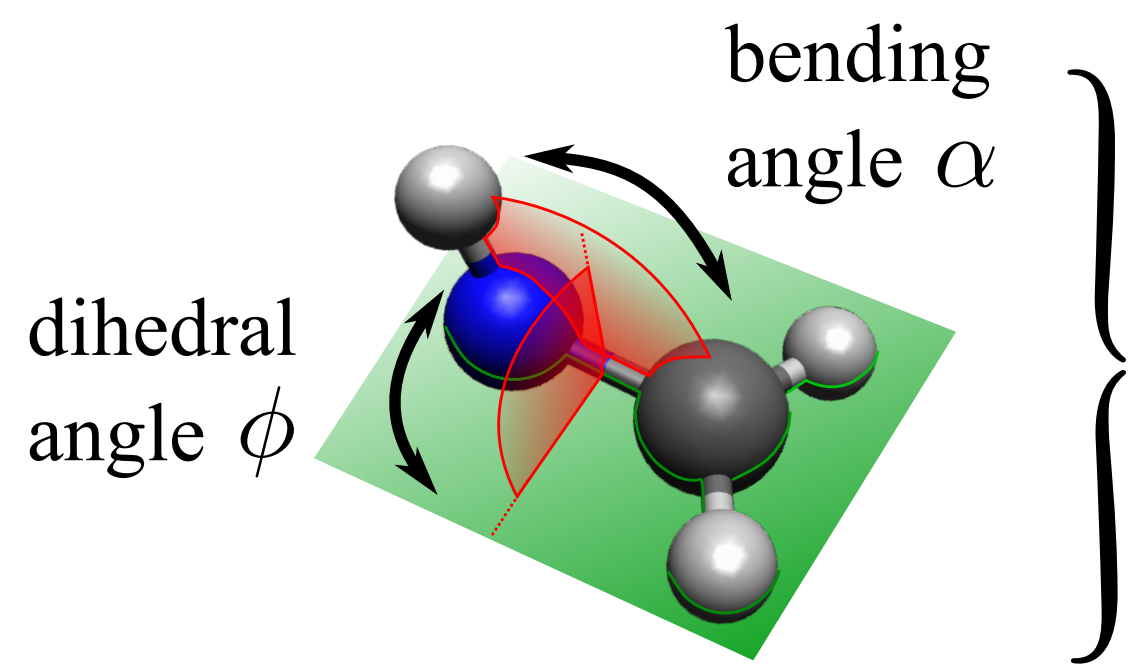
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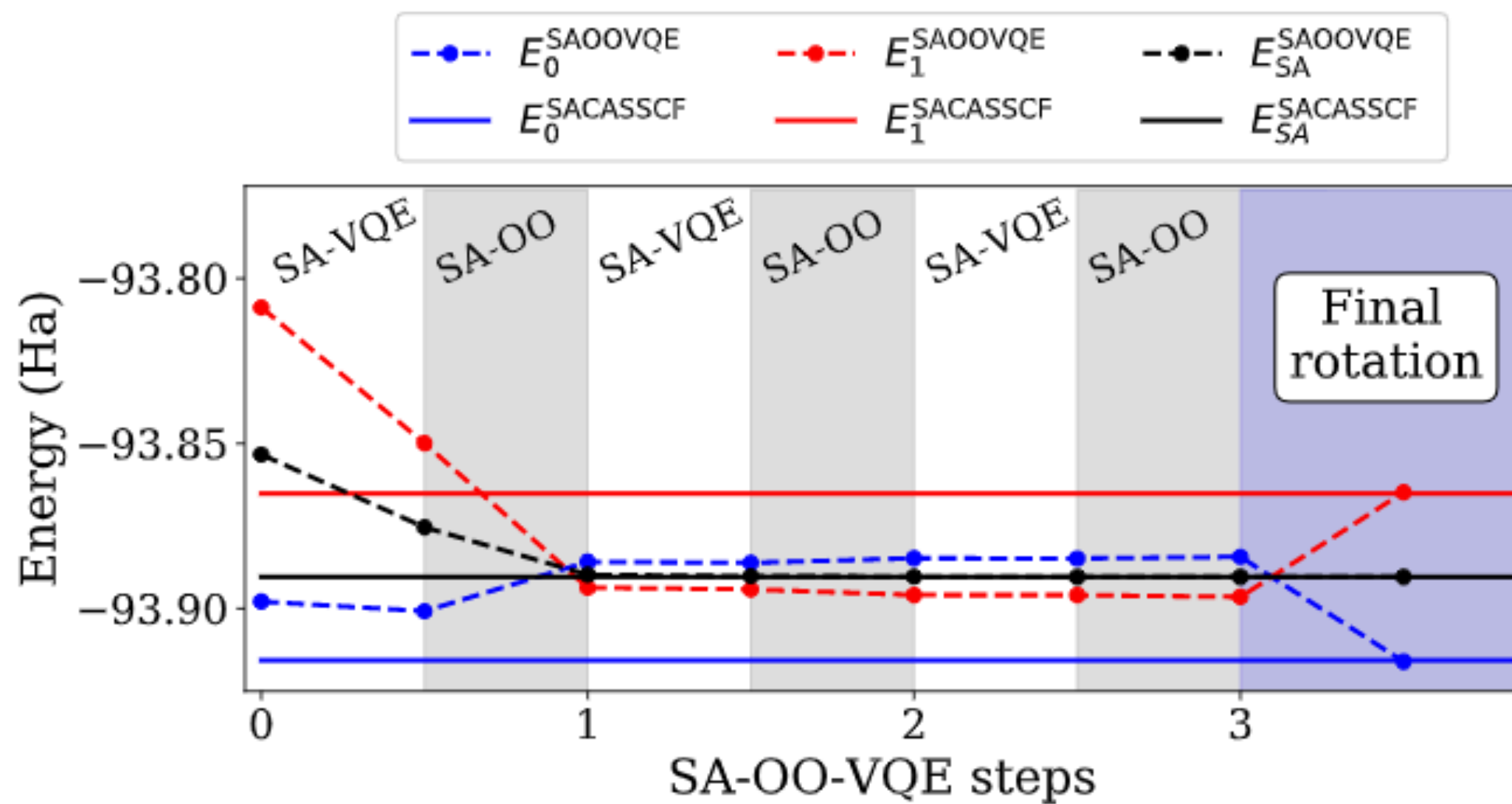
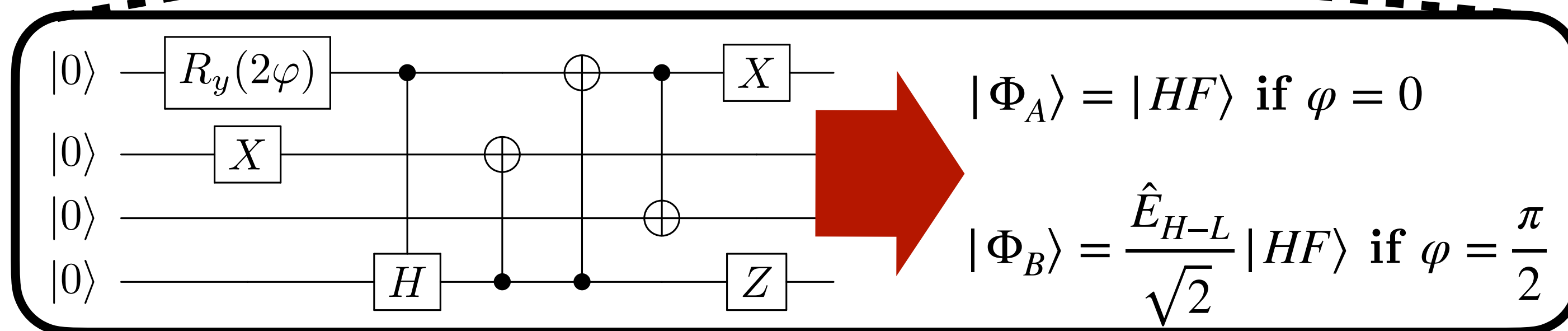
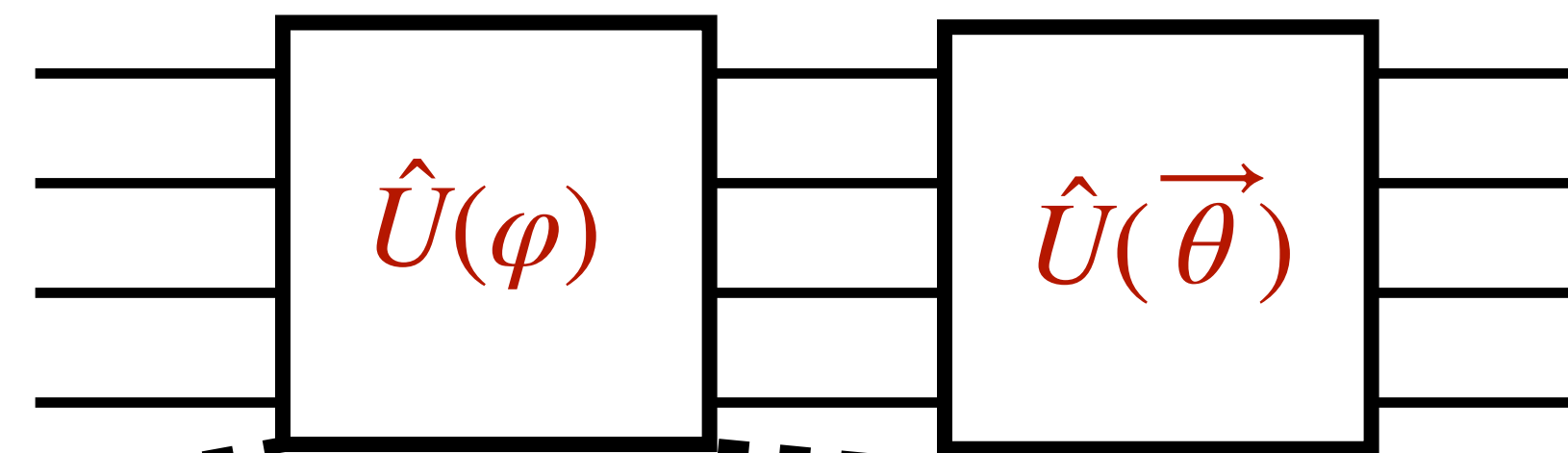
**Toy-model with a conical intersection**



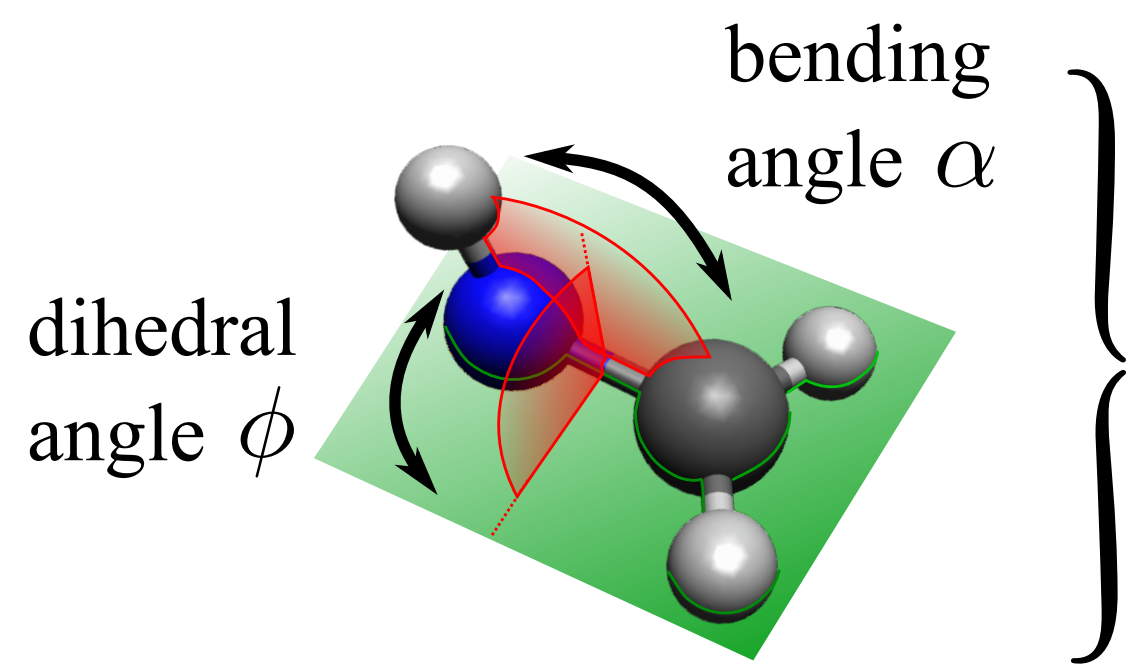
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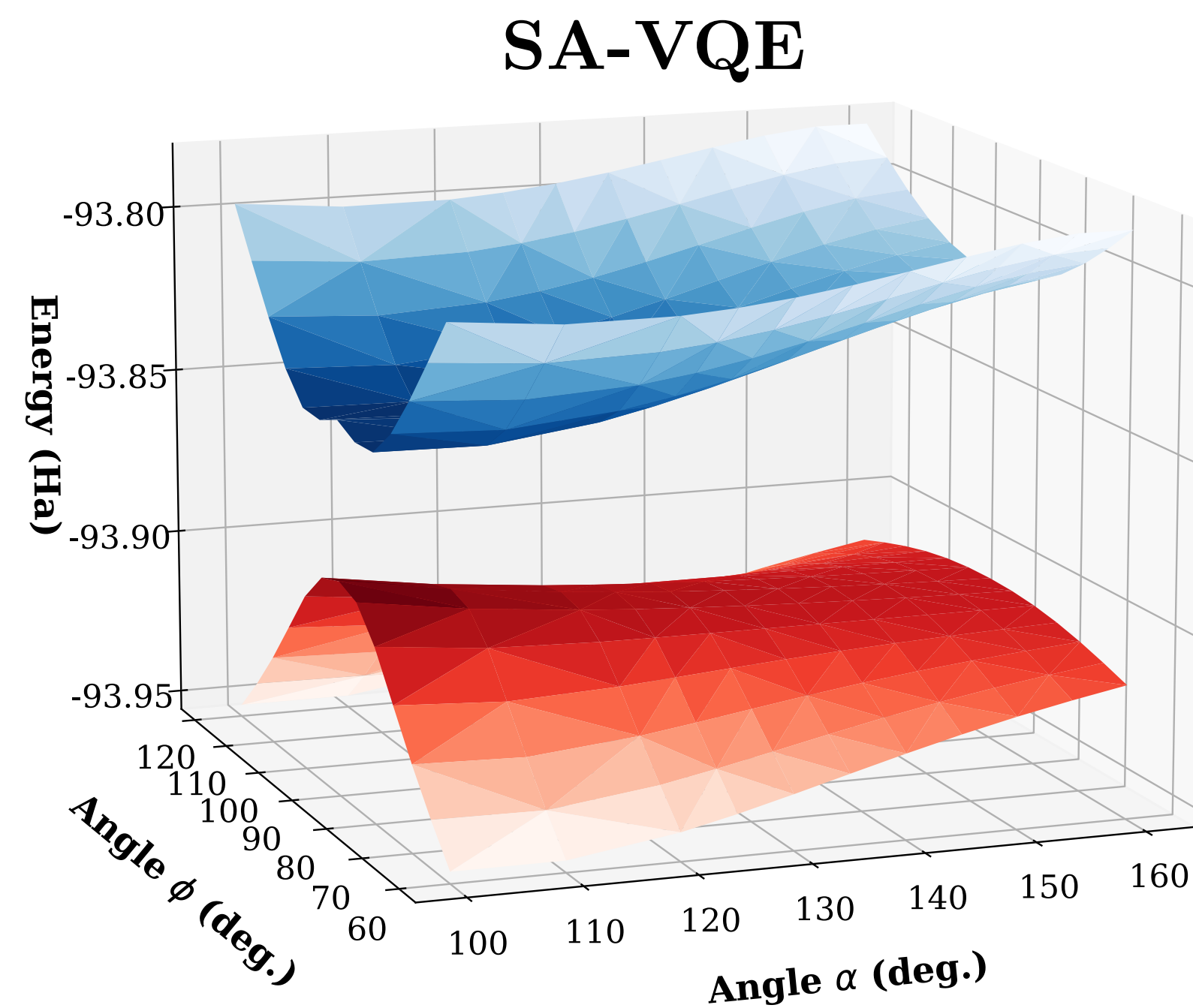
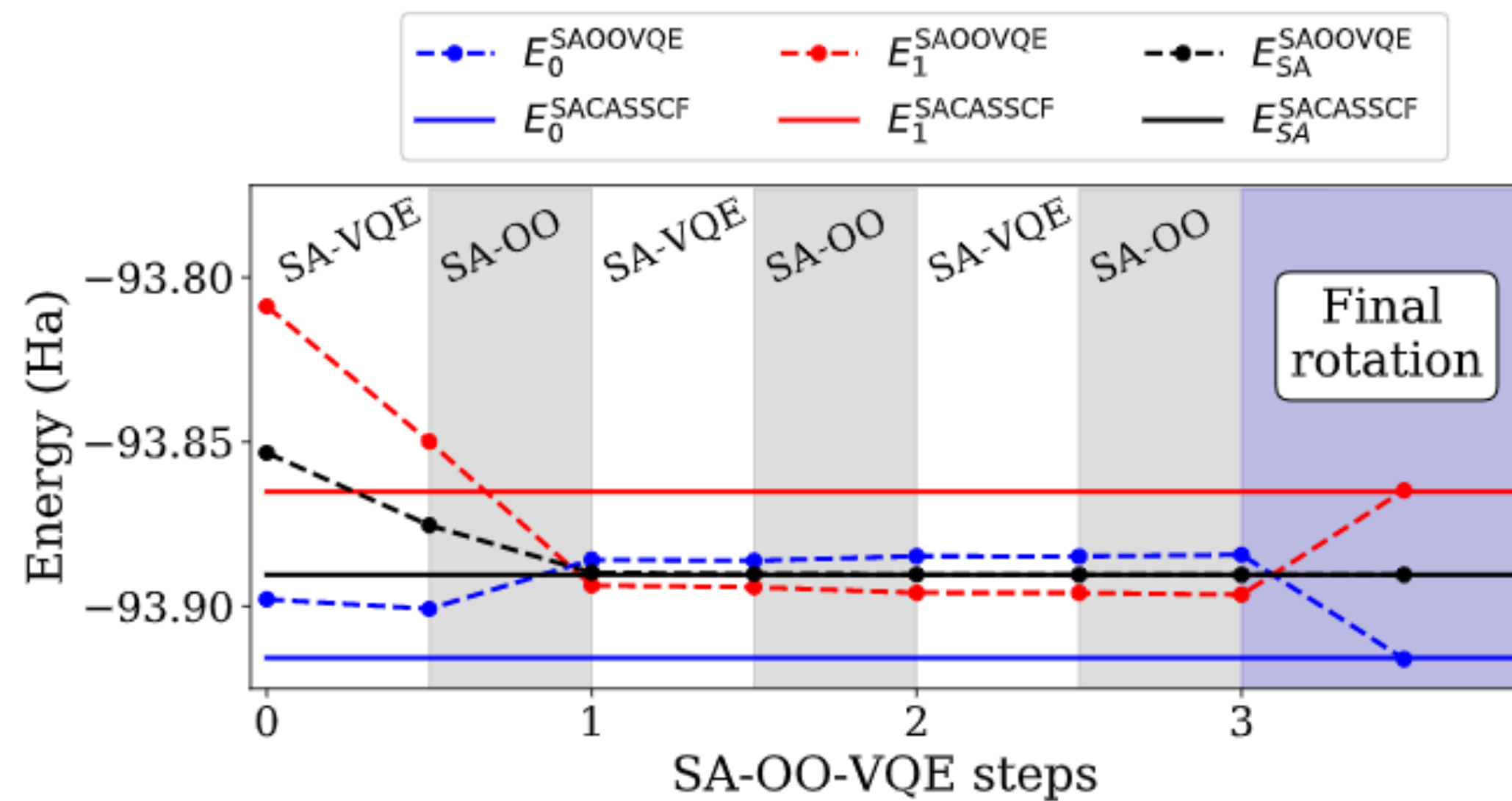
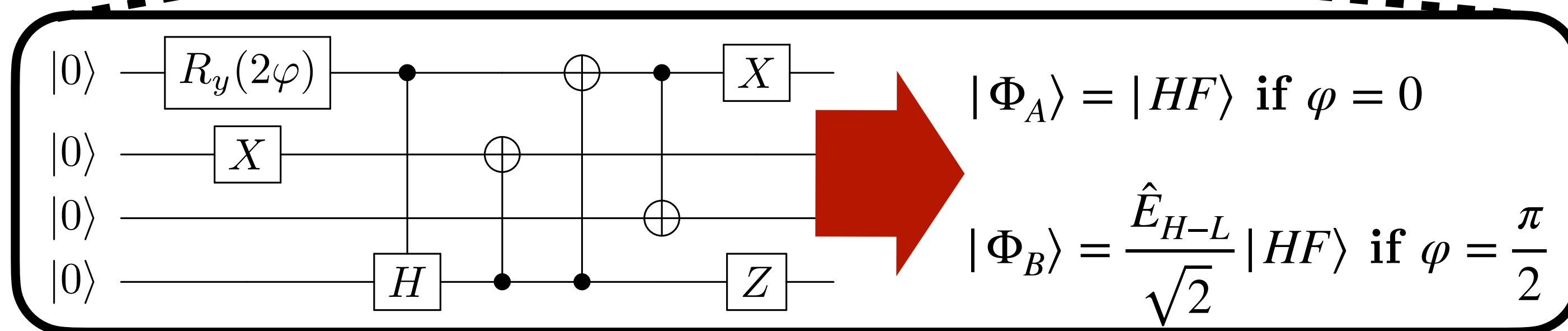
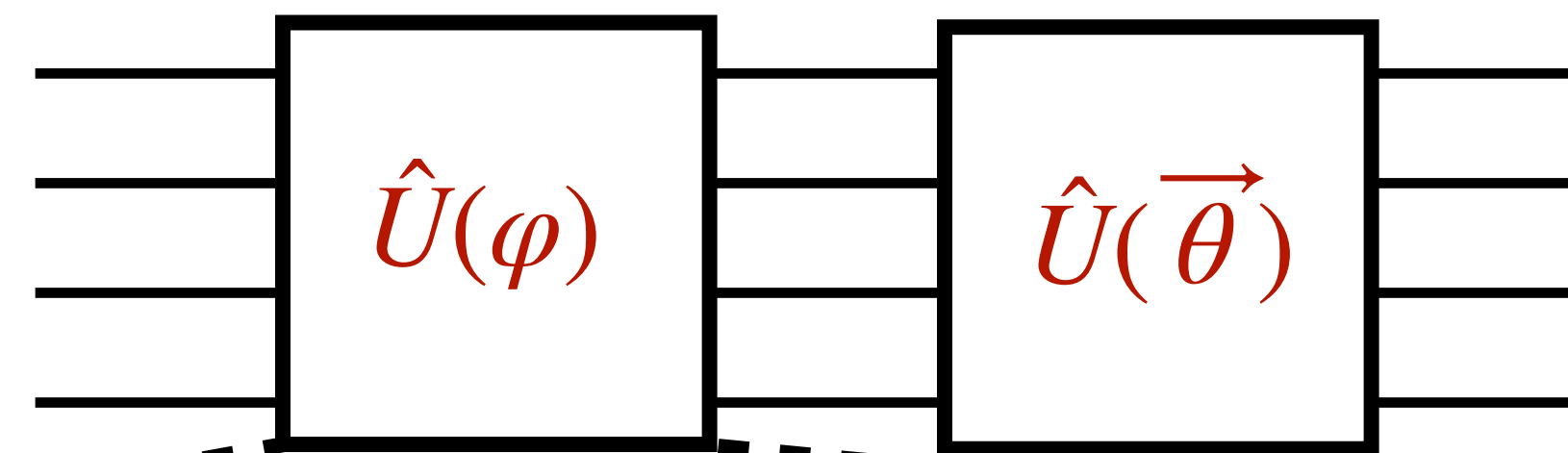
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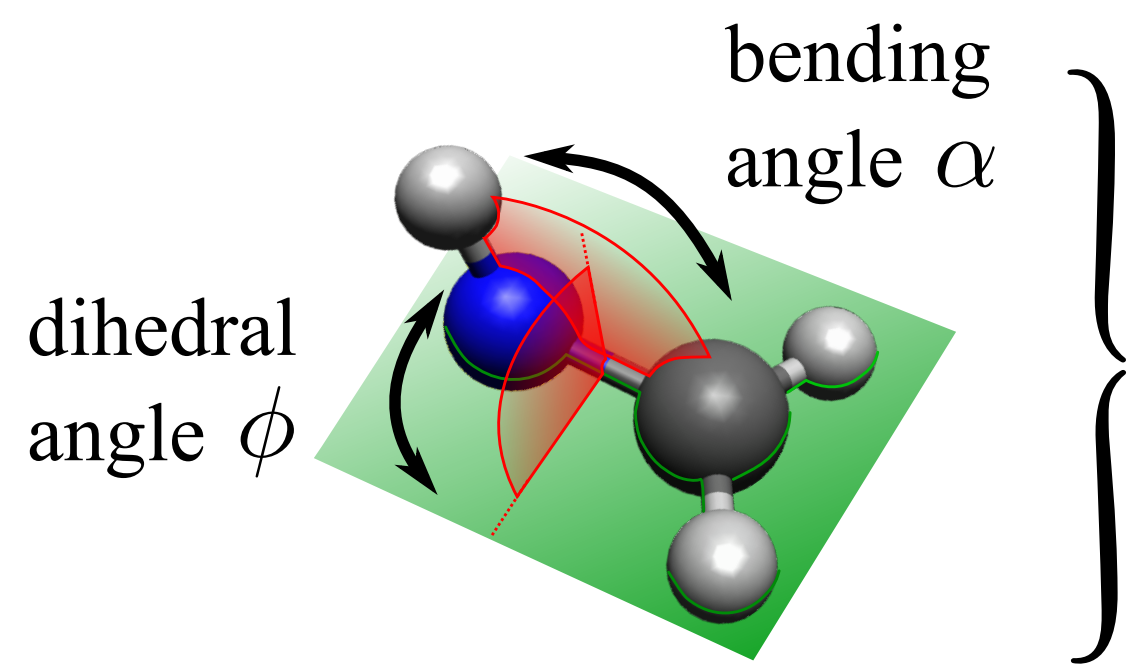
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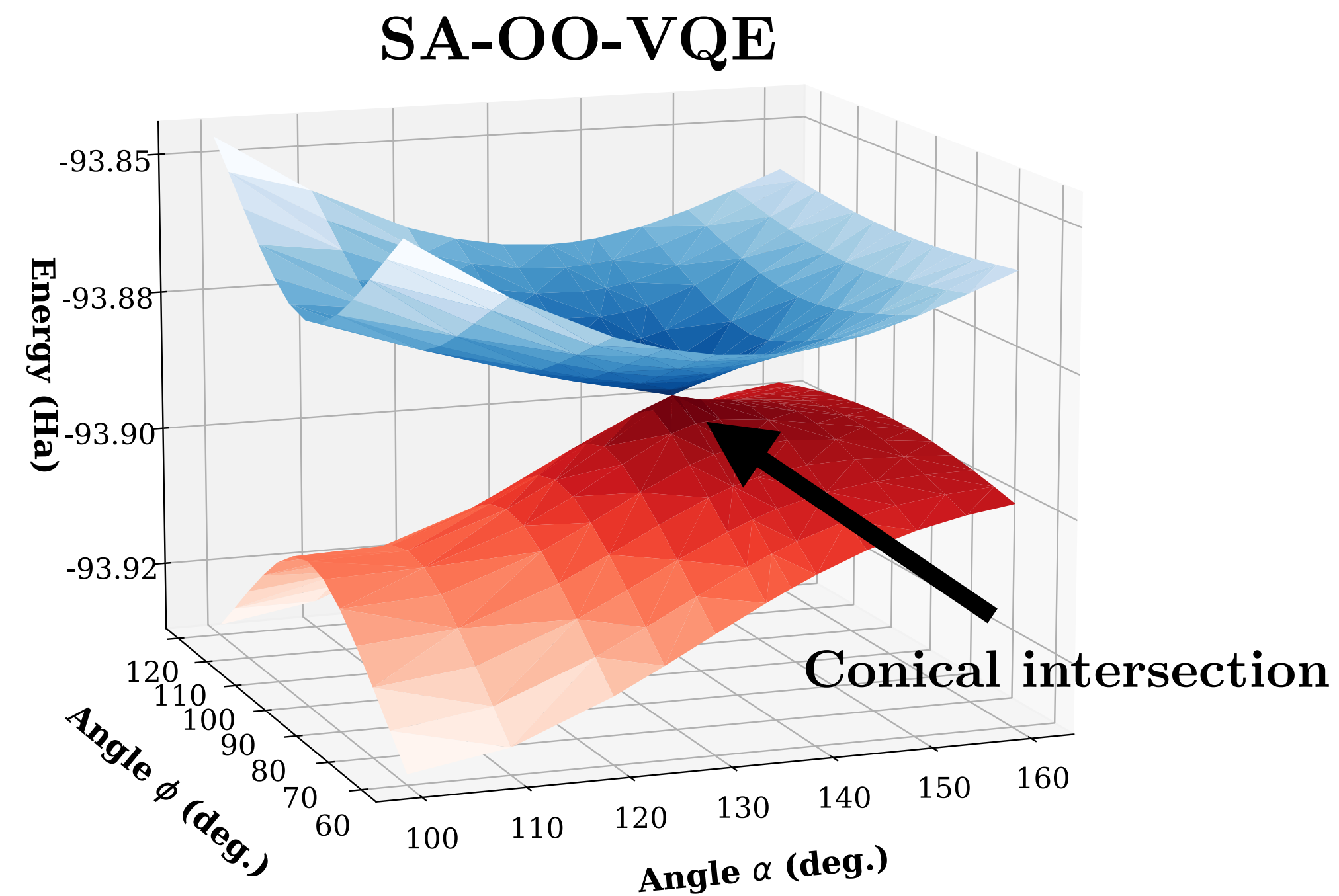
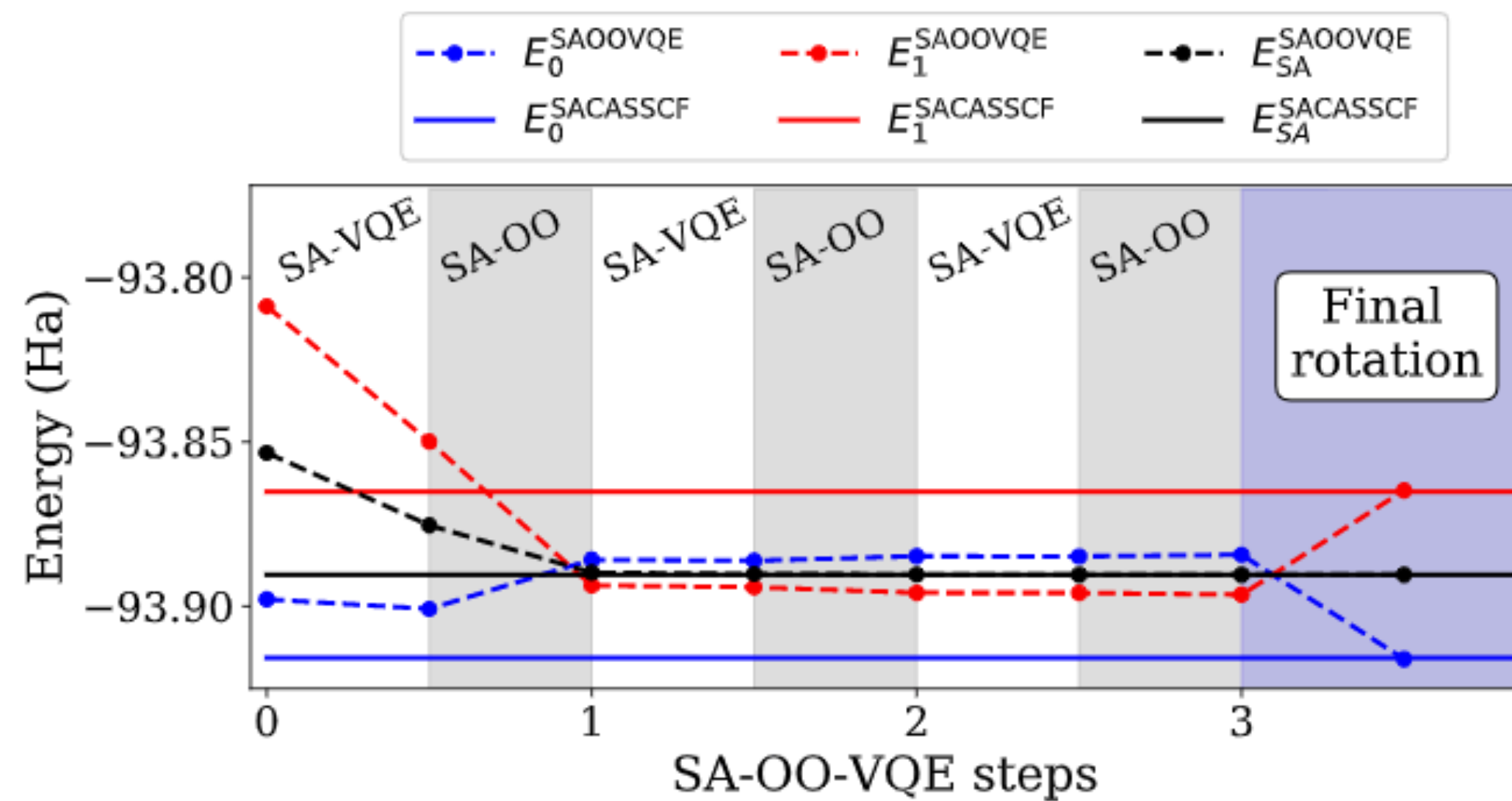
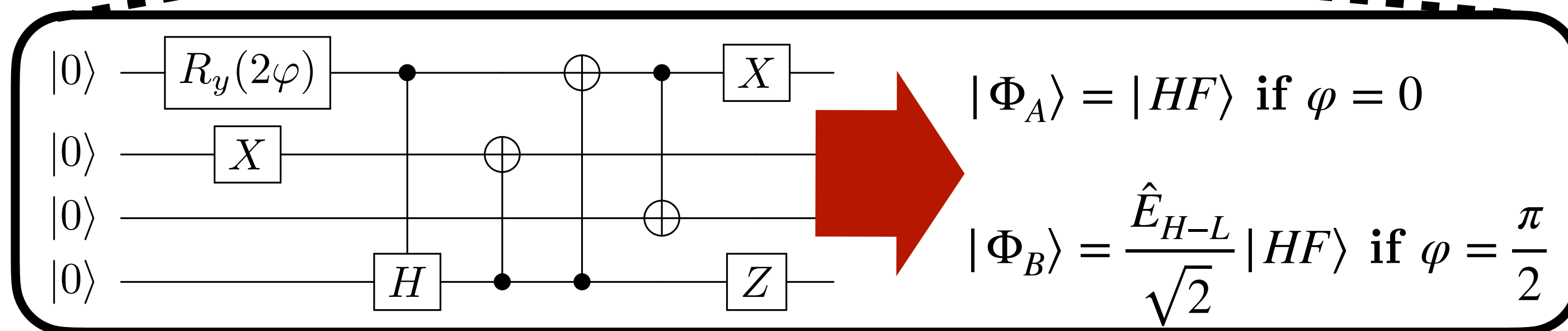
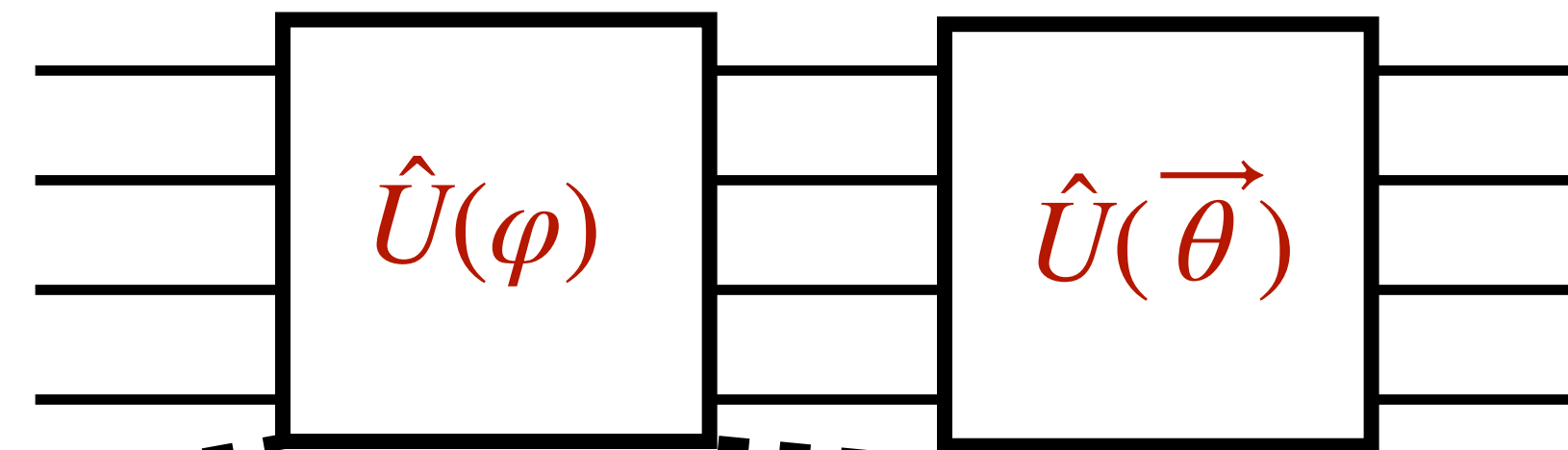
Toy-model with a conical intersection



### III) SA-OO-VQE: Some results



Toy-model with a conical intersection



### III) SA-OO-VQE: Some results

#### Estimation of analytical derivatives

##### Nuclear derivatives

$$\frac{dE_I}{dx}$$

Nuclear forces with respect  
to coordinate “  $x$  ”

##### Non-adiabatic couplings

$$D_{IJ} = \langle \Psi_I | \frac{d}{dx} \Psi_J \rangle$$

Coupling between two states  
through nuclear vibrations

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##### Non-adiabatic couplings

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#### Lagrange multipliers method

$$E_I \longrightarrow \mathcal{L}_I = E_I + \sum_{pq} \bar{\kappa}_{pq}^I \frac{\partial E^{SA}}{\partial \kappa_{pq}} + \sum_n \bar{\theta}_n^I \frac{\partial E^{SA}}{\partial \theta_n} \longrightarrow \frac{\partial \mathcal{L}_I}{\partial \kappa_{pq}^I} = \frac{\partial \mathcal{L}_I}{\partial \theta_n^I} = \frac{\partial \mathcal{L}_I}{\partial \bar{\kappa}_{pq}^I} = \frac{\partial \mathcal{L}_I}{\partial \bar{\theta}_n^I} = 0$$

$$\begin{pmatrix} \mathbf{H}^{OO} & \mathbf{H}^{OC} \\ \mathbf{H}^{CO} & \mathbf{H}^{CC} \end{pmatrix} \begin{pmatrix} \bar{\kappa}^I \\ \bar{\theta}^I \end{pmatrix} = - \begin{pmatrix} \mathbf{G}^{O,I} \\ \mathbf{G}^{C,I} \end{pmatrix}$$

$$\frac{dE_I}{dx} = \sum_{pq} \frac{\partial h_{pq}}{\partial x} \gamma_{pq}^{I,eff} + \frac{1}{2} \sum_{pqrs} \frac{\partial g_{pqrs}}{\partial x} \Gamma_{pqrs}^{I,eff} + \sum_J \sum_n w_J \bar{\theta}_n^I G_n^{C,J} \left( \frac{\partial \hat{H}}{\partial x} \right)$$

### III) SA-OO-VQE: Some results

#### Estimation of analytical derivatives

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$\frac{dE_I}{dx}$  Nuclear forces with respect to coordinate "x"

##### Non-adiabatic couplings

$D_{IJ} = \langle \Psi_I | \frac{d}{dx} \Psi_J \rangle$  Coupling between two states through nuclear vibrations

#### Lagrange multipliers method

$$E_I \longrightarrow \mathcal{L}_I = E_I + \sum_{pq} \bar{\kappa}_{pq}^I \frac{\partial E^{SA}}{\partial \kappa_{pq}} + \sum_n \bar{\theta}_n^I \frac{\partial E^{SA}}{\partial \theta_n} \longrightarrow \frac{\partial \mathcal{L}_I}{\partial \kappa_{pq}^I} = \frac{\partial \mathcal{L}_I}{\partial \theta_n^I} = \frac{\partial \mathcal{L}_I}{\partial \bar{\kappa}_{pq}^I} = \frac{\partial \mathcal{L}_I}{\partial \bar{\theta}_n^I} = 0$$

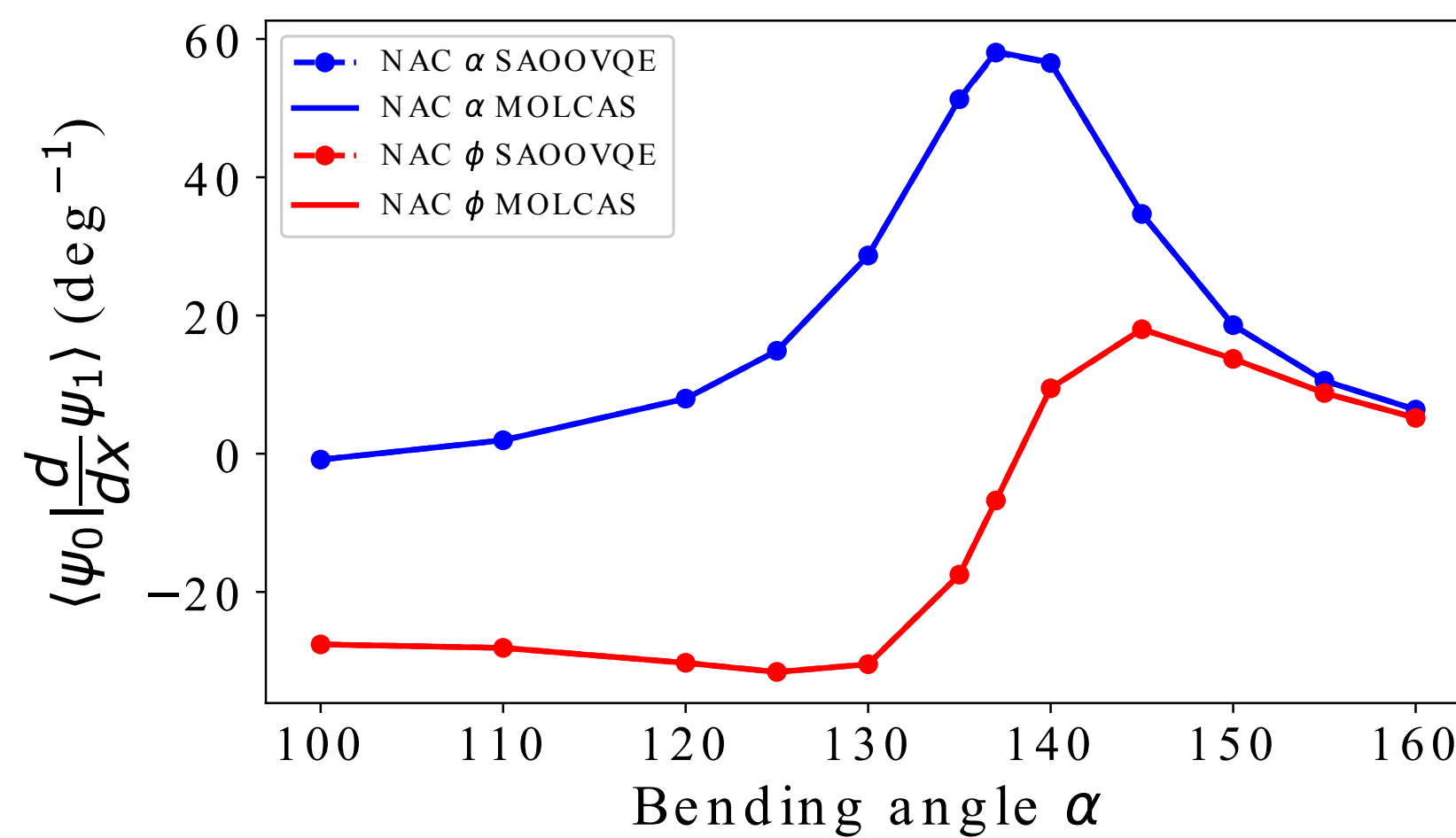
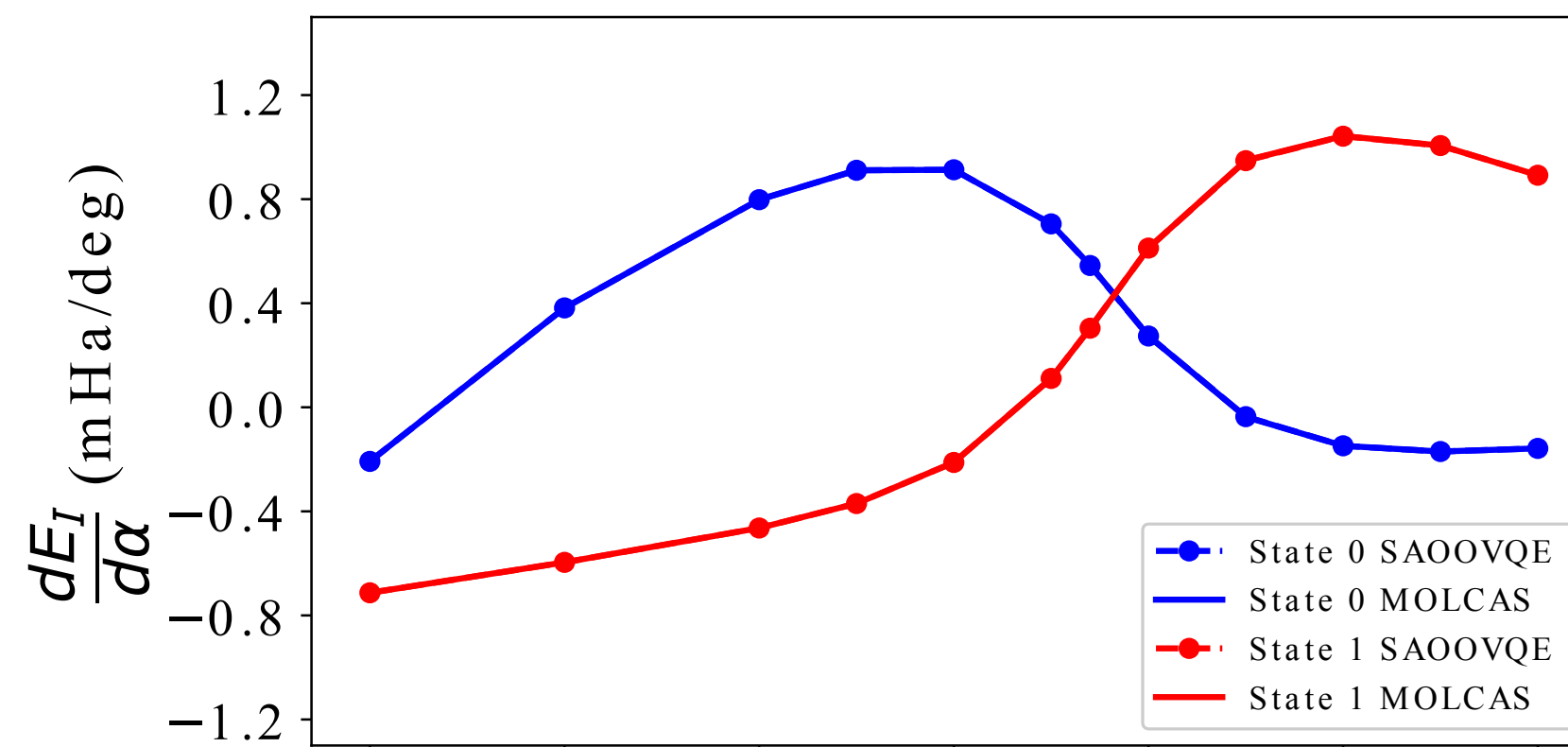
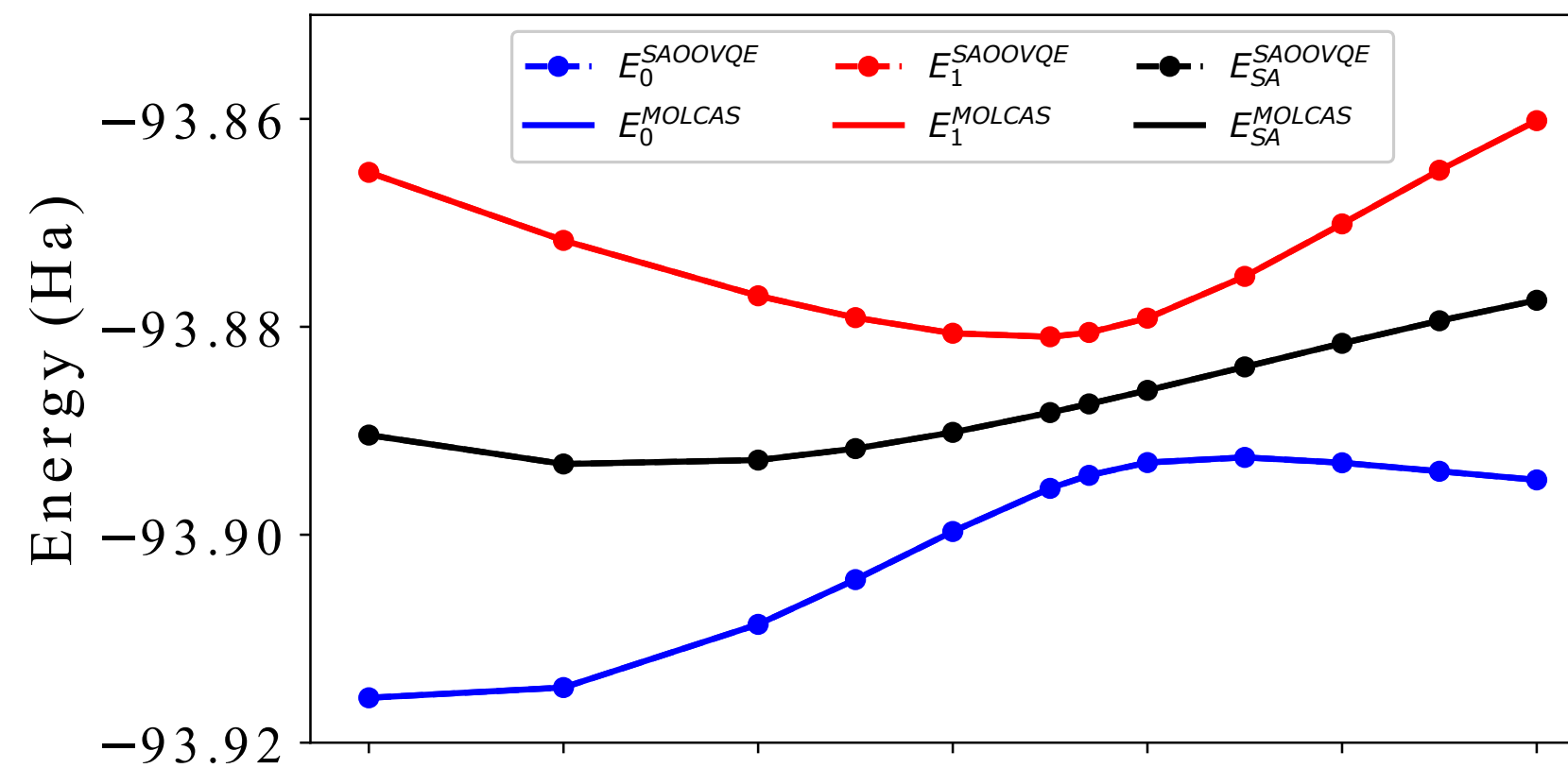
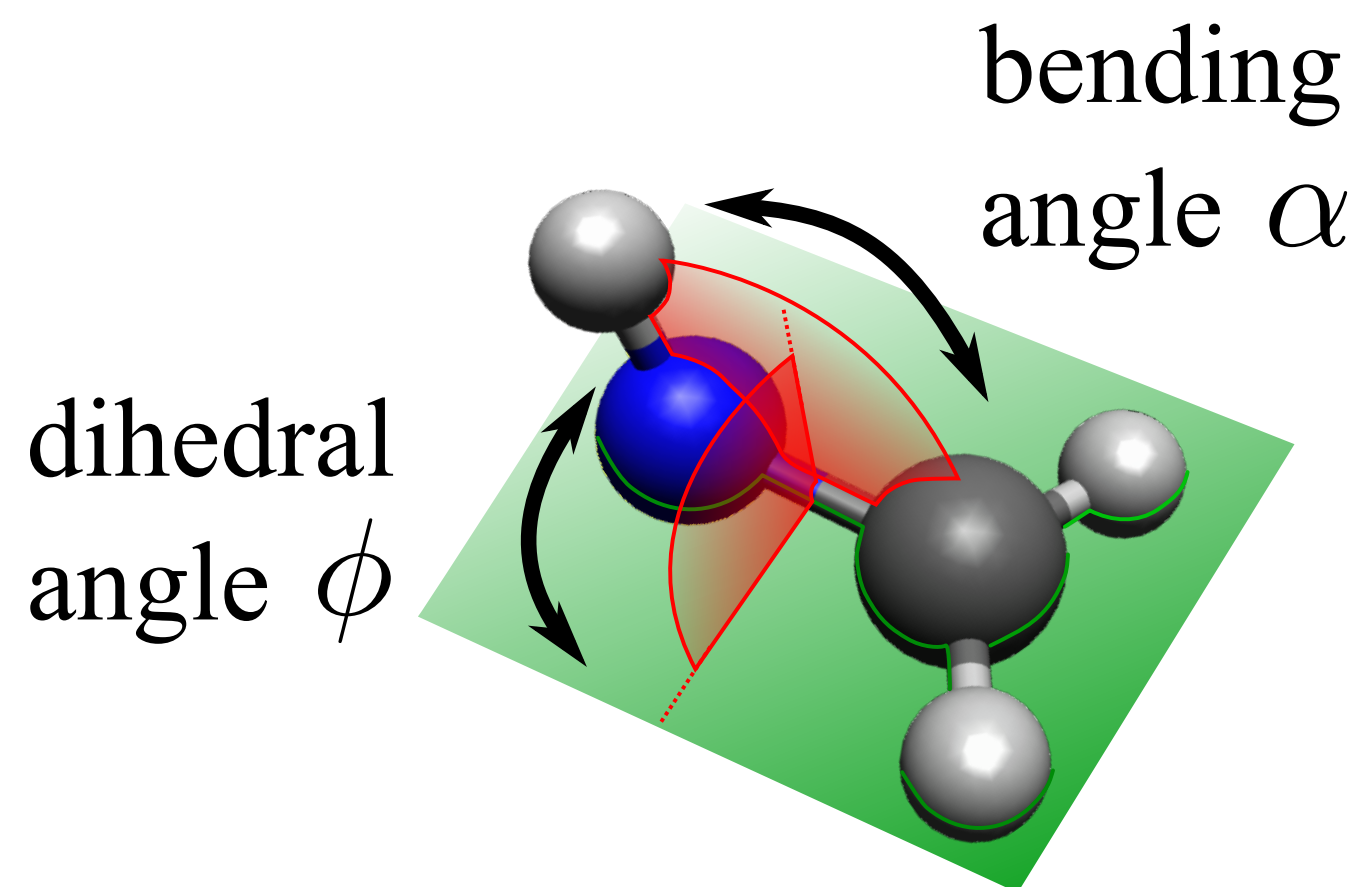
$$\frac{dE_I}{dx} = \sum_{pq} \frac{\partial h_{pq}}{\partial x} \gamma_{pq}^{I,eff} + \frac{1}{2} \sum_{pqrs} \frac{\partial g_{pqrs}}{\partial x} \Gamma_{pqrs}^{I,eff} + \sum_J \sum_n w_J \bar{\theta}_n^I G_n^{C,J} \left( \frac{\partial \hat{H}}{\partial x} \right)$$

$$\begin{pmatrix} \mathbf{H}^{OO} & \mathbf{H}^{OC} \\ \mathbf{H}^{CO} & \mathbf{H}^{CC} \end{pmatrix} \begin{pmatrix} \bar{\kappa}^I \\ \bar{\theta}^I \end{pmatrix} = - \begin{pmatrix} \mathbf{G}^{O,I} \\ \mathbf{G}^{C,I} \end{pmatrix}$$

Can be measured out of the circuit !



### III) SA-OO-VQE: Some results



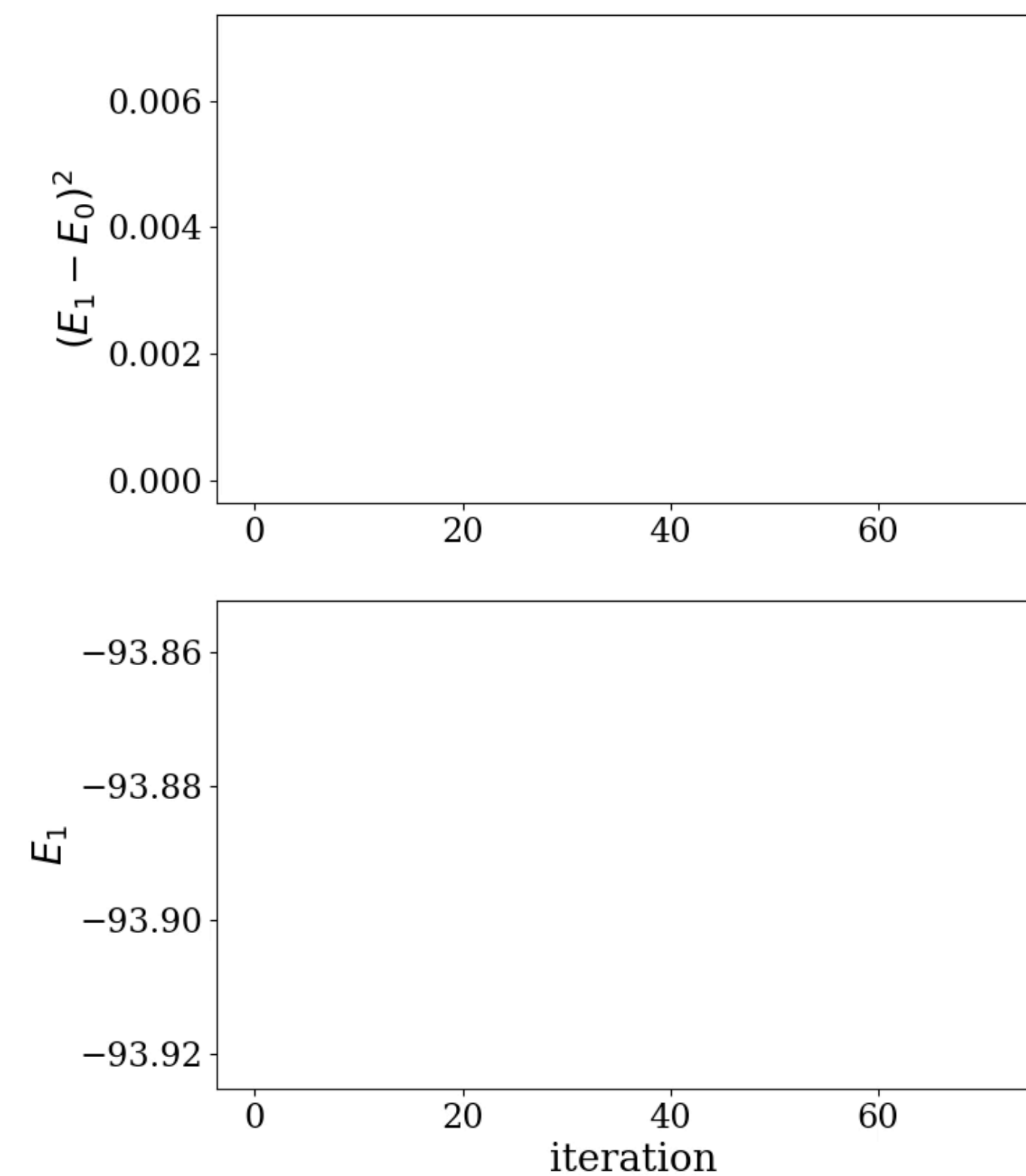
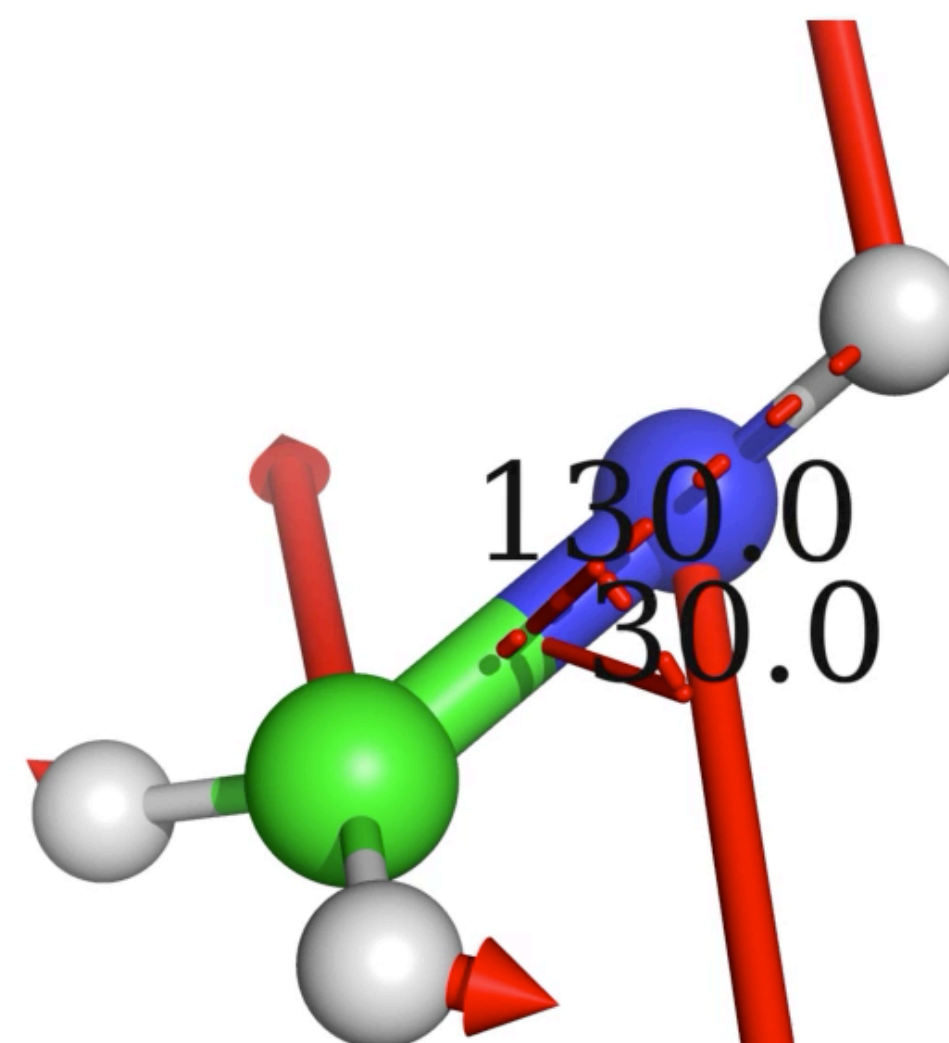
### III) SA-OO-VQE: Some results

*Ingredients:*

- Nuclear gradients
- Non-adiabatic couplings

Research of  
Minimal-energy  
conical-intersection  
(MECI)

### Evolution of the geometry optimisation with SA-OO-VQE



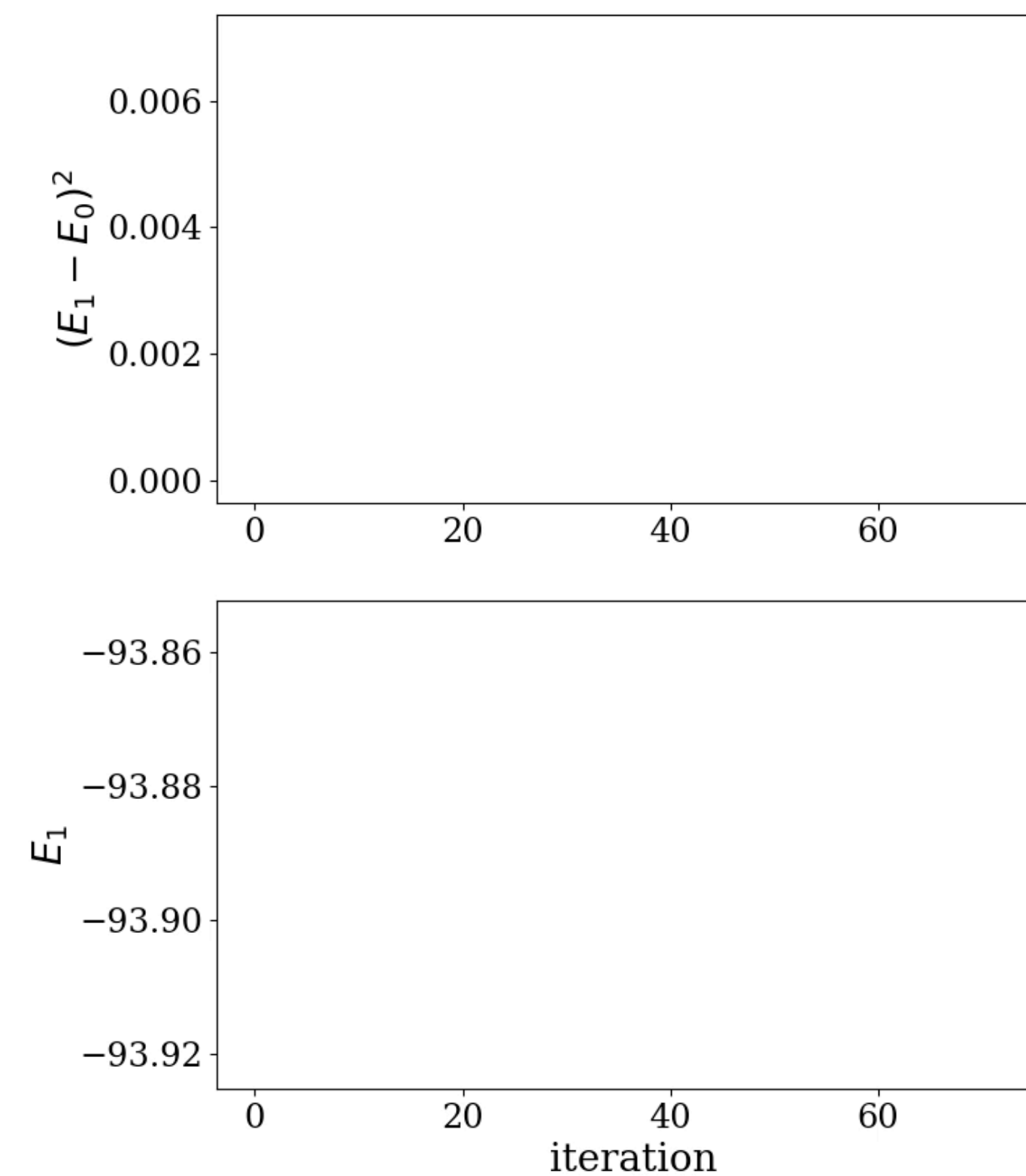
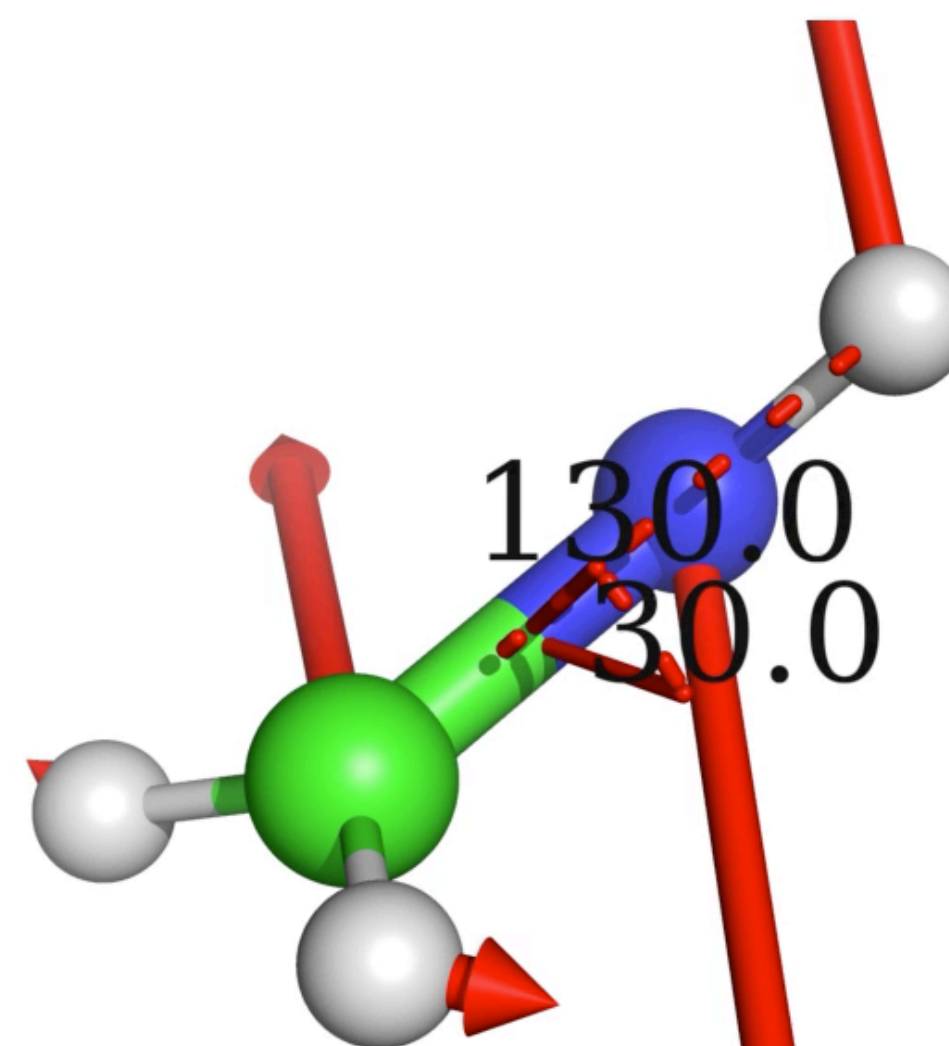
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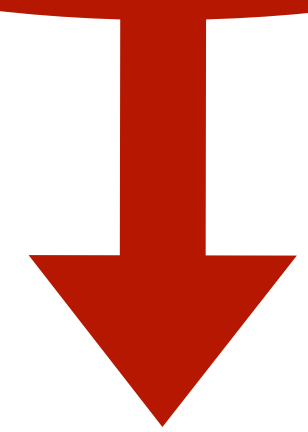
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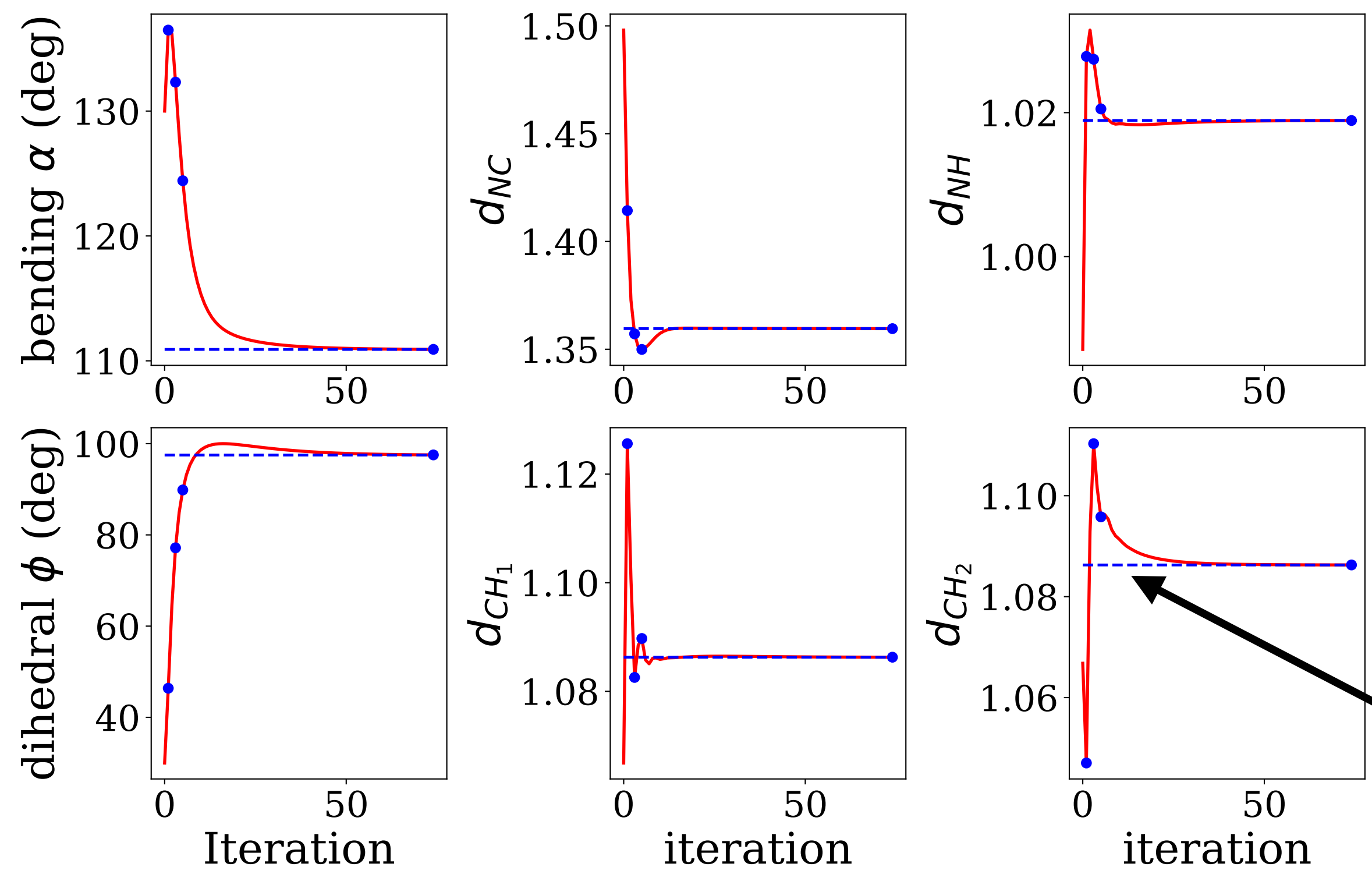
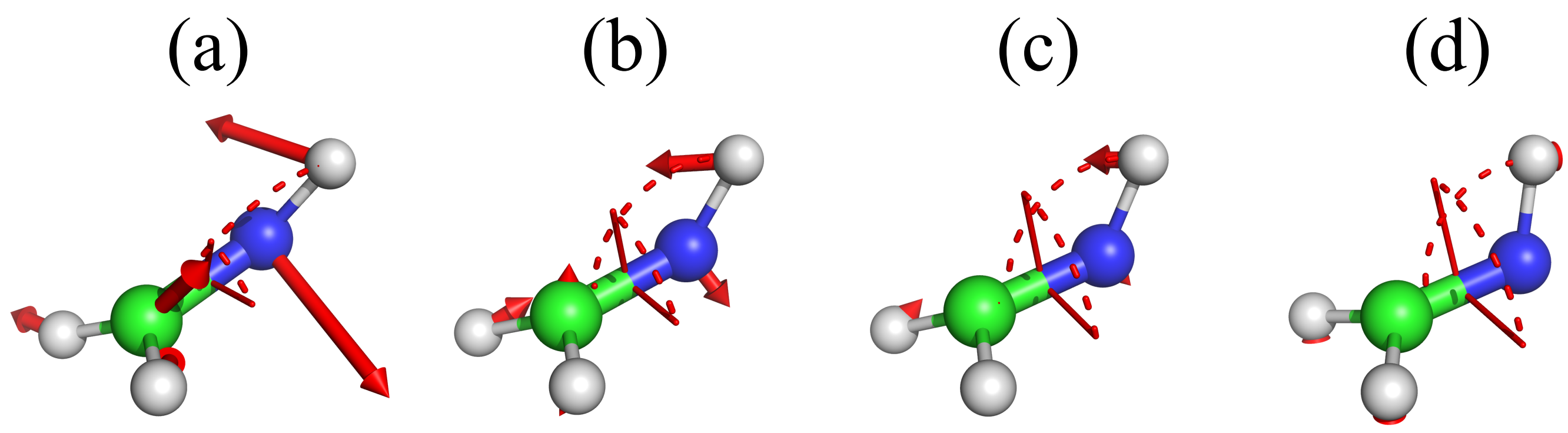
### III) SA-OO-VQE: Some results

*Ingredients:*

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**Research of Minimal-energy conical-intersection (MECI)**



MECI with SA-CASSCF (OpenMolcas)

# Content

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- I) General introduction
- II) Describing conical intersections on near term quantum computers
- III) SA-OO-VQE: Some results
- IV) Take home messages**

## IV) Take home messages

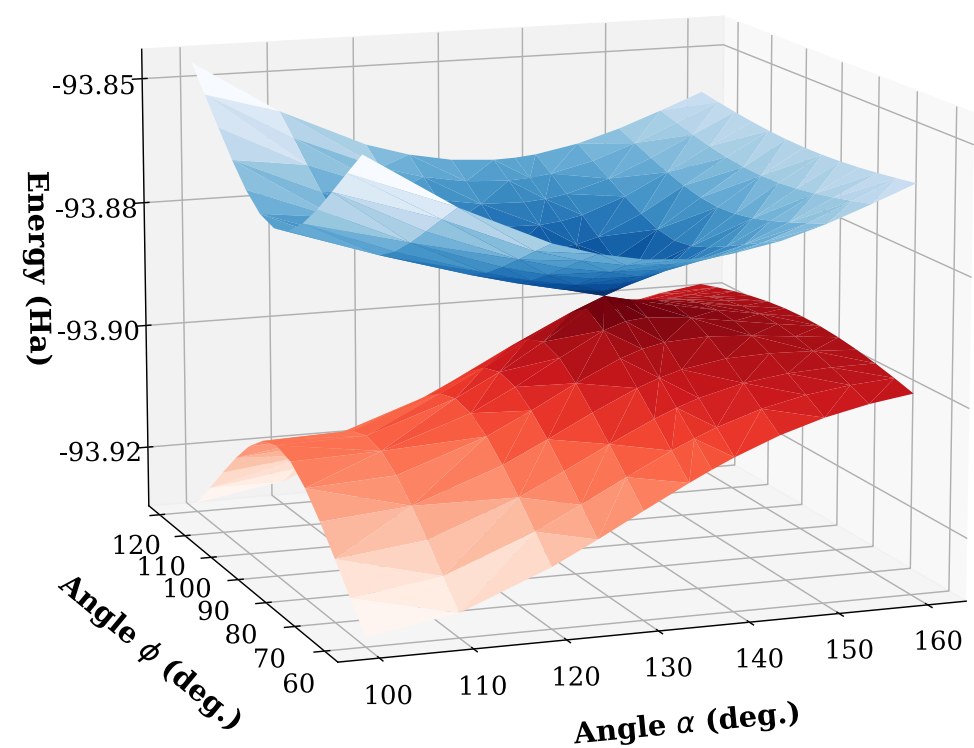
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**SA-OO-VQE**

# IV) Take home messages

SA-OO-VQE

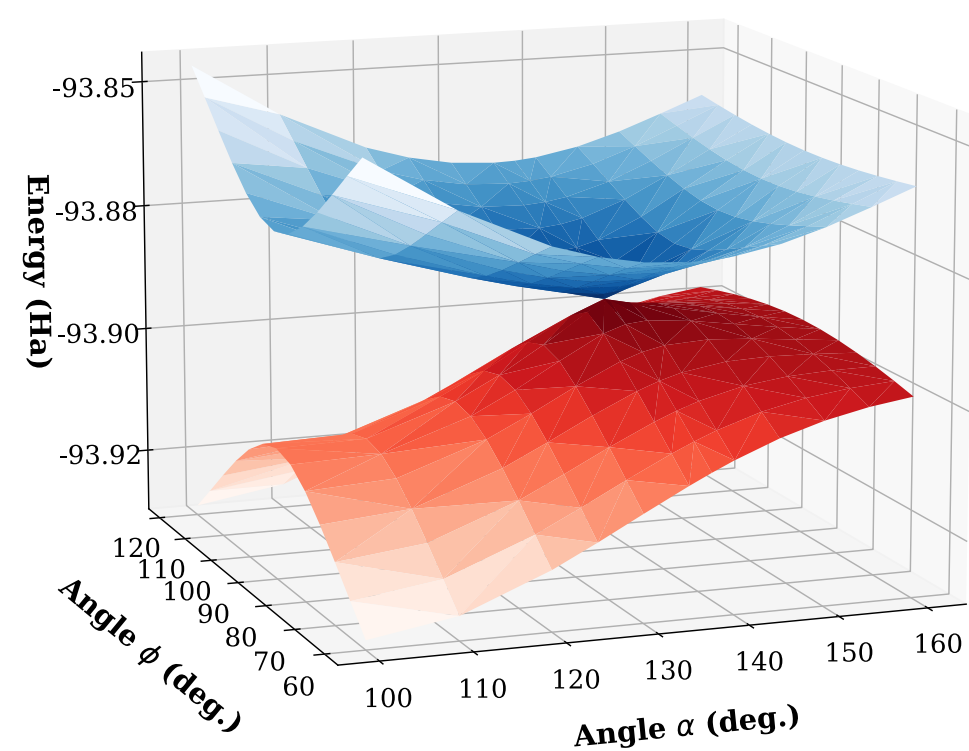
Potential energy surfaces



## IV) Take home messages

SA-OO-VQE

Potential energy surfaces



Analytical derivatives

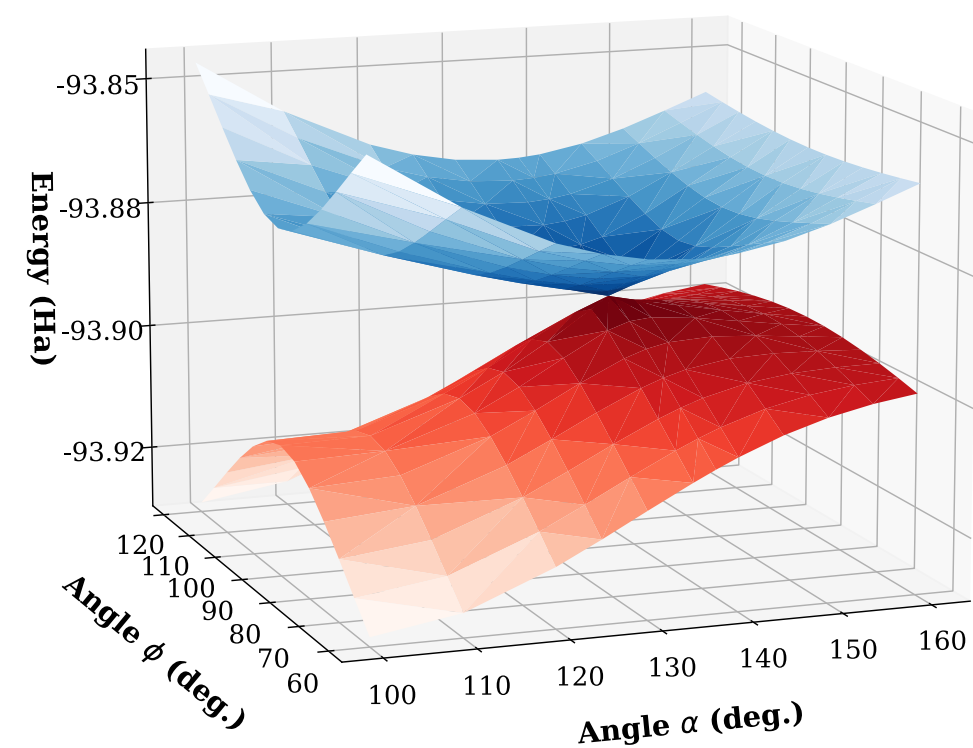
$$\frac{dE_I}{dx} \quad D_{IJ} = \langle \Psi_I | \frac{d}{dx} \Psi_J \rangle$$



# IV) Take home messages

## SA-OO-VQE

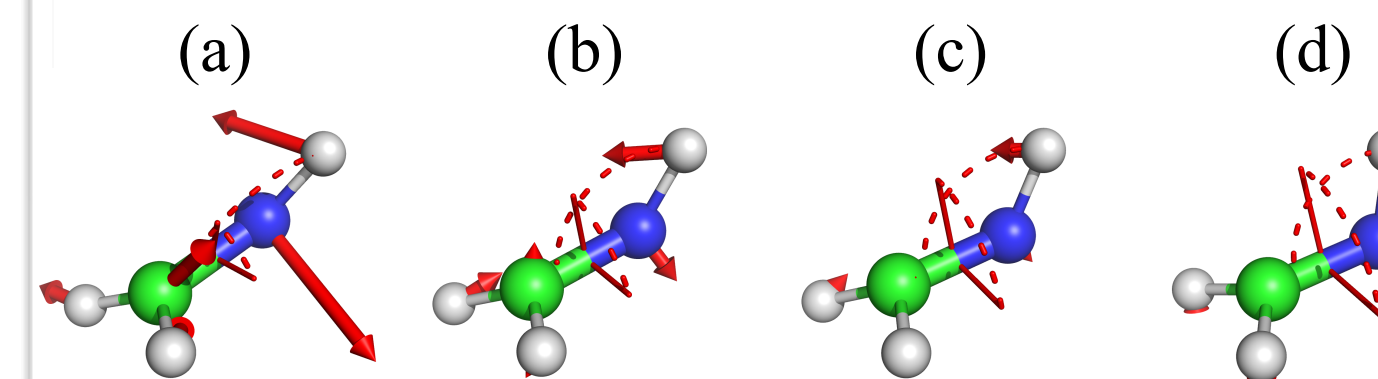
### Potential energy surfaces



### Analytical derivatives

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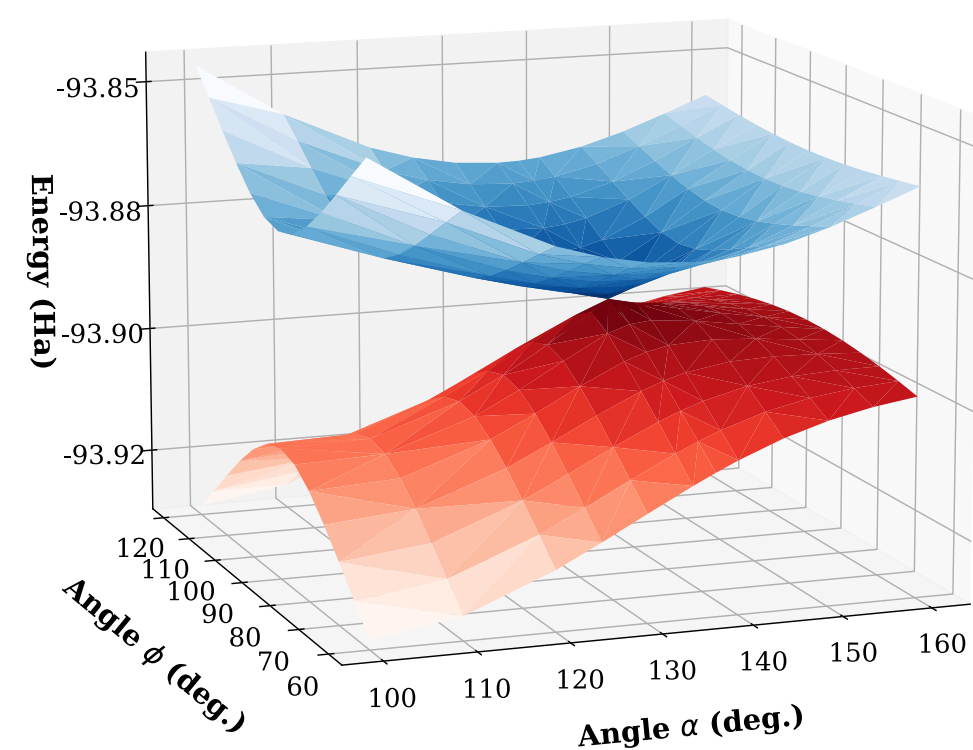
### MECI optimisation



# IV) Take home messages

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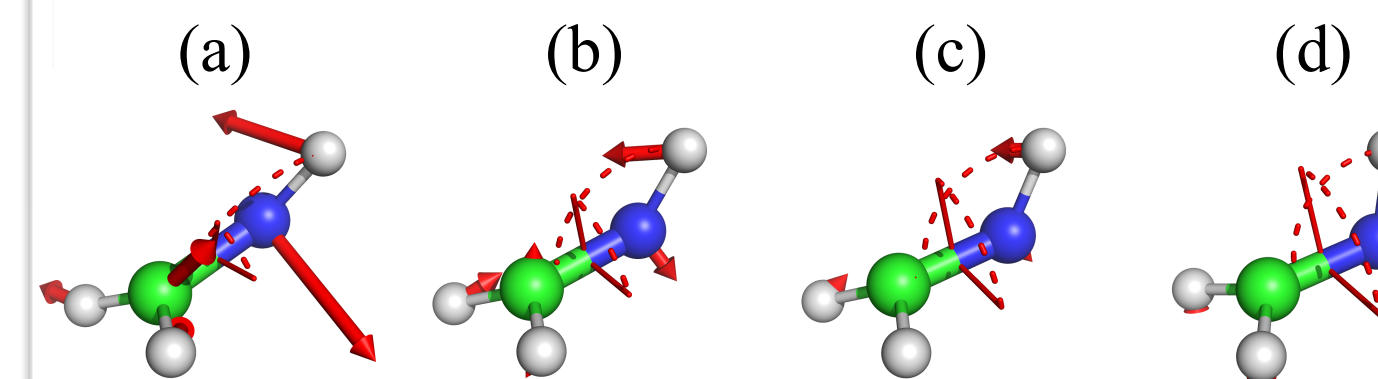
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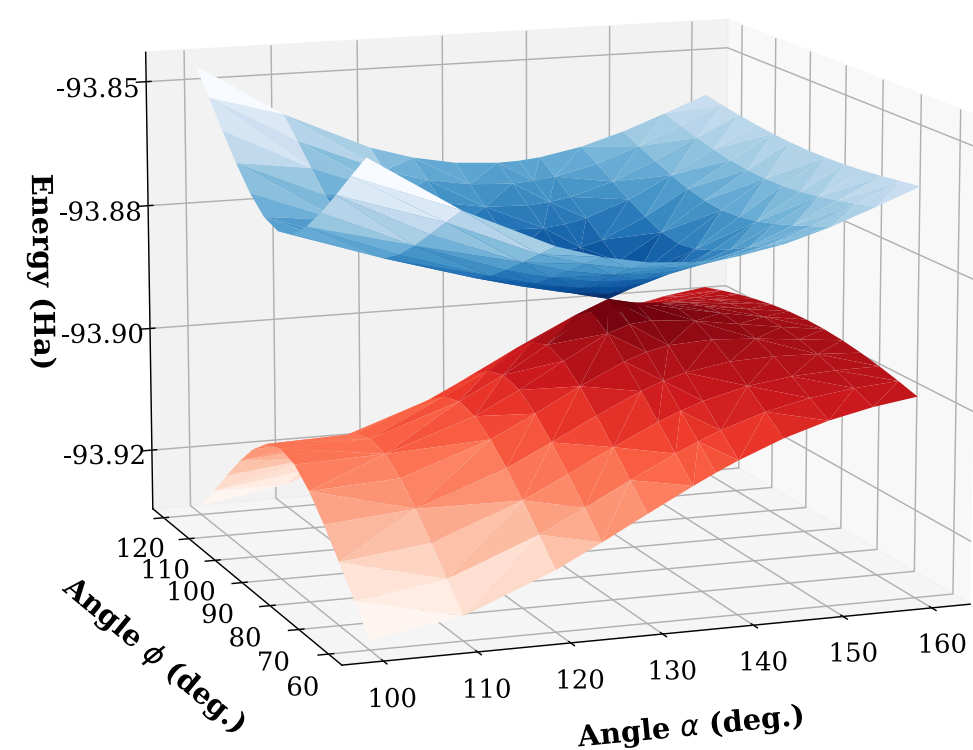


**SA-OO-VQE = Quantum analog of SA-CASSCF (a reference for degeneracies!)**

## IV) Take home messages

### SA-OO-VQE

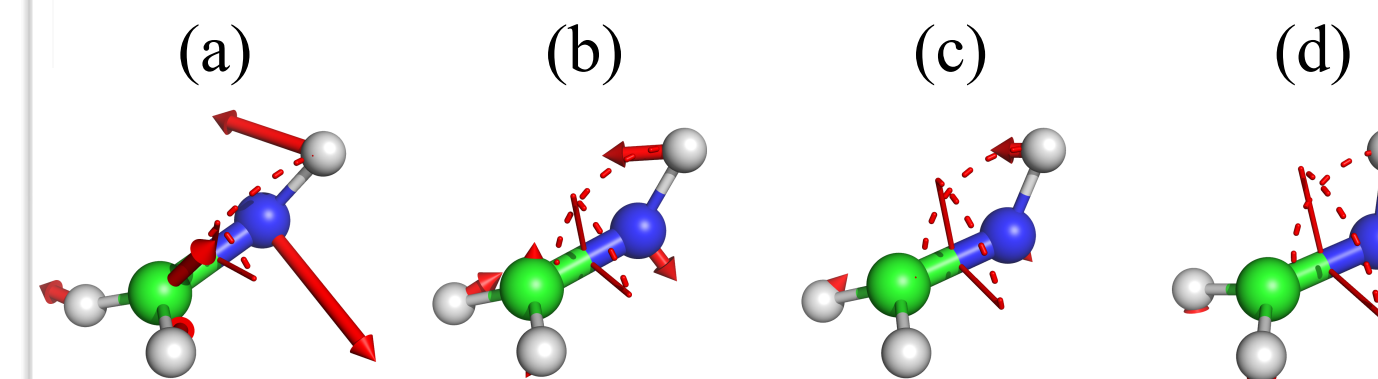
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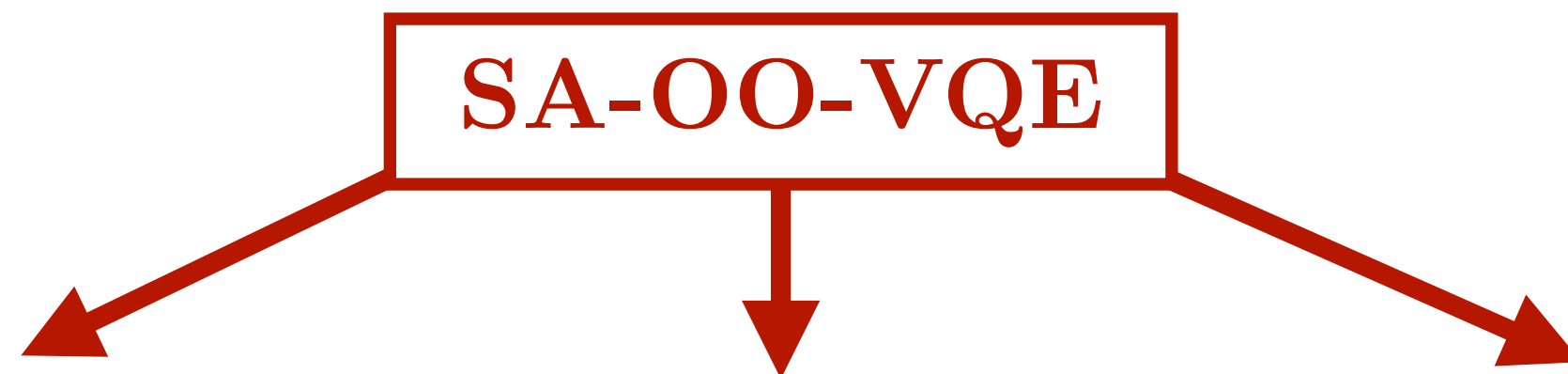
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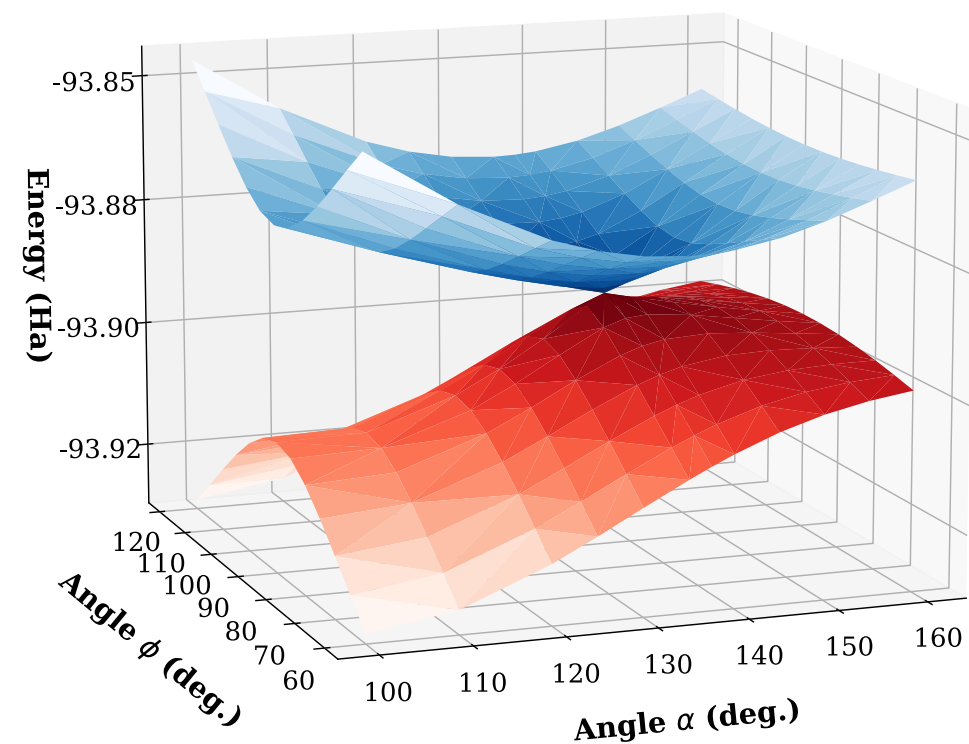
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Next steps:

# IV) Take home messages



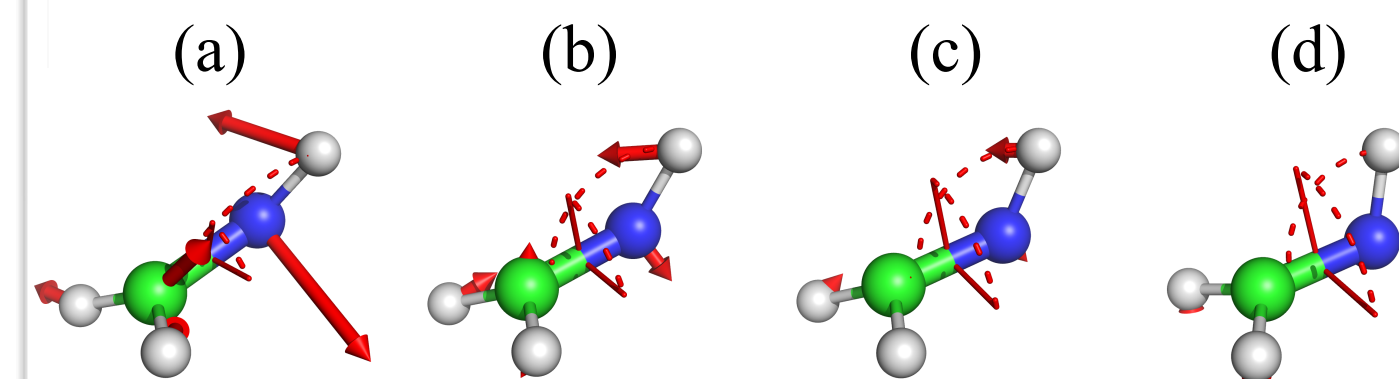
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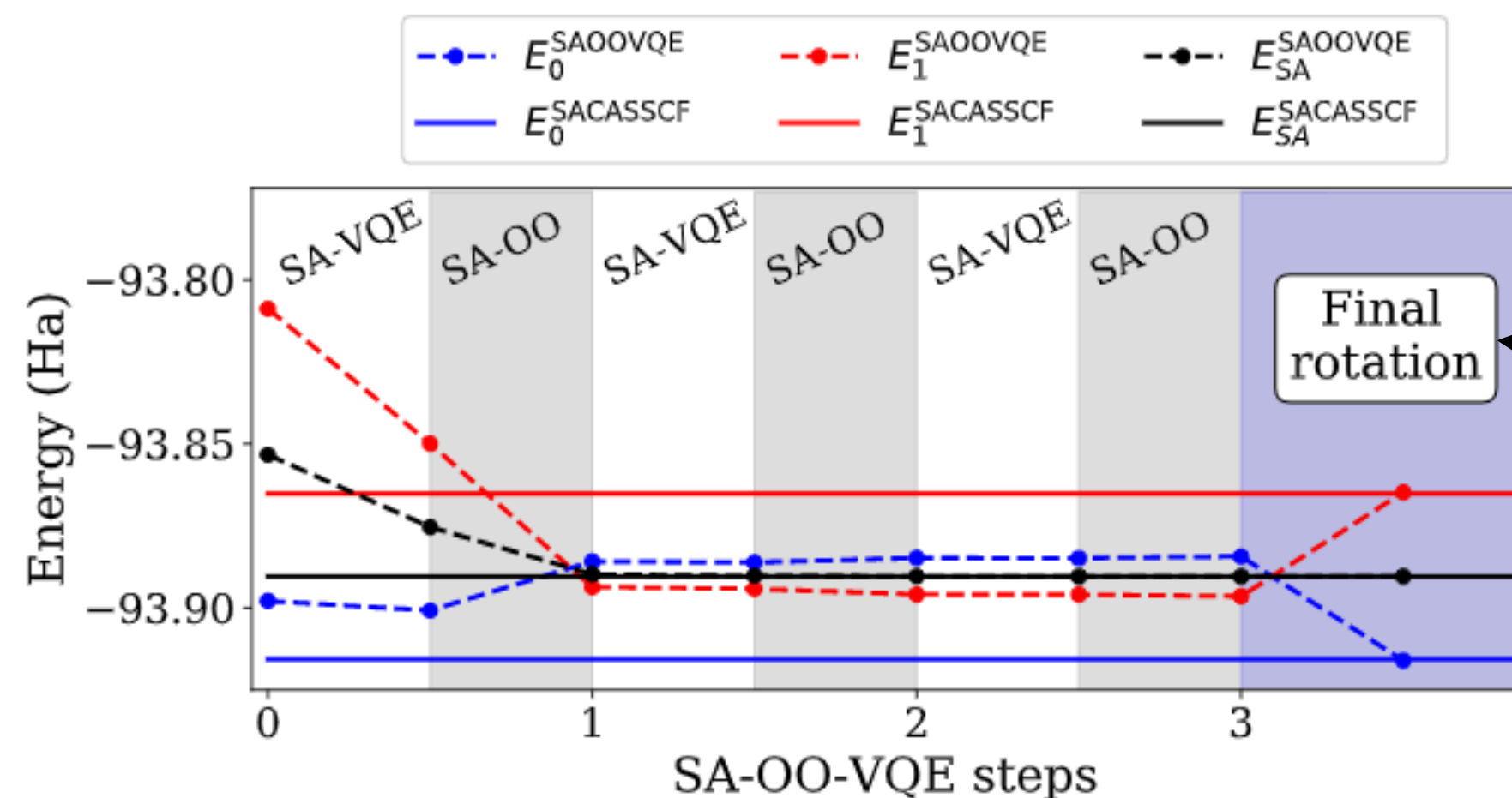
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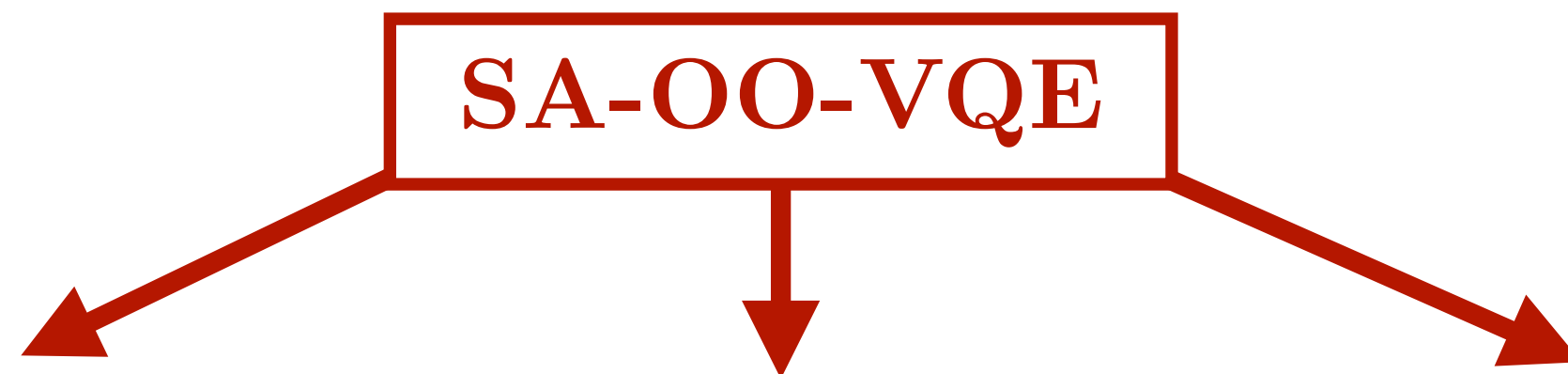
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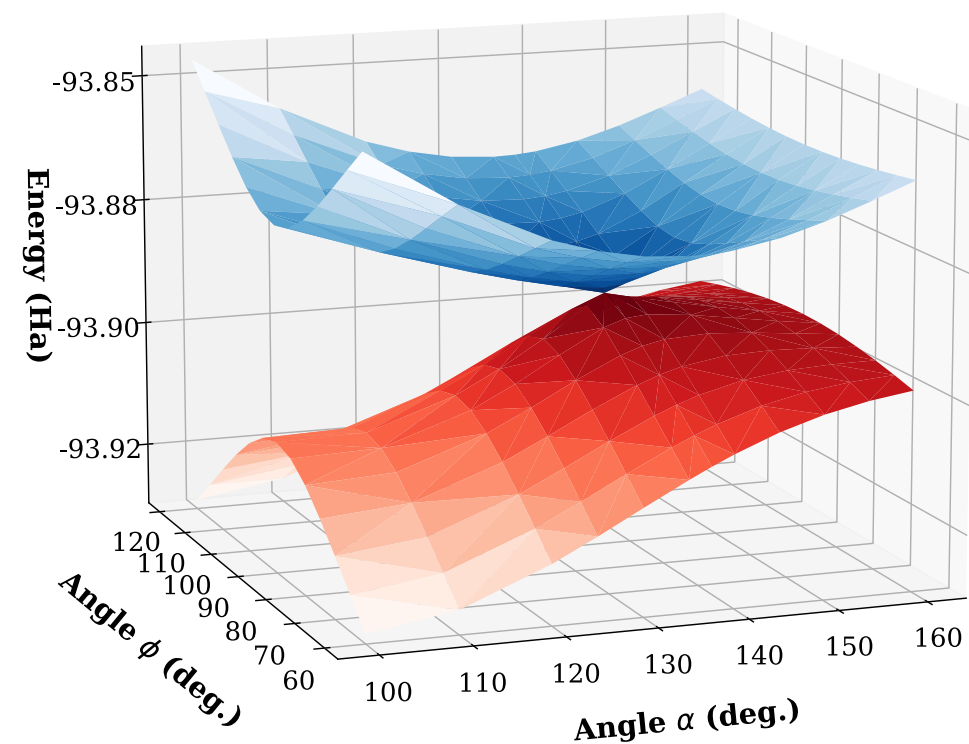
*Next steps:*

1) Switching to **diabatic states** ?

# IV) Take home messages



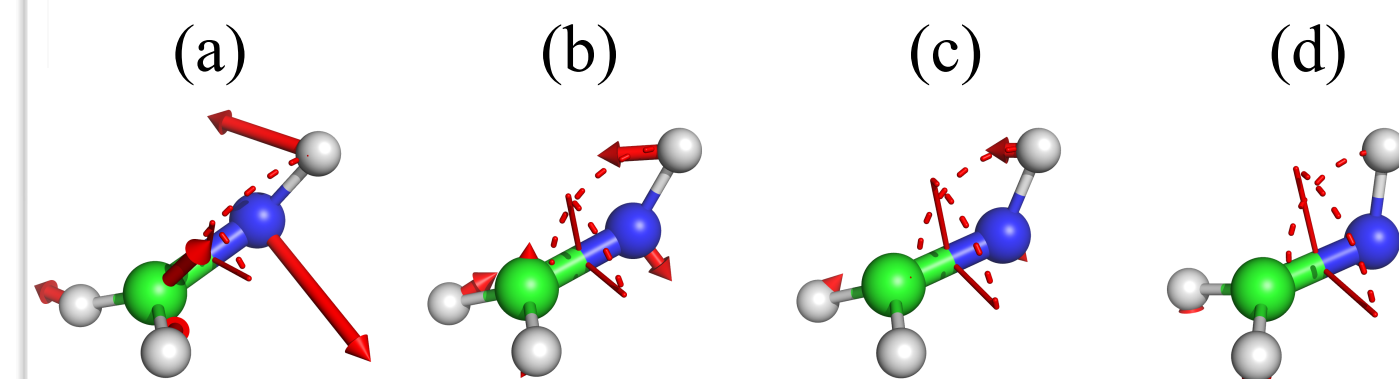
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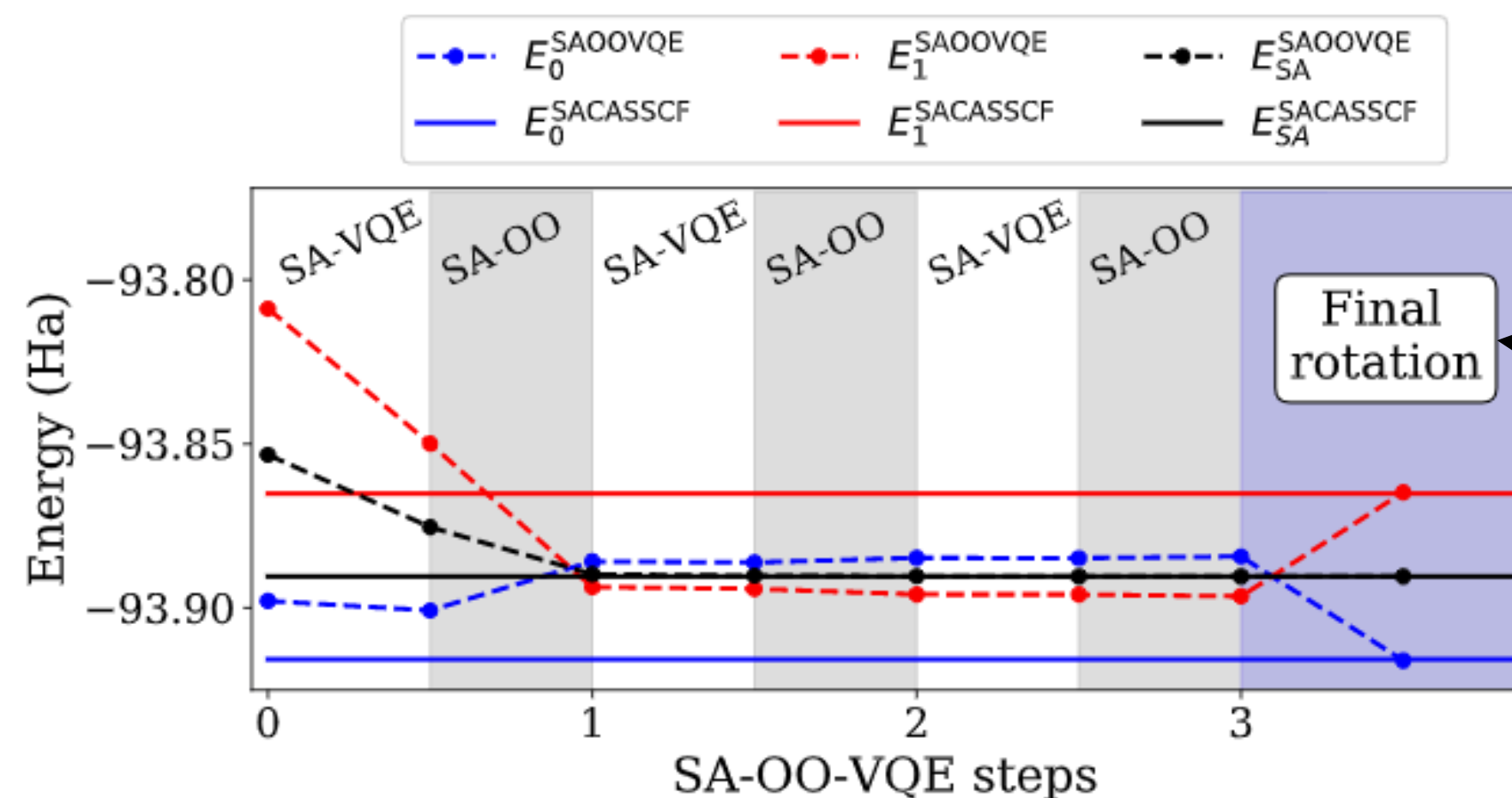
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## MECI optimisation



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Next steps:

- 1) Switching to **diabatic states** ?
- 2) Application to **quantum dynamics** ?

Thanks to my colleagues



Emiel Koridon, Benjamin Lasorne, Bruno Senjean,  
Lucas Visscher and Thomas O'Brien



Thanks a lot for your  
attention !