Quantum Chemistry & Quantum Computing

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Quantum Chemistry & Quantum Computing

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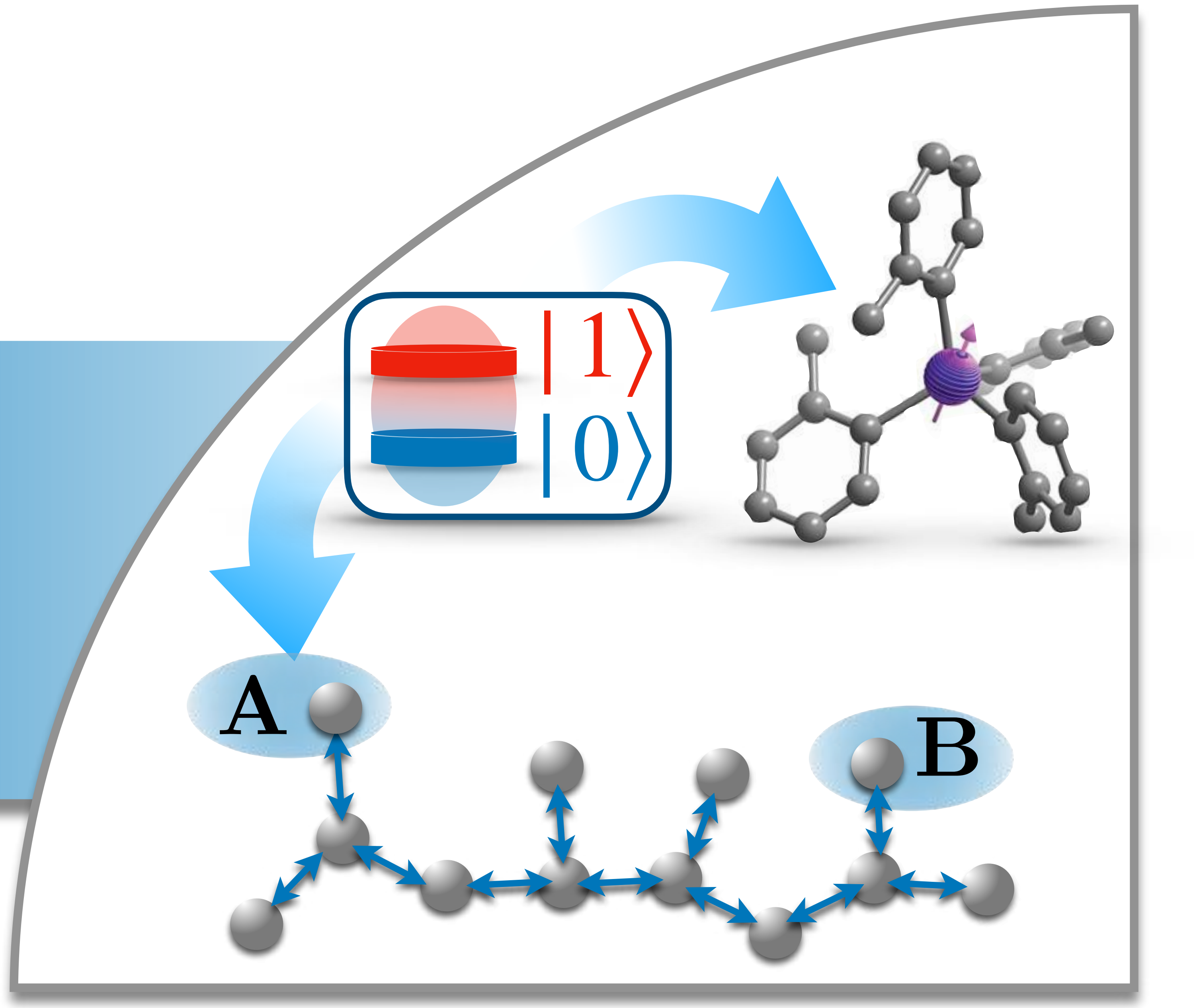
Quantum Chemistry & Quantum Computing

Quantum Hardware



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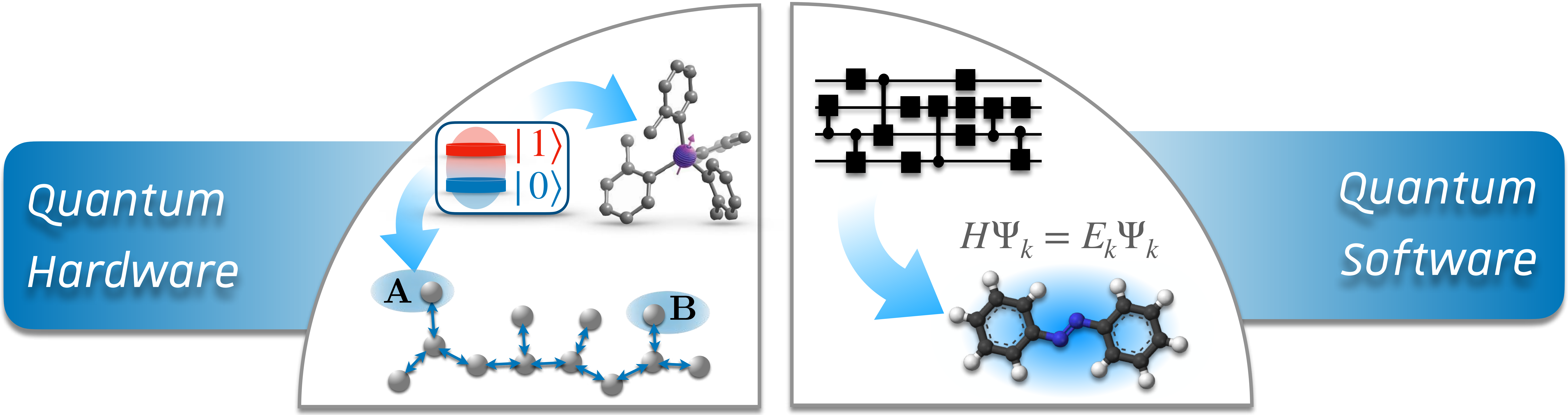
Quantum Chemistry & Quantum Computing



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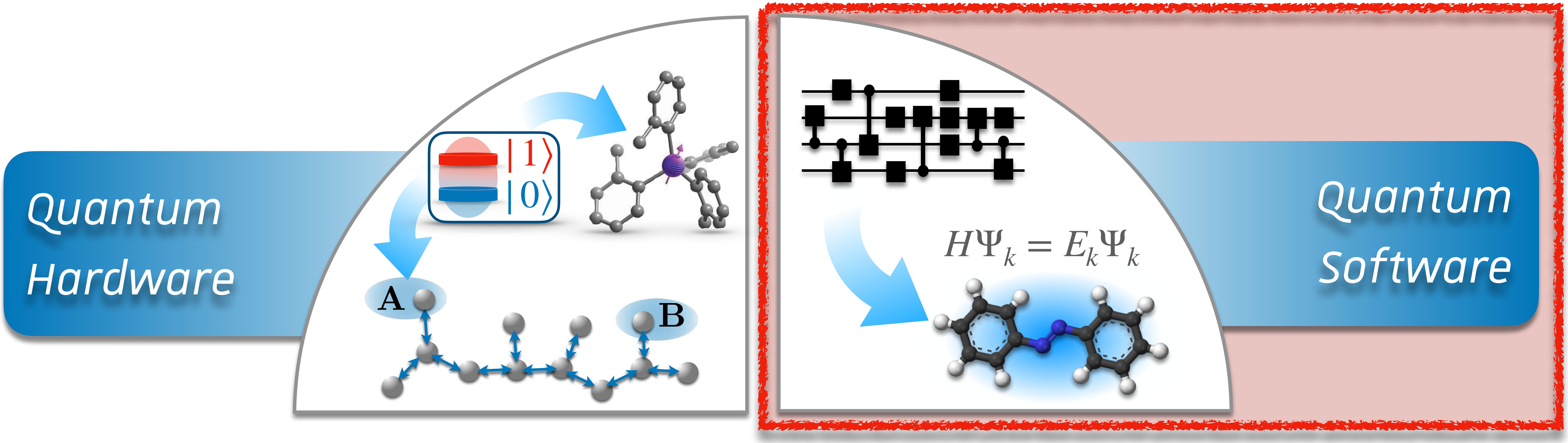
Quantum Chemistry & Quantum Computing



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Summary

I) Introduction to quantum computing

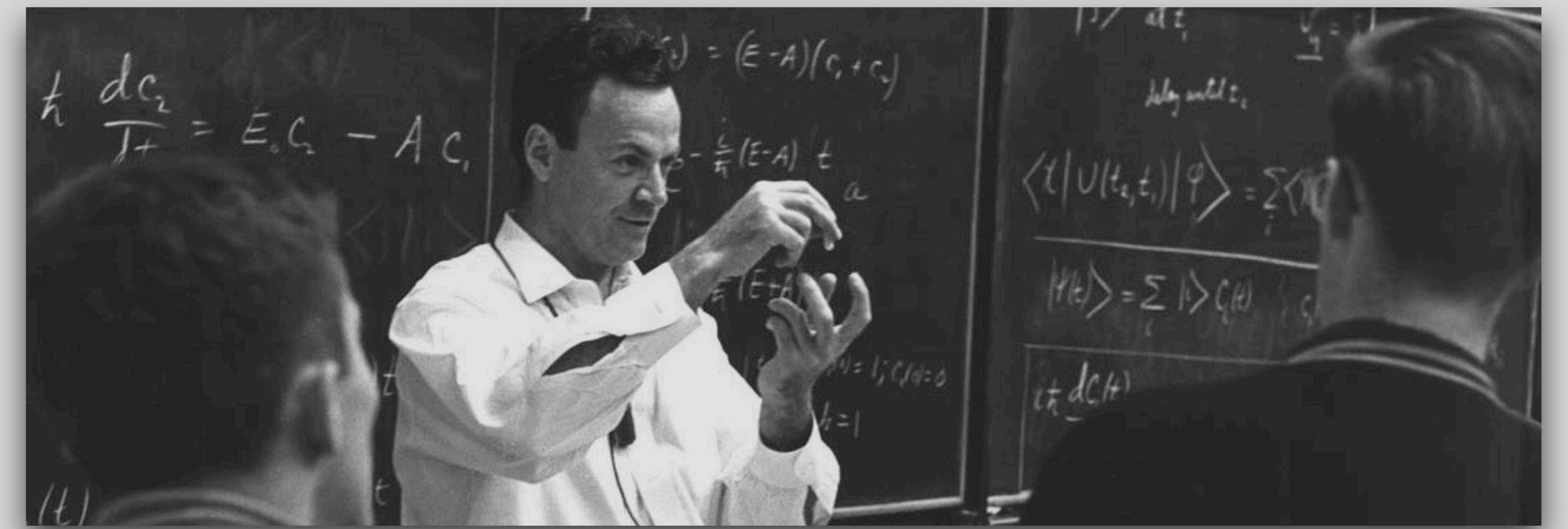
II) From quantum computing to chemistry

III) Quantum algorithm for photochemistry

IV) Take home messages

I) Introduction to quantum computing

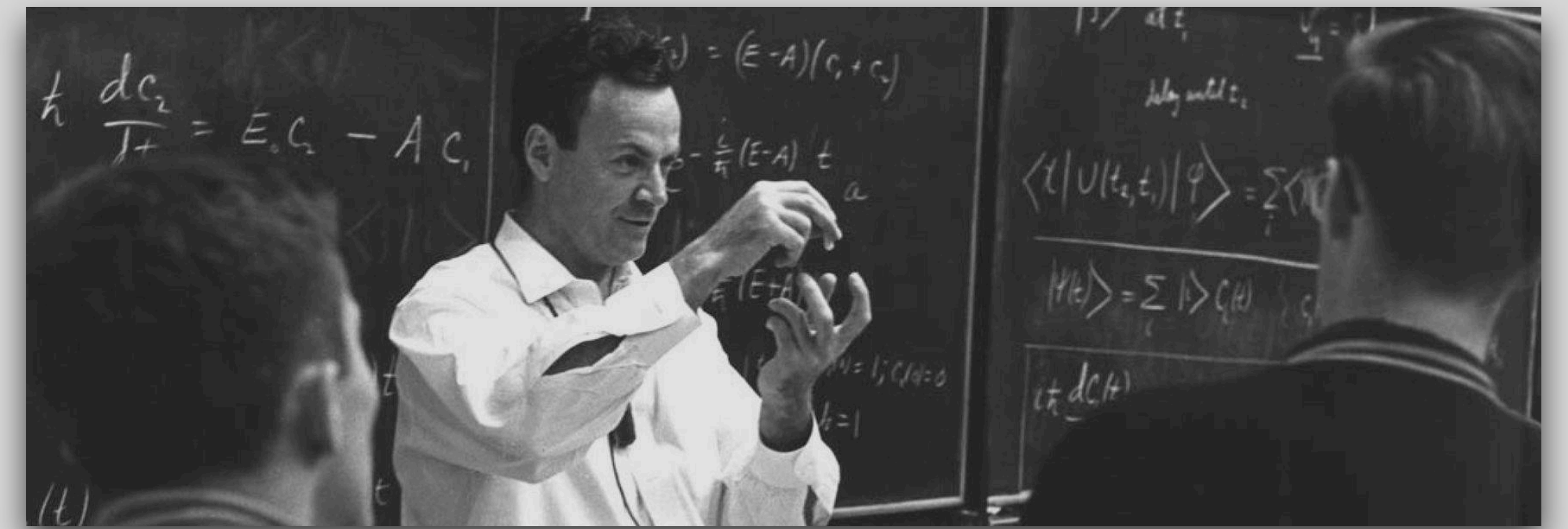
I) Introduction to quantum computing



-Richard P. Feynman

“Nature (e.g. atoms, molecules …) isn't classical and if you want to make a simulation of nature, you'd better make it quantum mechanical.”

I) Introduction to quantum computing



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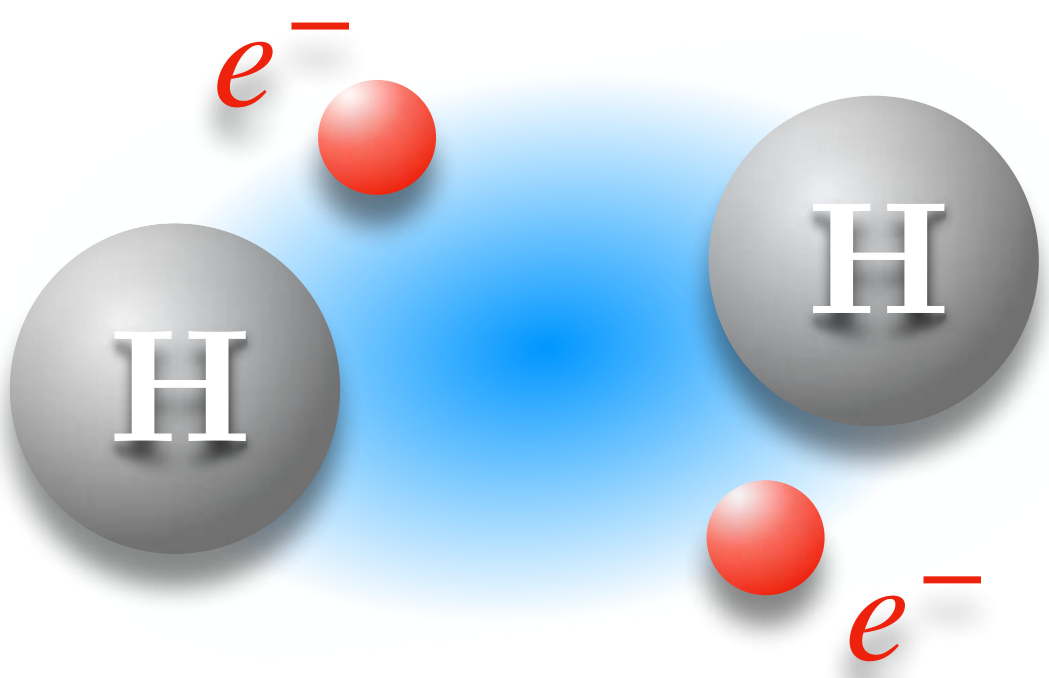
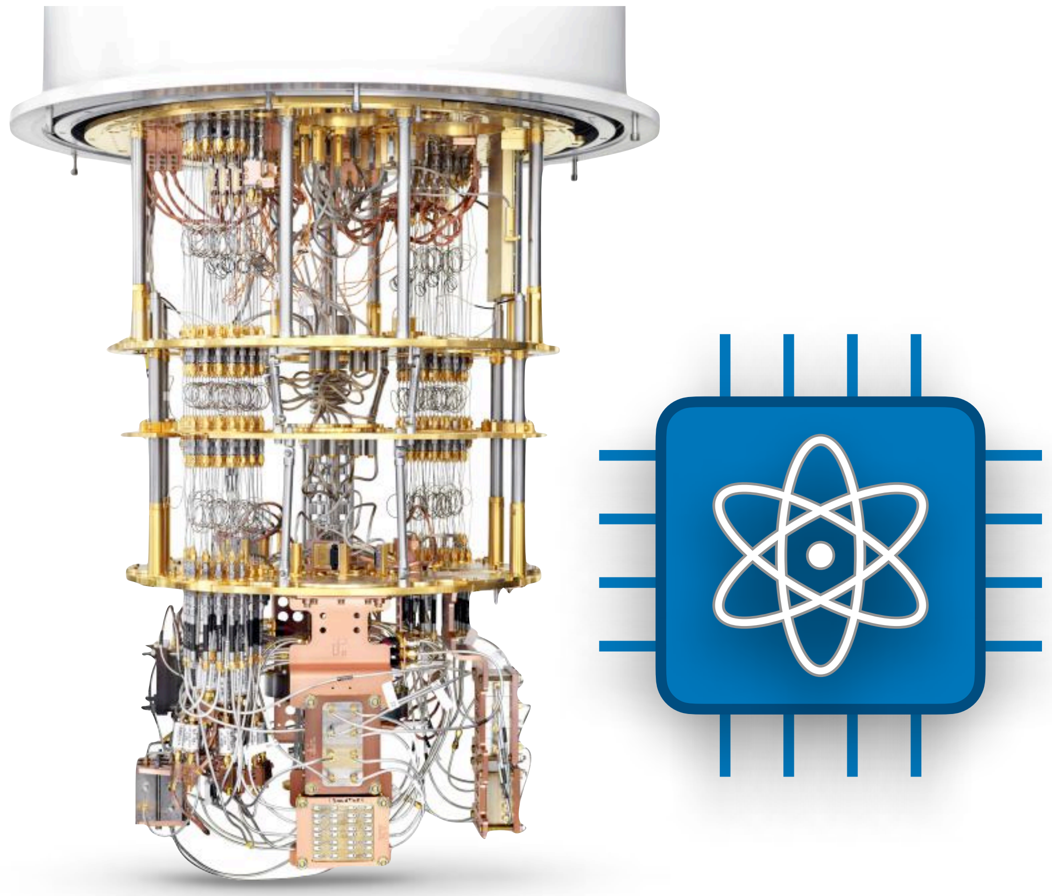
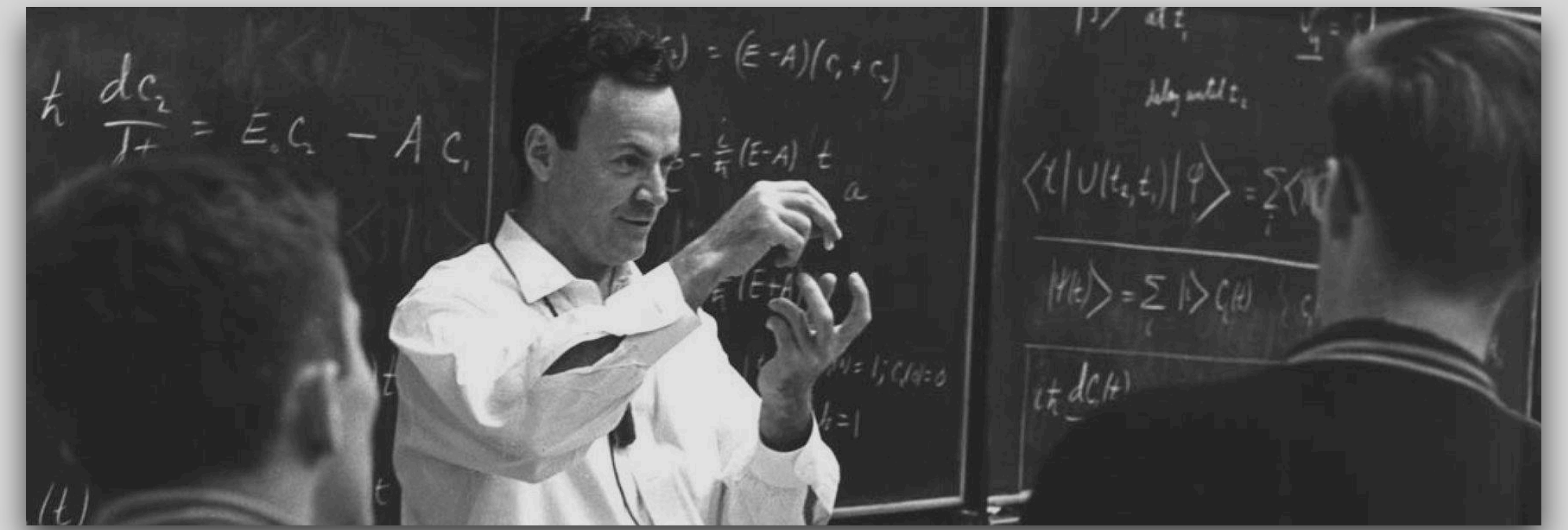
Quantum Chemistry





Quantum Computer

I) Introduction to quantum computing



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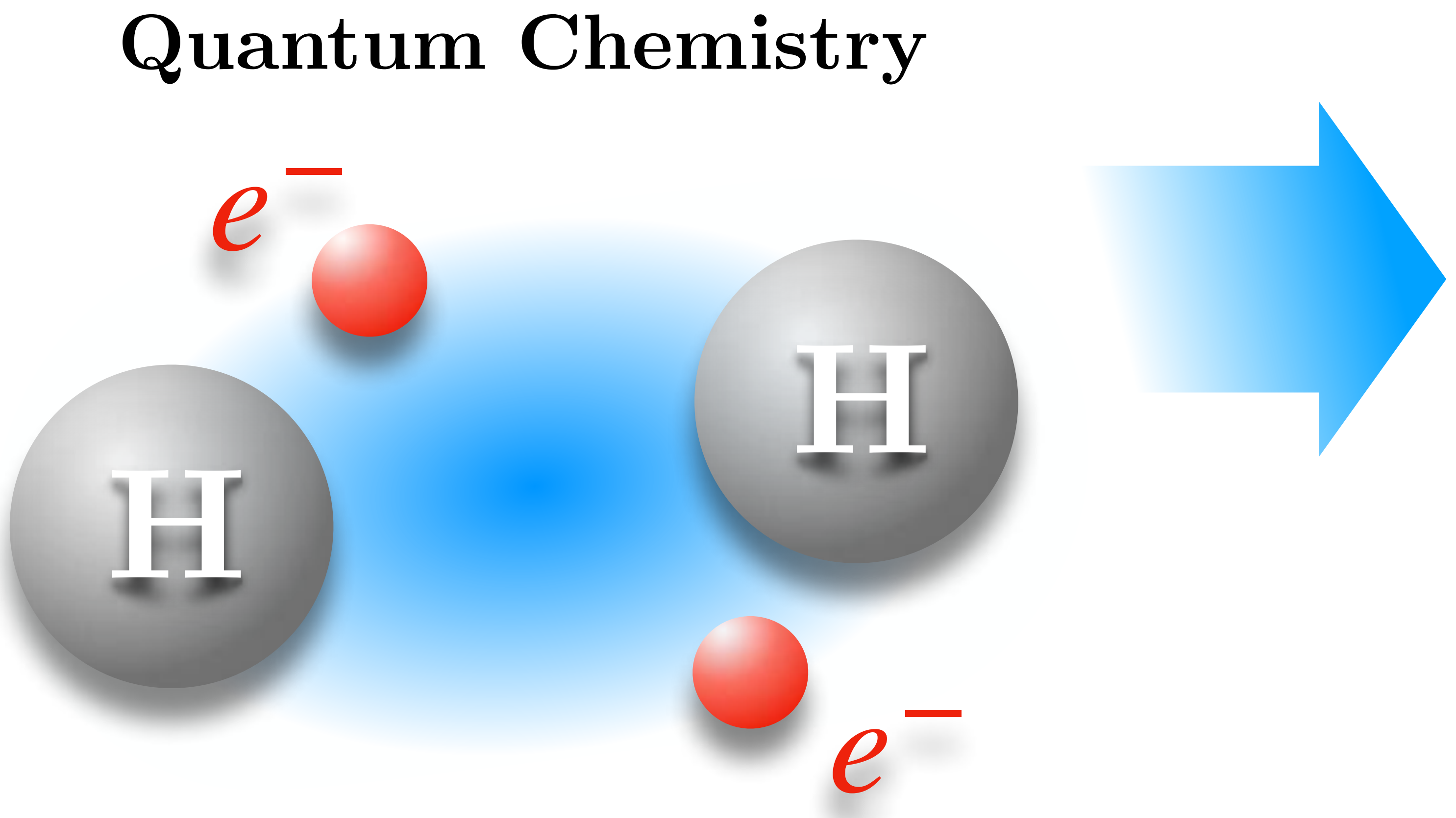
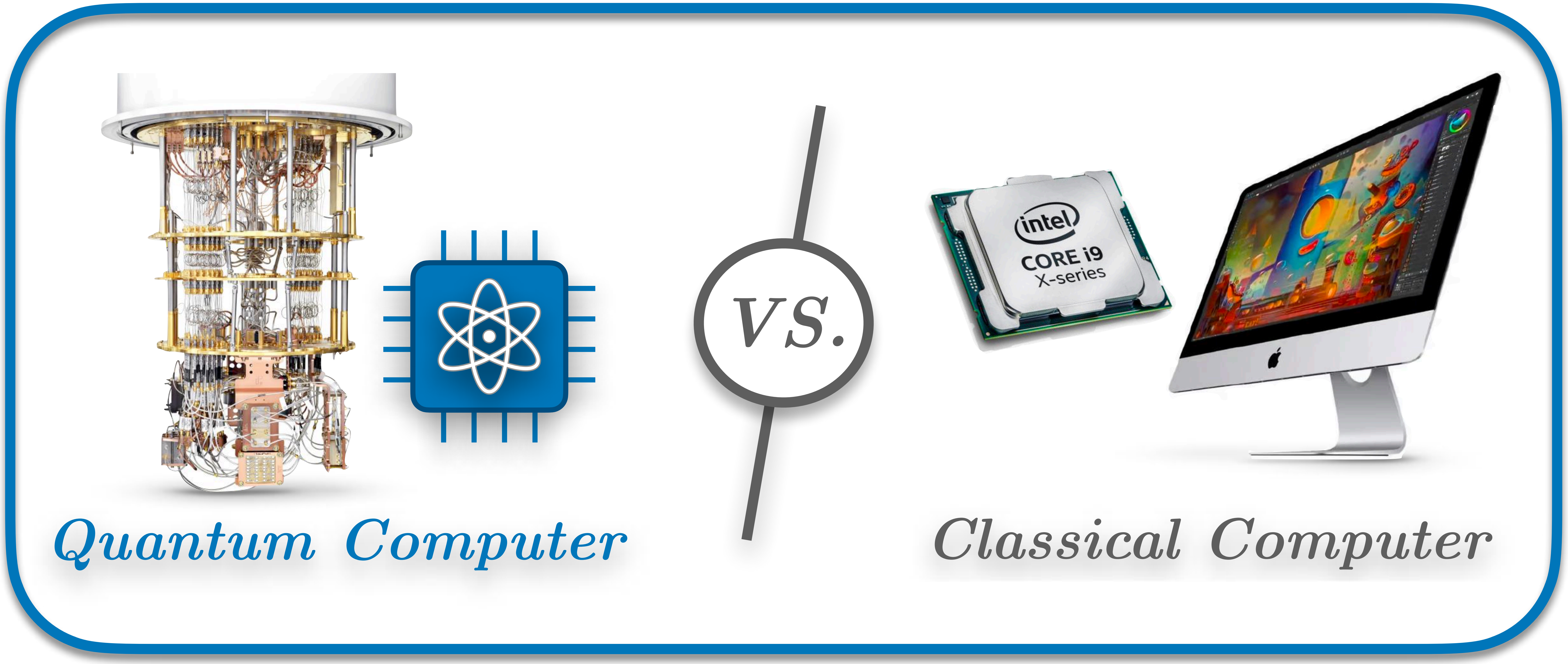


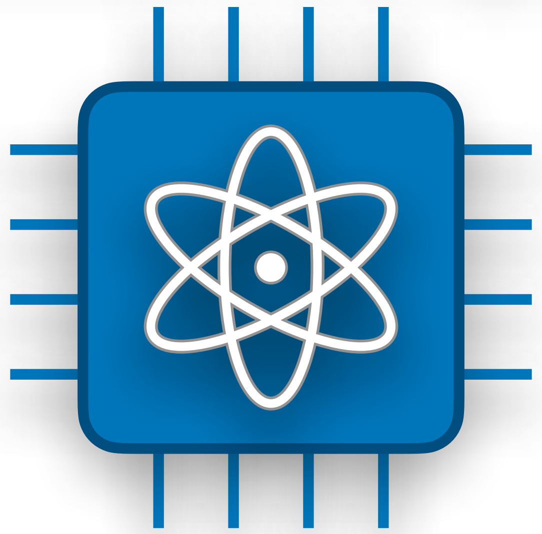


I) Introduction to quantum computing

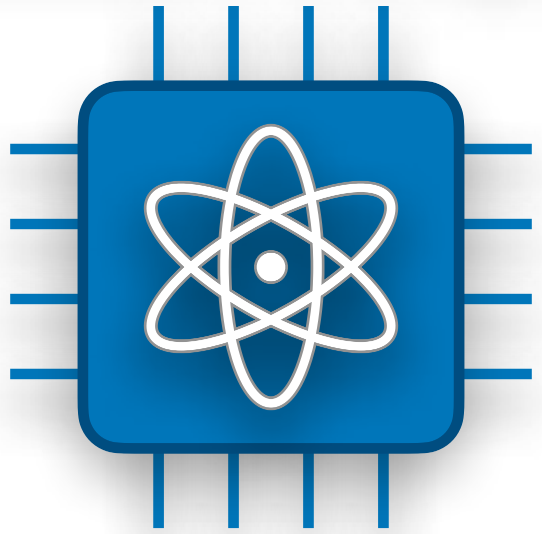
Classical Computer

VS.

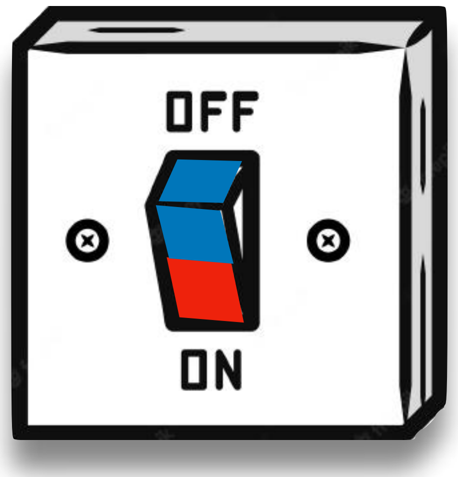
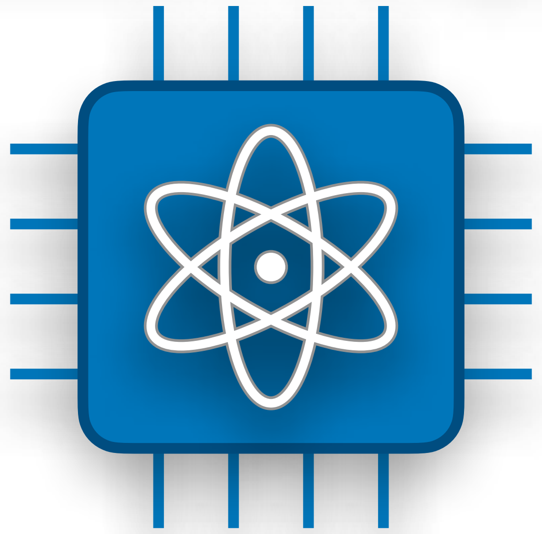
Quantum Computer



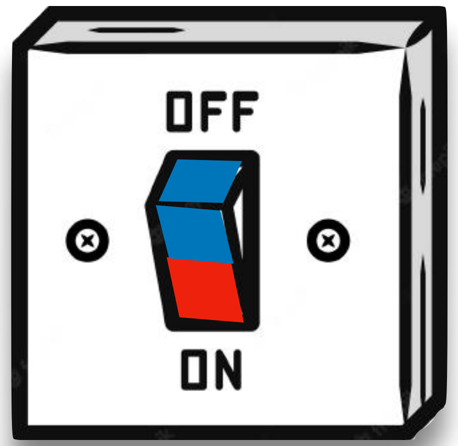
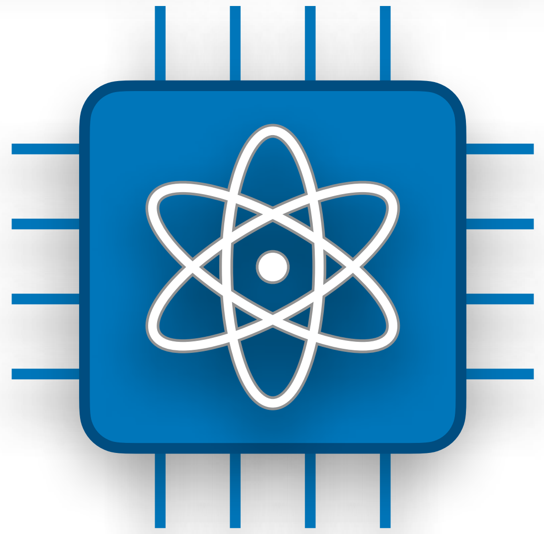
I) Introduction to quantum computing

	Unit of Information	Basic Logic	Prog. Langage
Classical Computer 			
VS.			
Quantum Computer 			

I) Introduction to quantum computing

	Unit of Information	Basic Logic	Prog. Langage
Classical Computer 	The Bit *0* *1* 		
VS. *Quantum Computer* 			

I) Introduction to quantum computing

	Unit of Information	Basic Logic	Prog. Langage
Classical Computer 	The Bit 0 1 		
VS.			
Quantum Computer 	The Qubit  $\|Q\rangle = c_0\|0\rangle + c_1\|1\rangle$		

I) Introduction to quantum computing

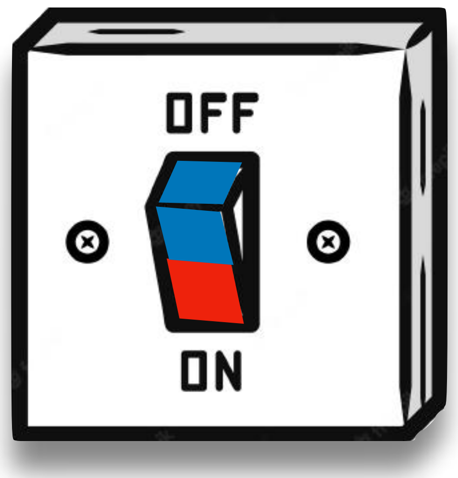
	Unit of Information	Basic Logic	Prog. Langage
Classical Computer	The Bit	Logical circuit	
VS.			
Quantum Computer	The Qubit		

Classical Computer

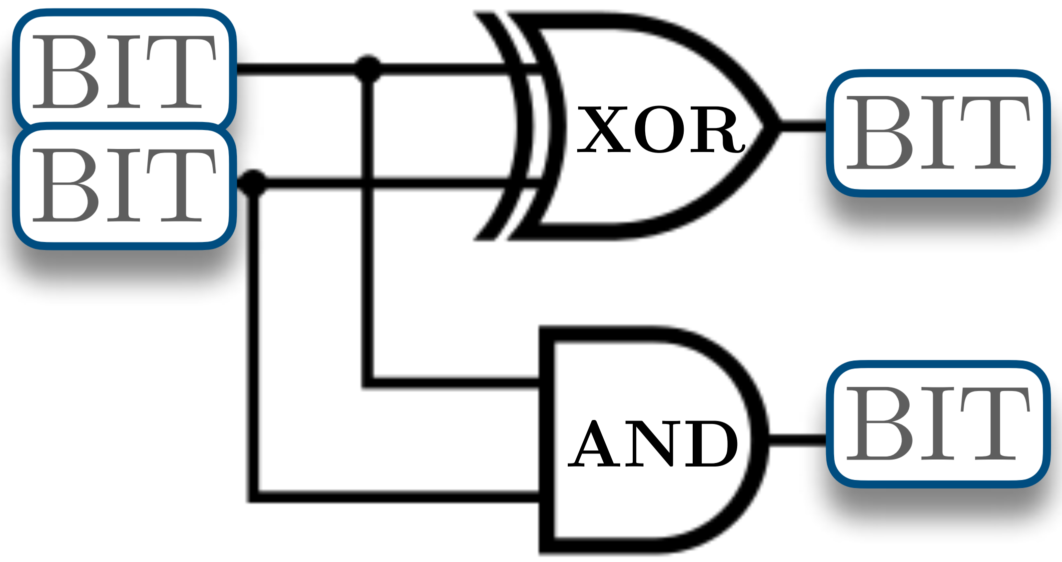
Unit of Information — The Bit

0

1

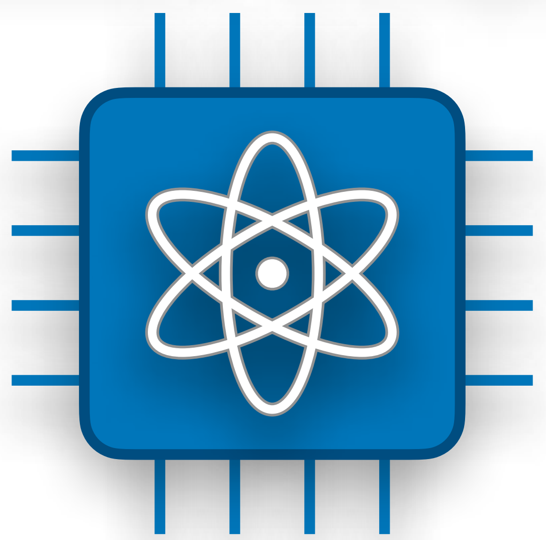


Basic Logic — Logical circuit

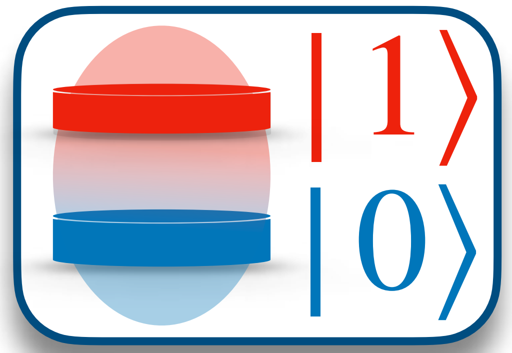


VS.

Quantum Computer



Unit of Information — The Qubit



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

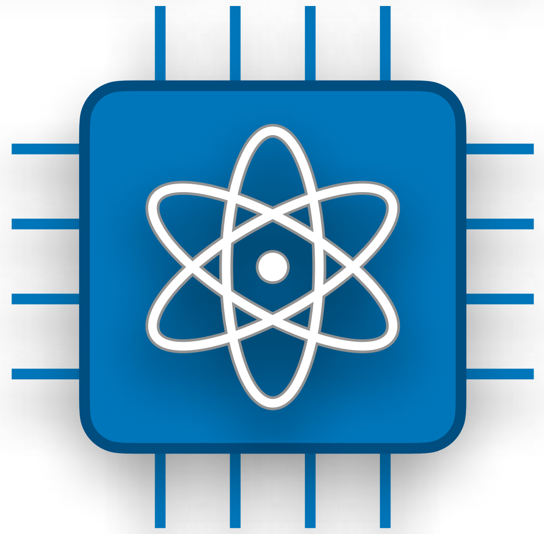
I) Introduction to quantum computing

	Unit of Information	Basic Logic	Prog. Langage

Classical Computer

VS.

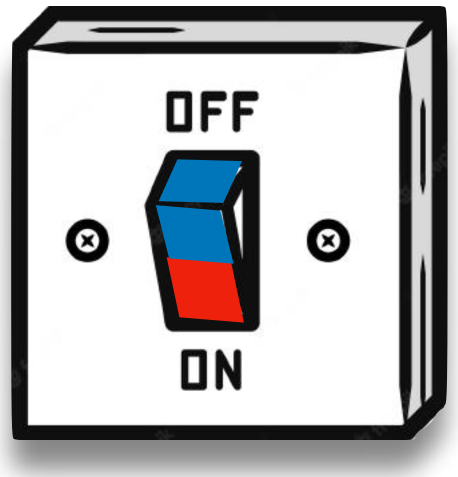
Quantum Computer



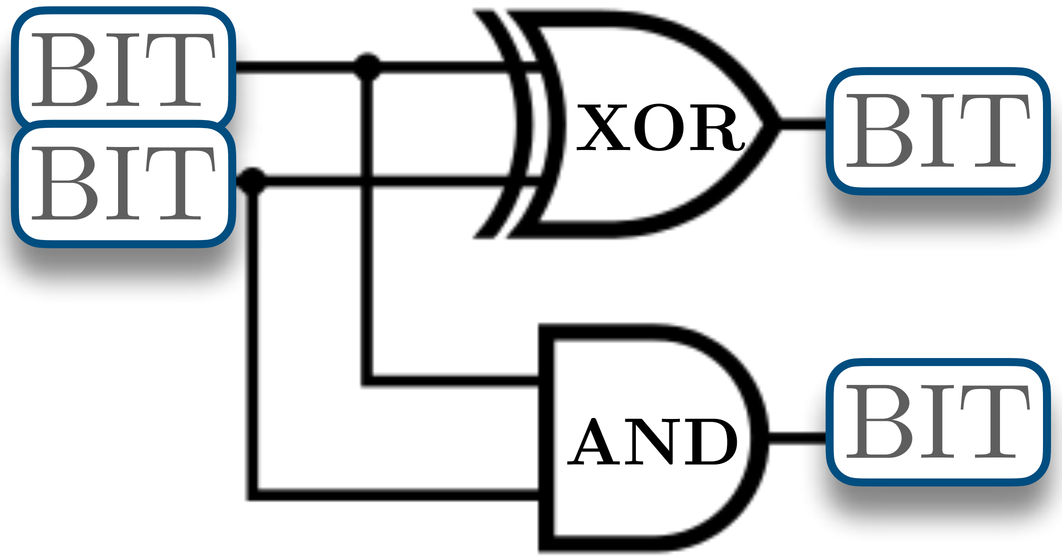
The Bit

0

1



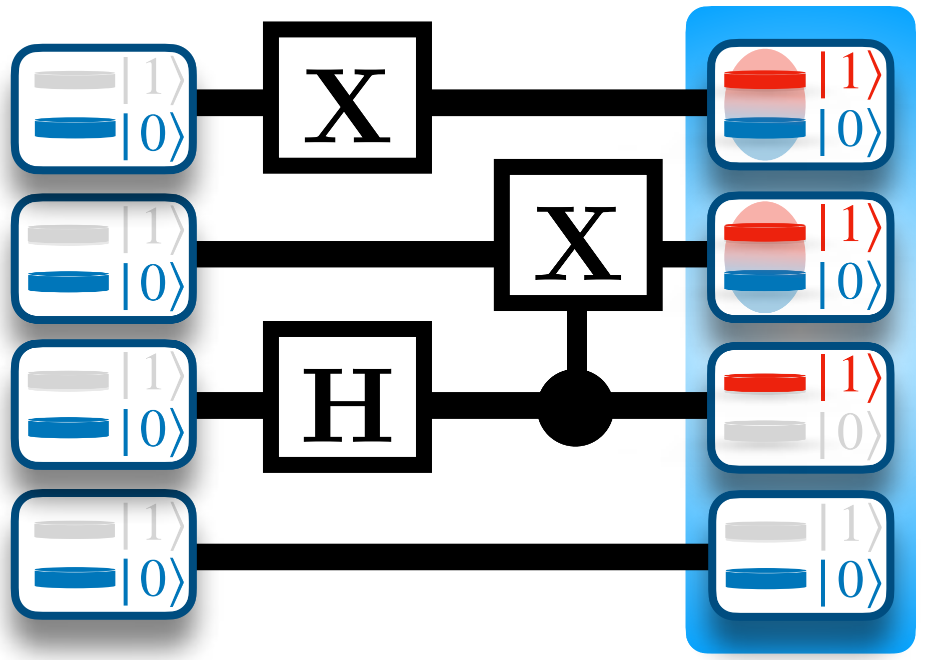
Logical circuit



The Qubit

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

Quantum Circuit

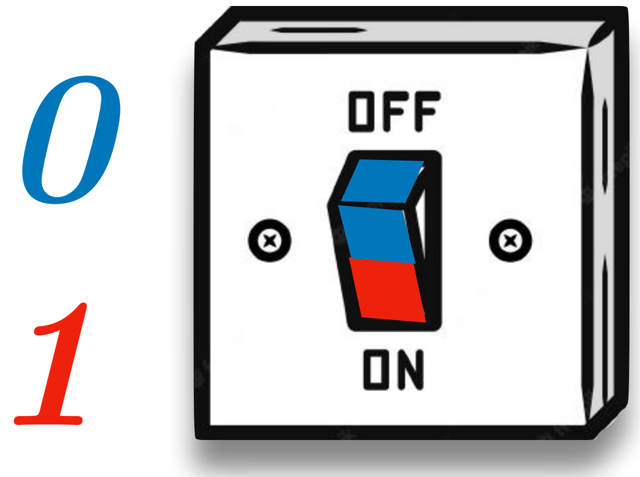


I) Introduction to quantum computing

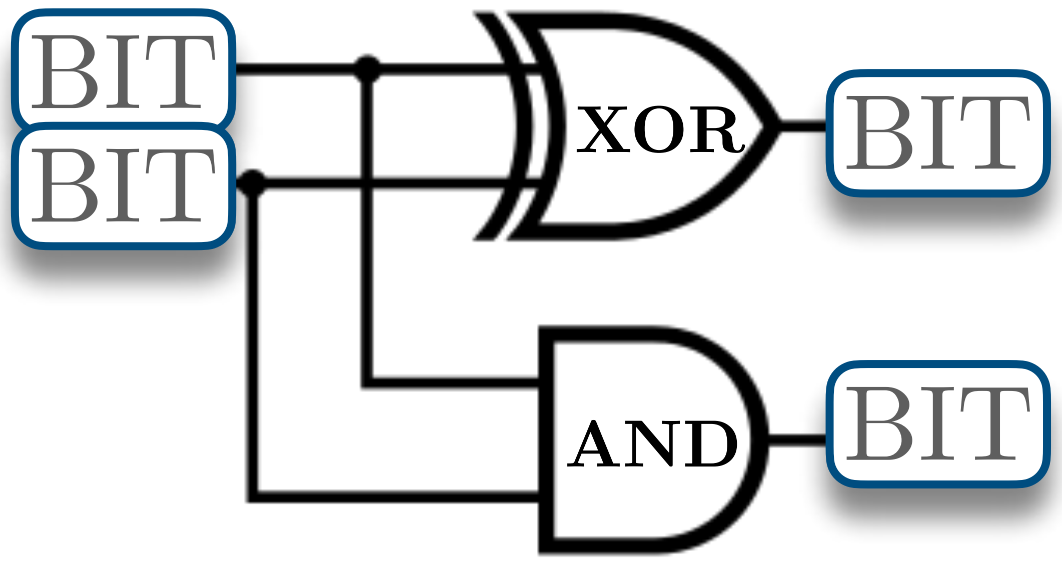
	Unit of Information	Basic Logic	Prog. Langage
Classical Computer	The Bit	Logical circuit	Fortran, C, Python ...
Quantum Computer	The Qubit	Quantum Circuit	

Classical Computer

The Bit



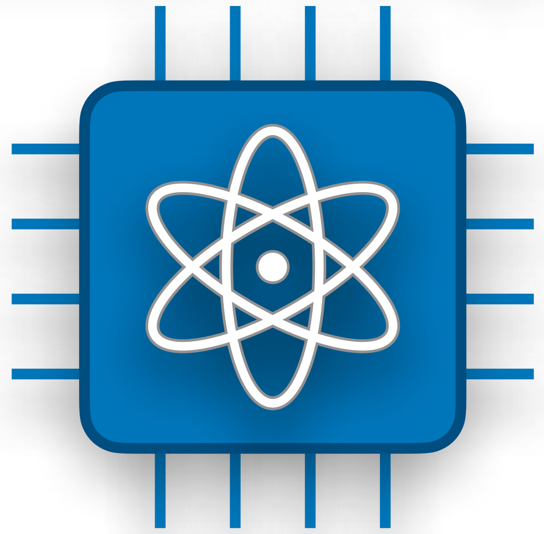
Logical circuit



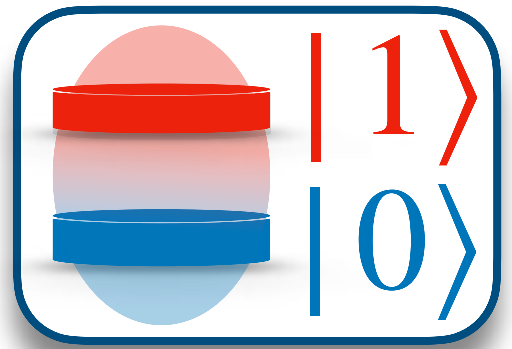
Fortran, C, Python ...

VS.

Quantum Computer

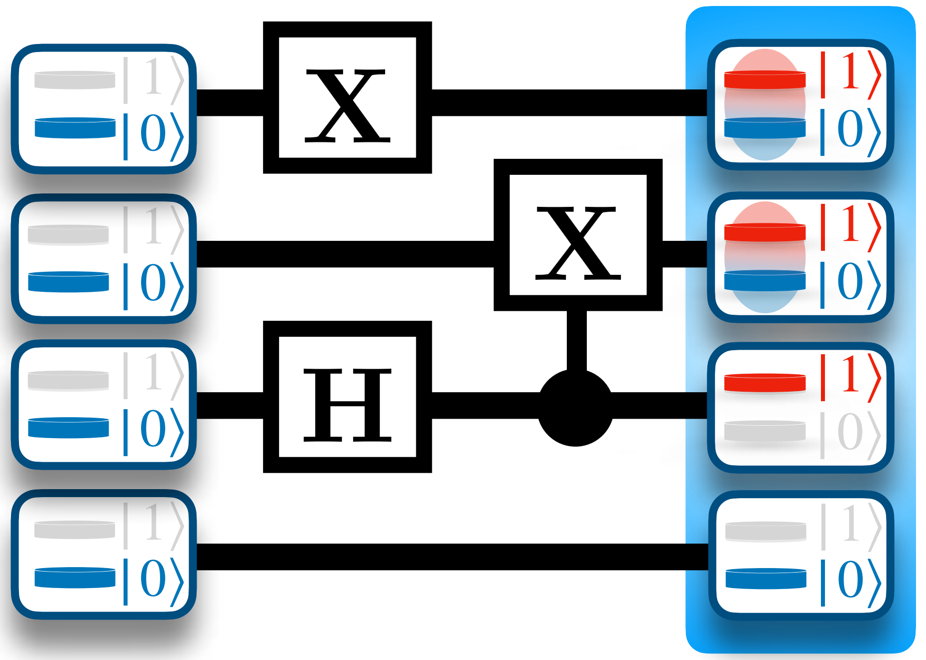


The Qubit

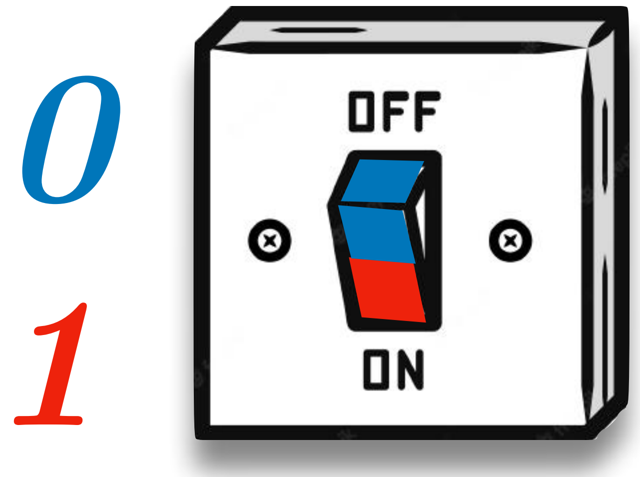
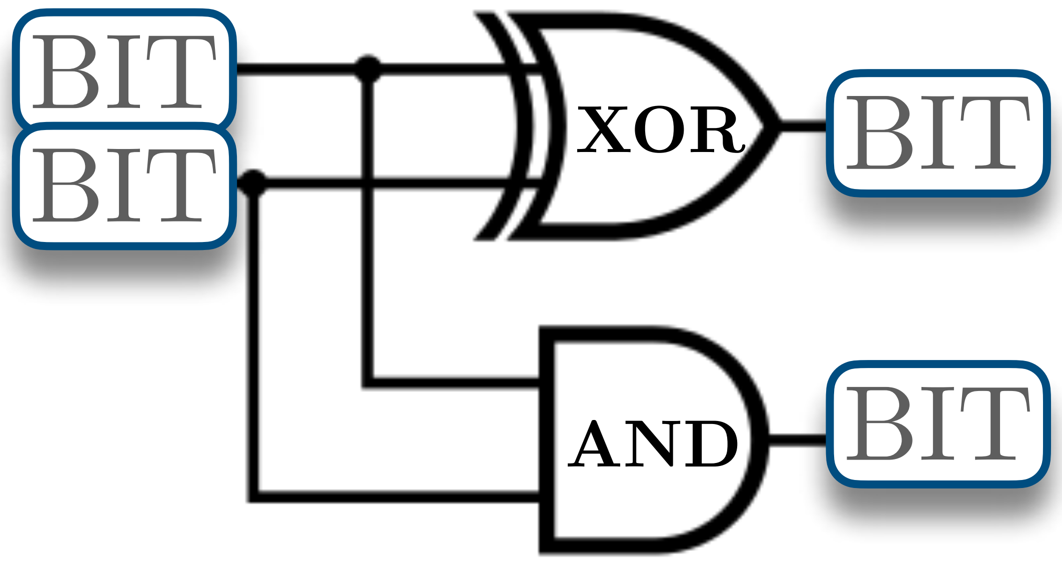
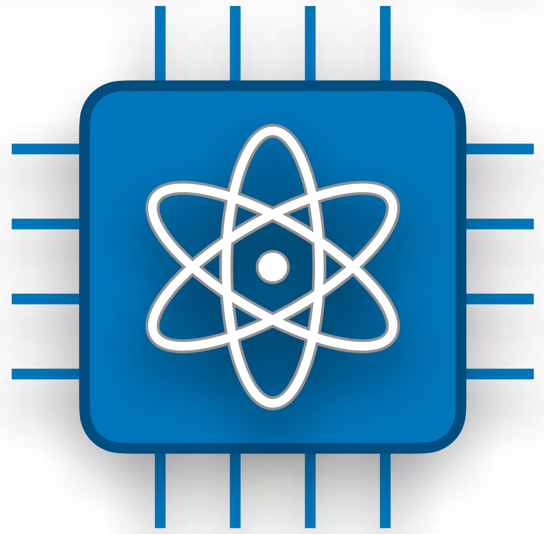
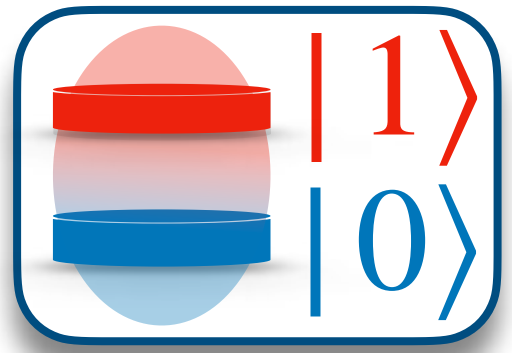
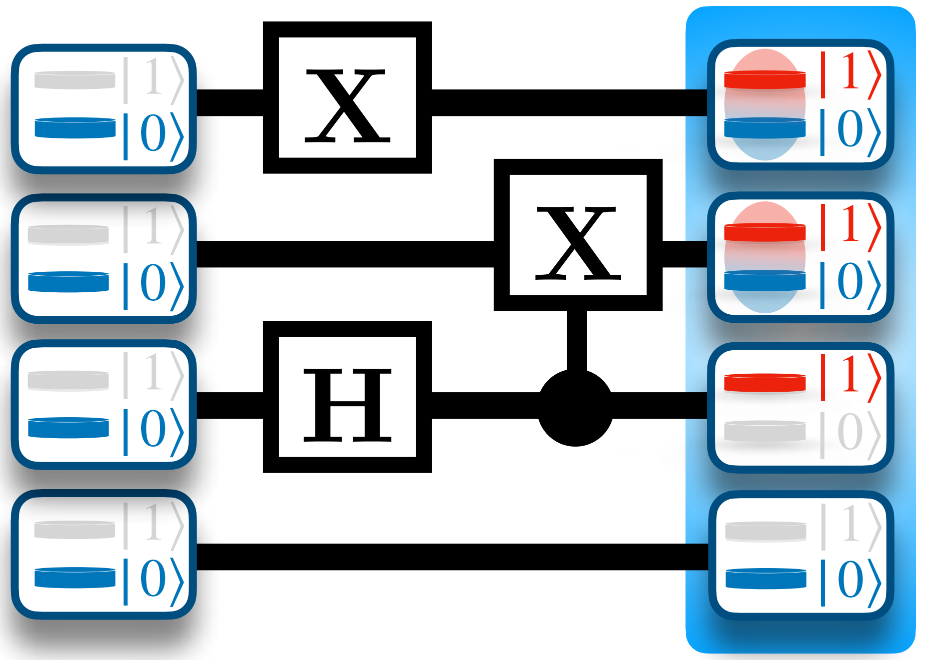
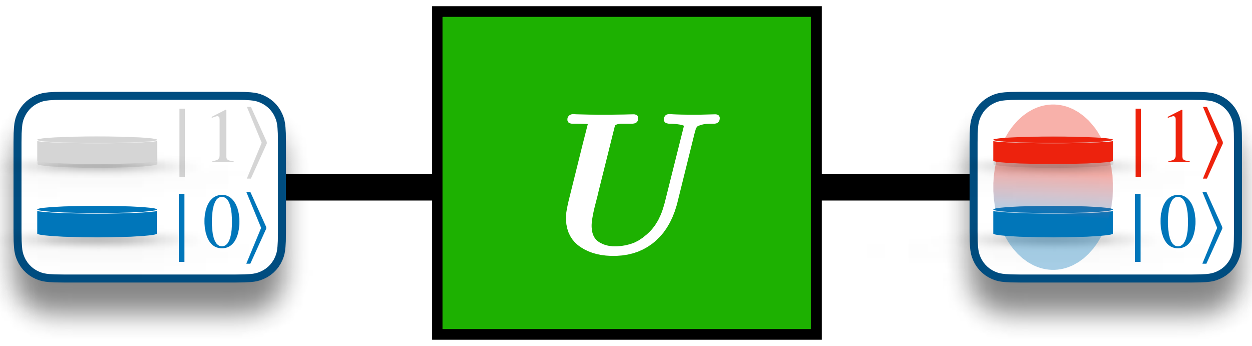


$$|Q\rangle = c_0|0\rangle + c_1|1\rangle$$

Quantum Circuit



I) Introduction to quantum computing

	Unit of Information	Basic Logic	Prog. Langage
Classical Computer 	The Bit 	Logical circuit 	Fortran, C, Python … 
VS.			
Quantum Computer 	The Qubit  $\lvert Q\rangle = c_0\lvert 0\rangle + c_1\lvert 1\rangle$	Quantum Circuit 	Quantum Physics ! (Unitary Transformations) 

I) Introduction to quantum computing

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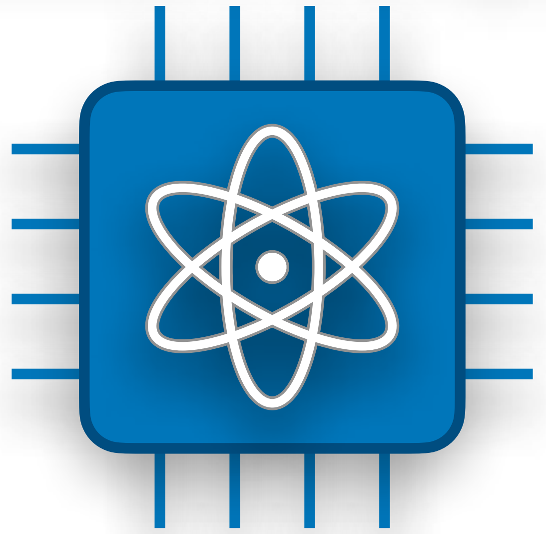
Classical Computer	The Bit	Logical circuit	Fortran, C, Python ...
Quantum Computer	The Qubit	Quantum Circuit	Quantum Physics ! (Unitary Transformations)

Classical Computer

VS.

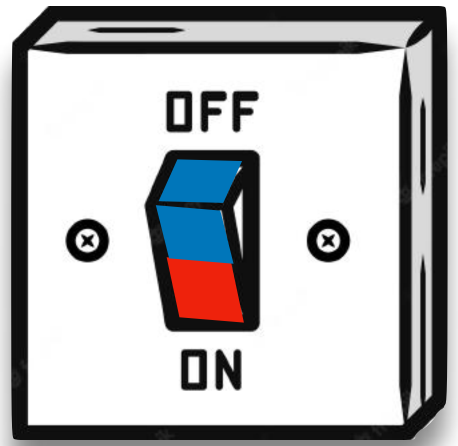
Quantum Computer



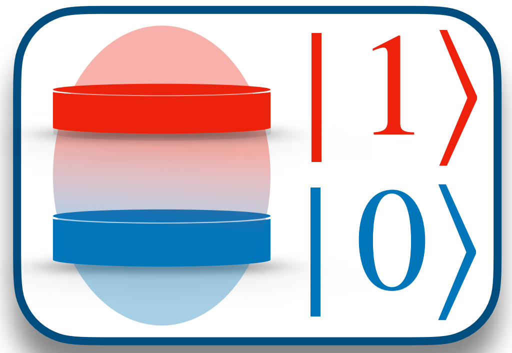
Unit of Information

The Bit

0
1



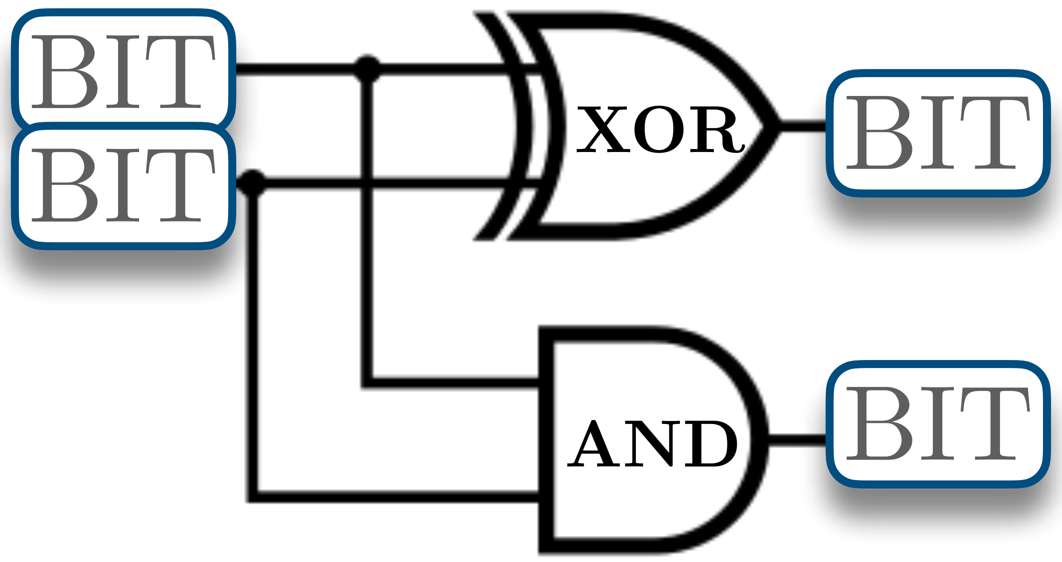
The Qubit



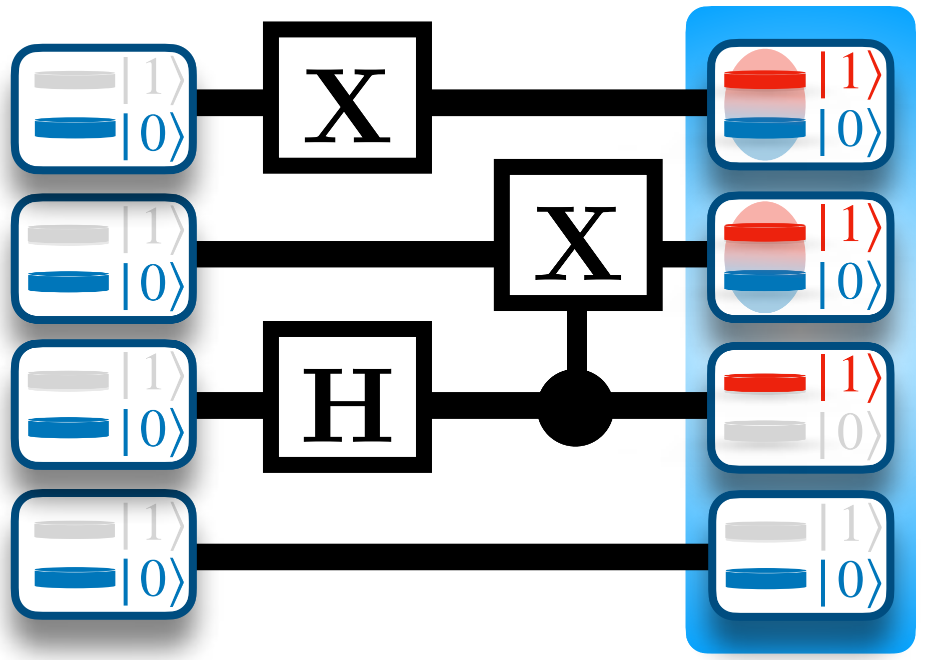
$$|Q\rangle = c_0|0\rangle + c_1|1\rangle$$

Basic Logic

Logical circuit



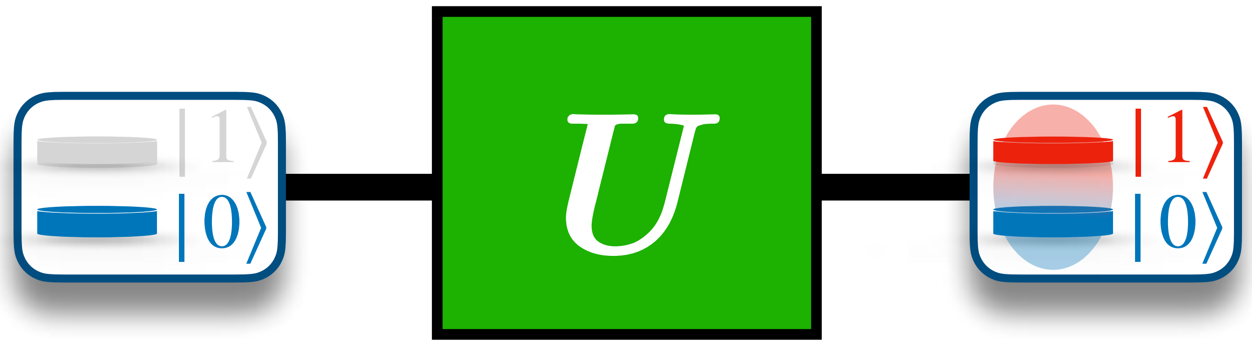
Quantum Circuit



Prog. Langage

Fortran, C, Python ...

Quantum Physics !
(Unitary Transformations)



QUESTION Why a Quantum computer is more powerful than a classical one ?

I) Introduction to quantum computing

ANSWER How to encode information in Qubits vs. Bits

I) Introduction to quantum computing

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2^N *Bitstrings* accessible from N (qu)bits

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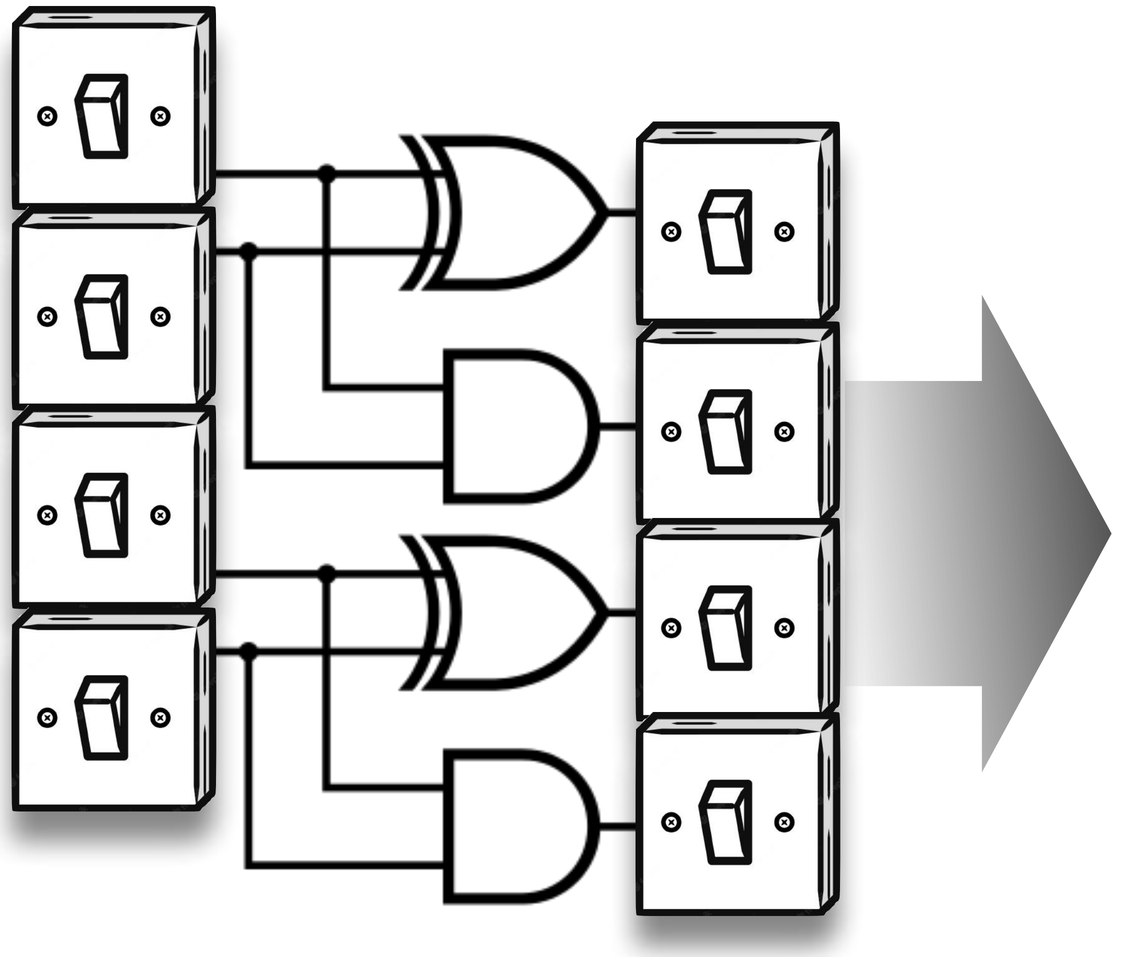

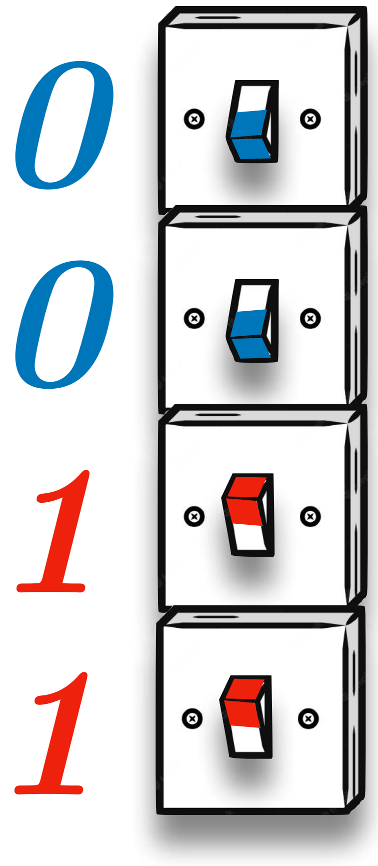

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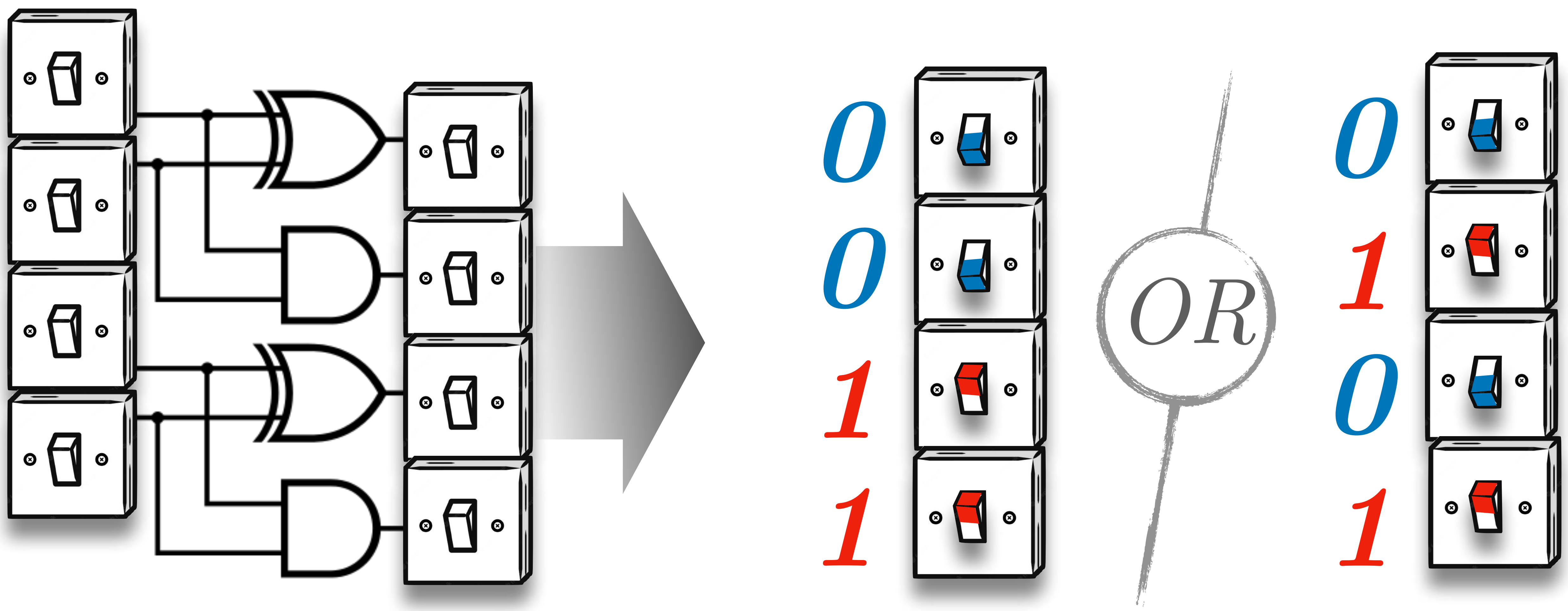

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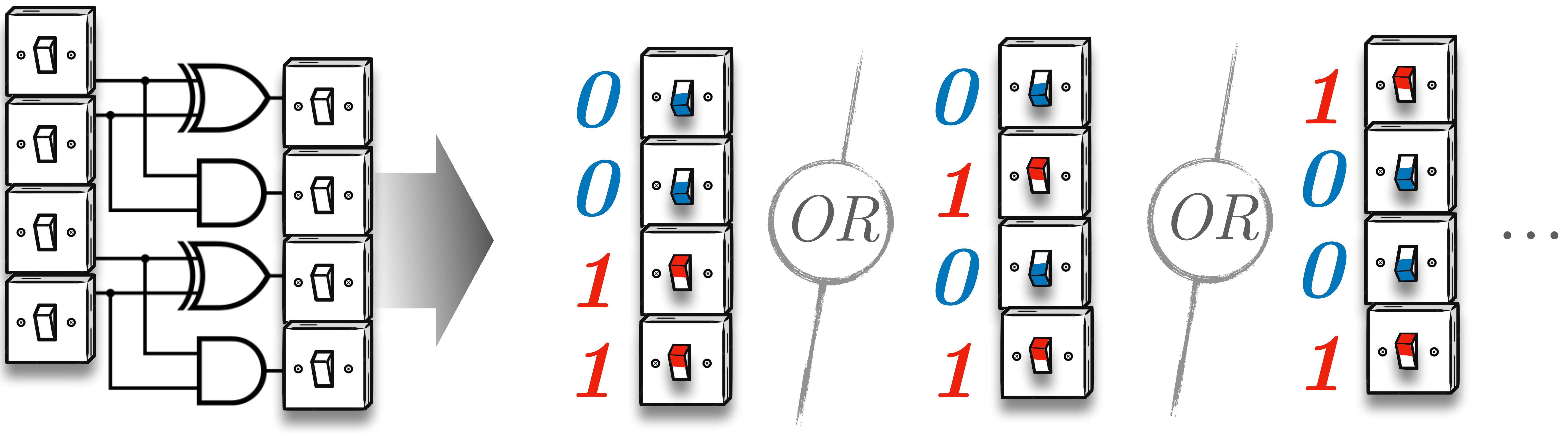

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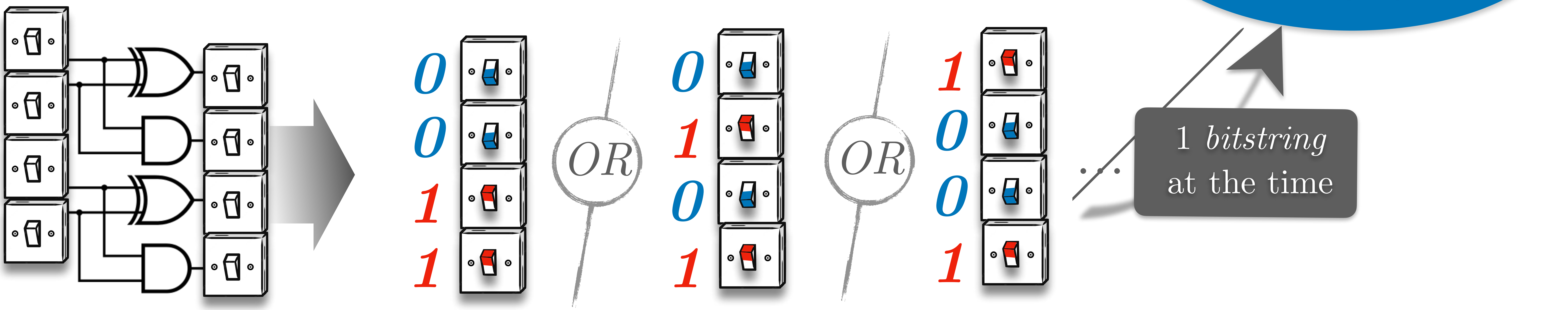

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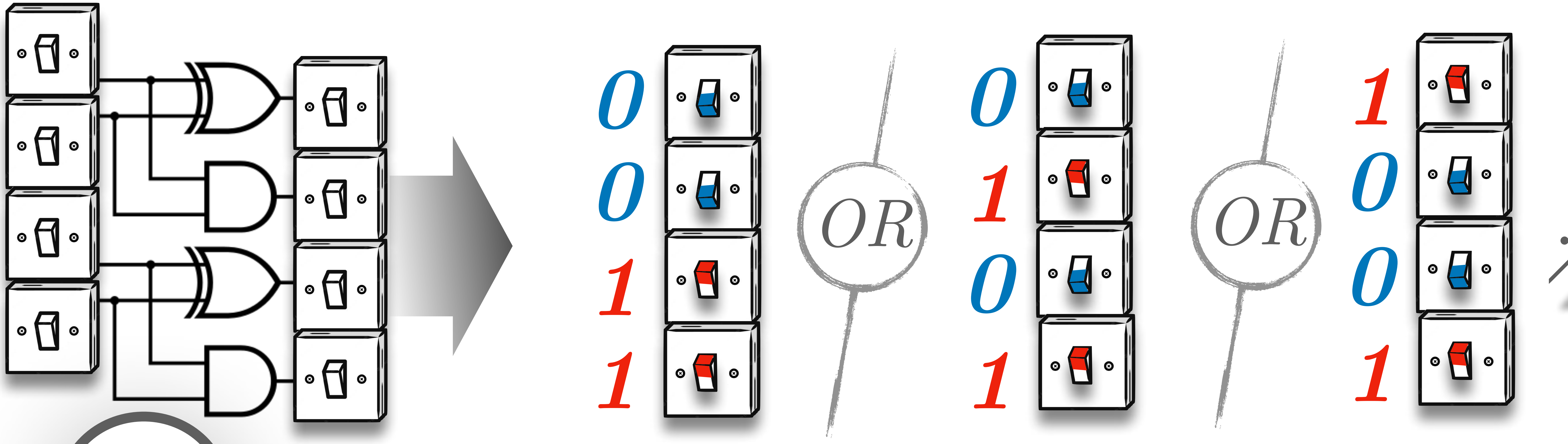
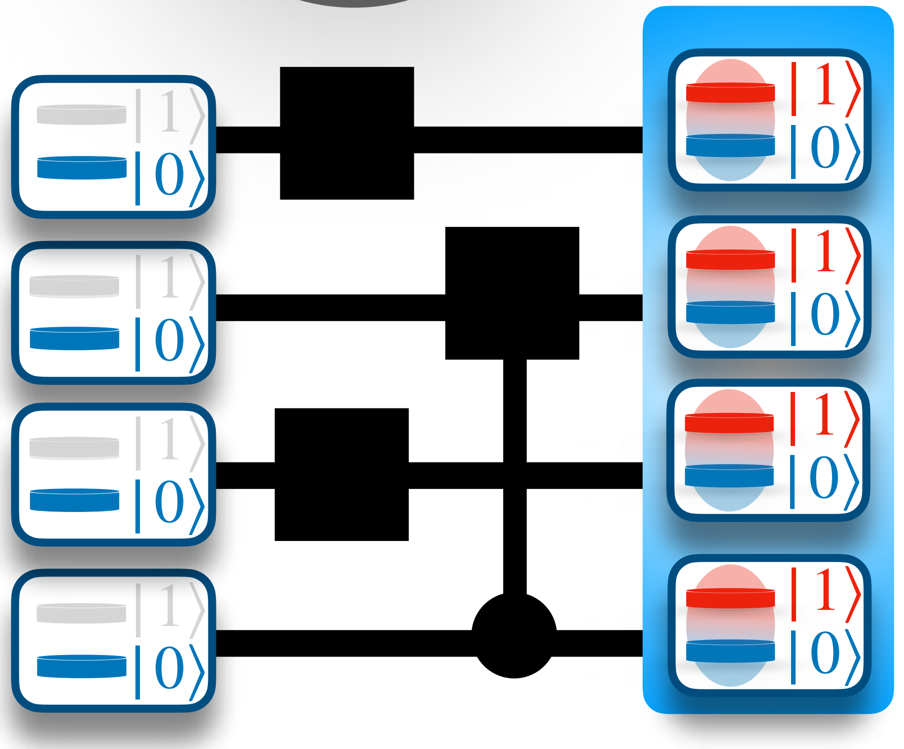


1 *bitstring* at the time

VS.



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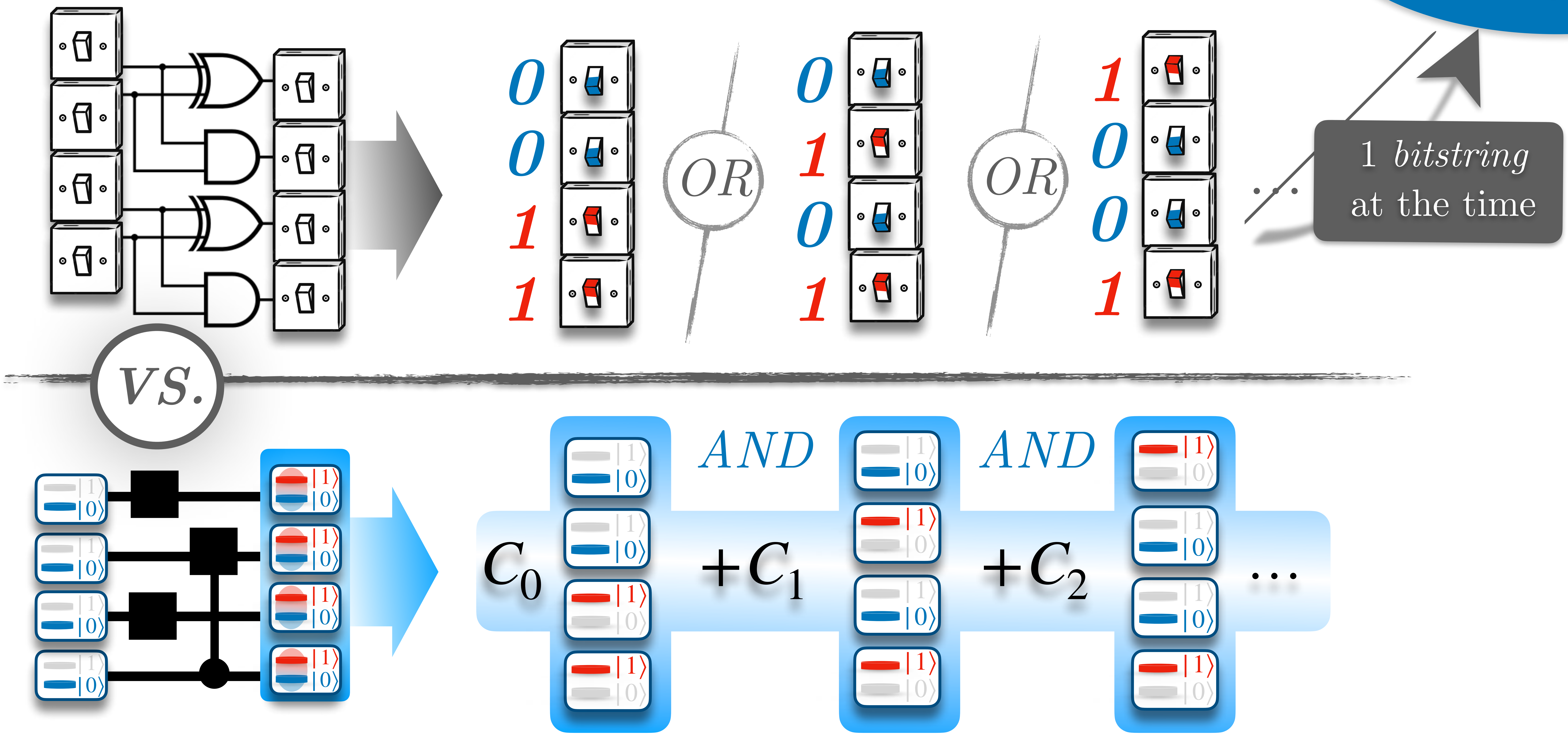

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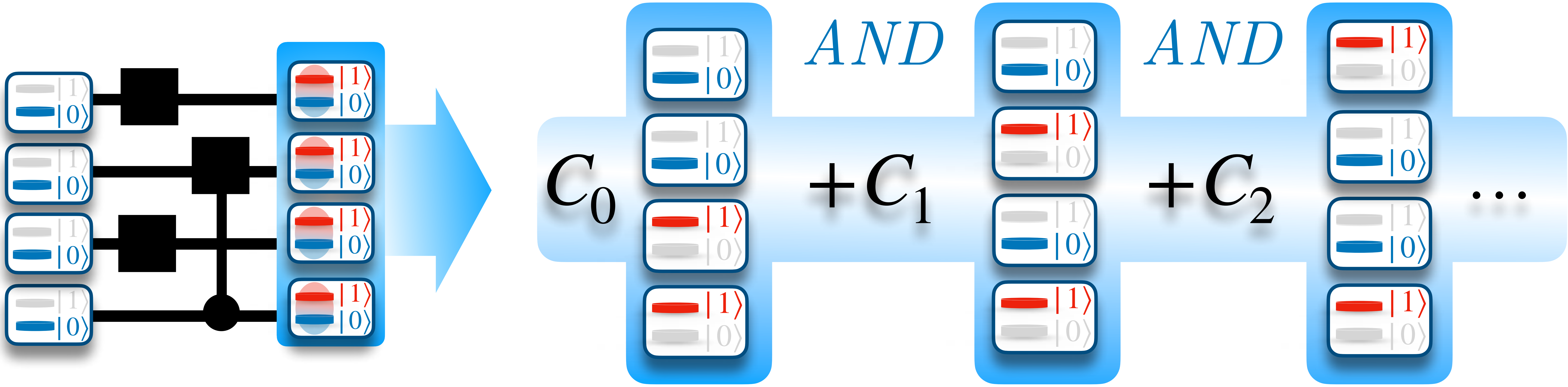
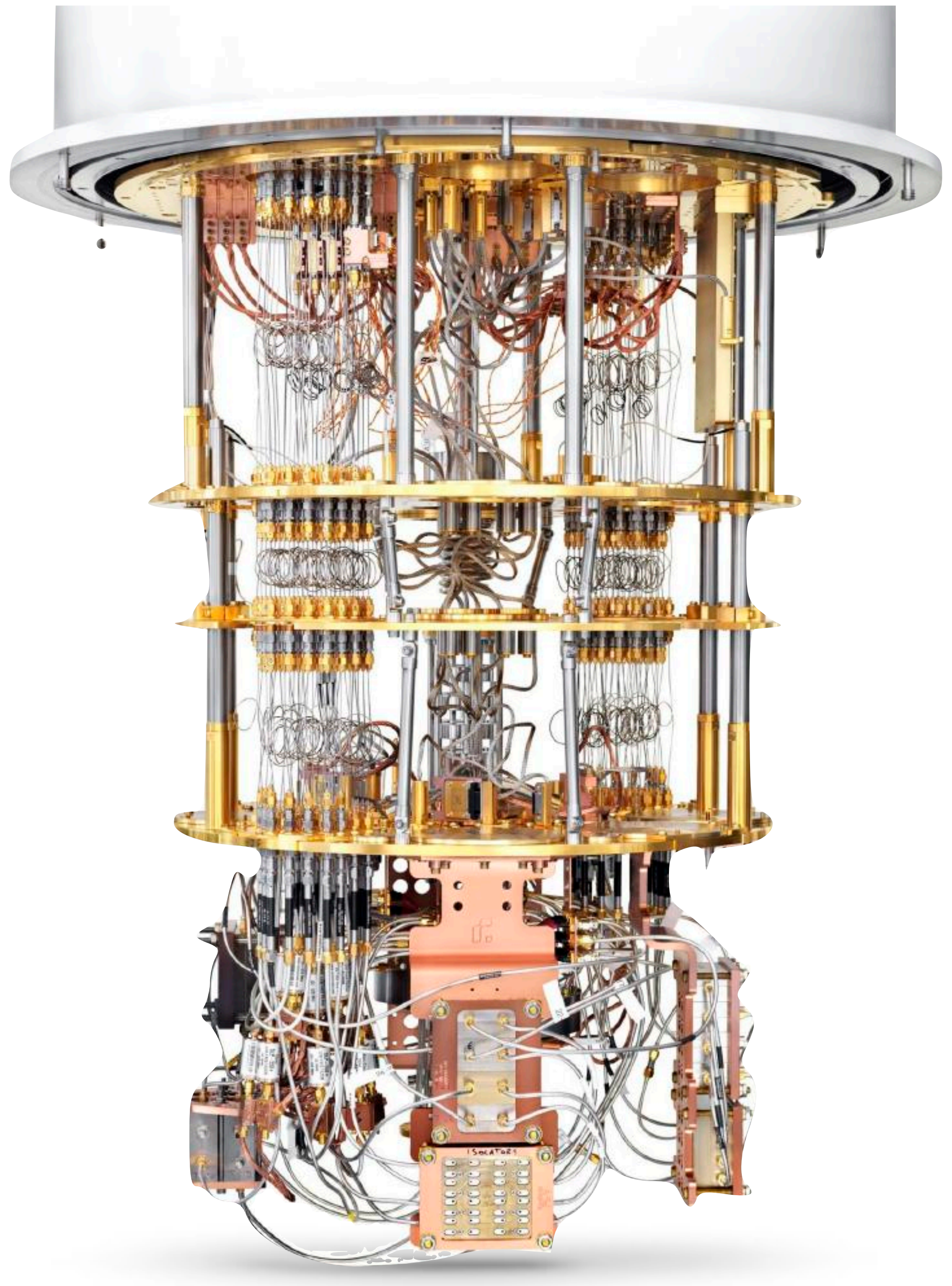
Exemple of Full Quantum Superposition



Let's build a quantum circuit !

I) Introduction to quantum computing



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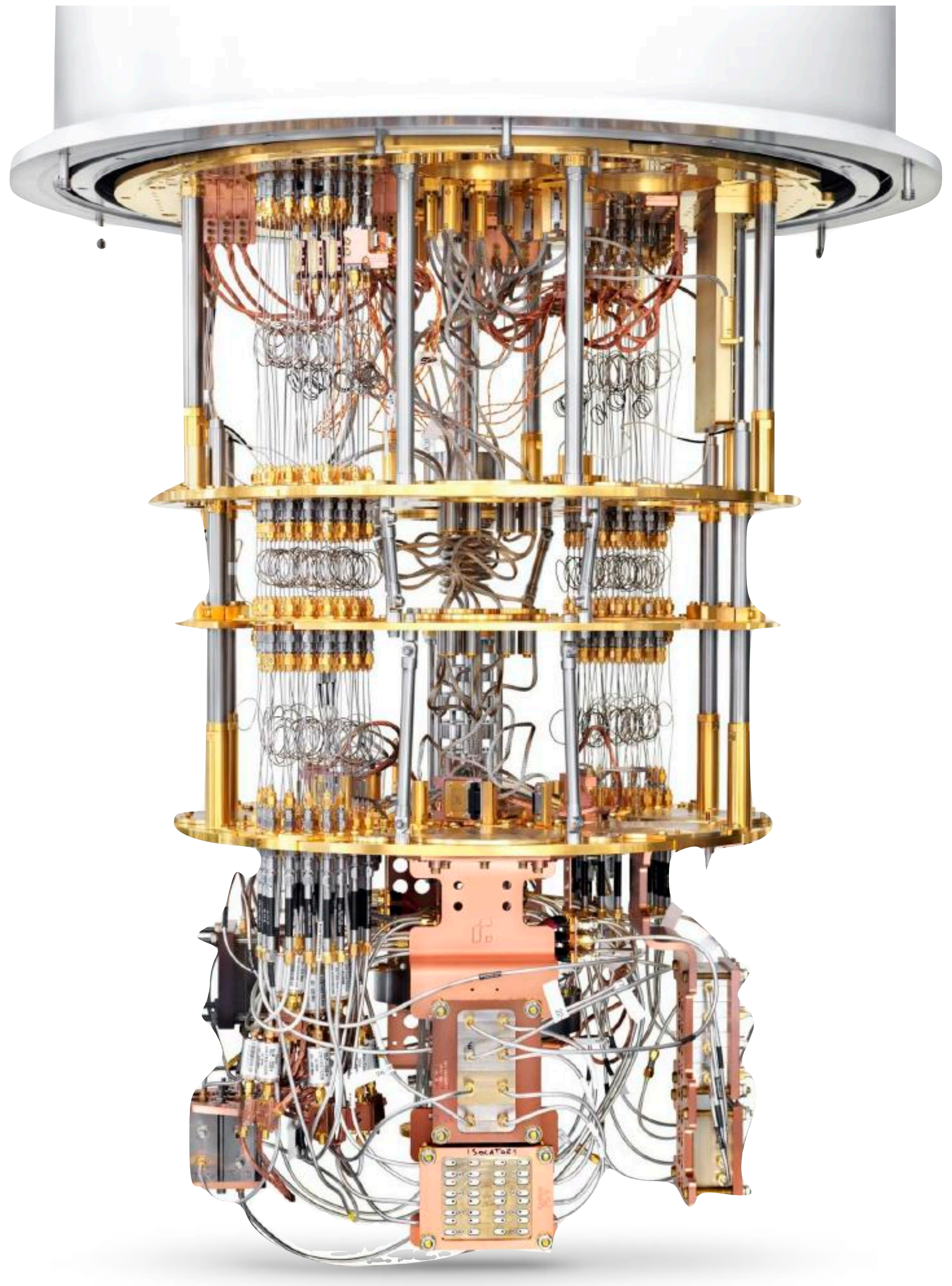
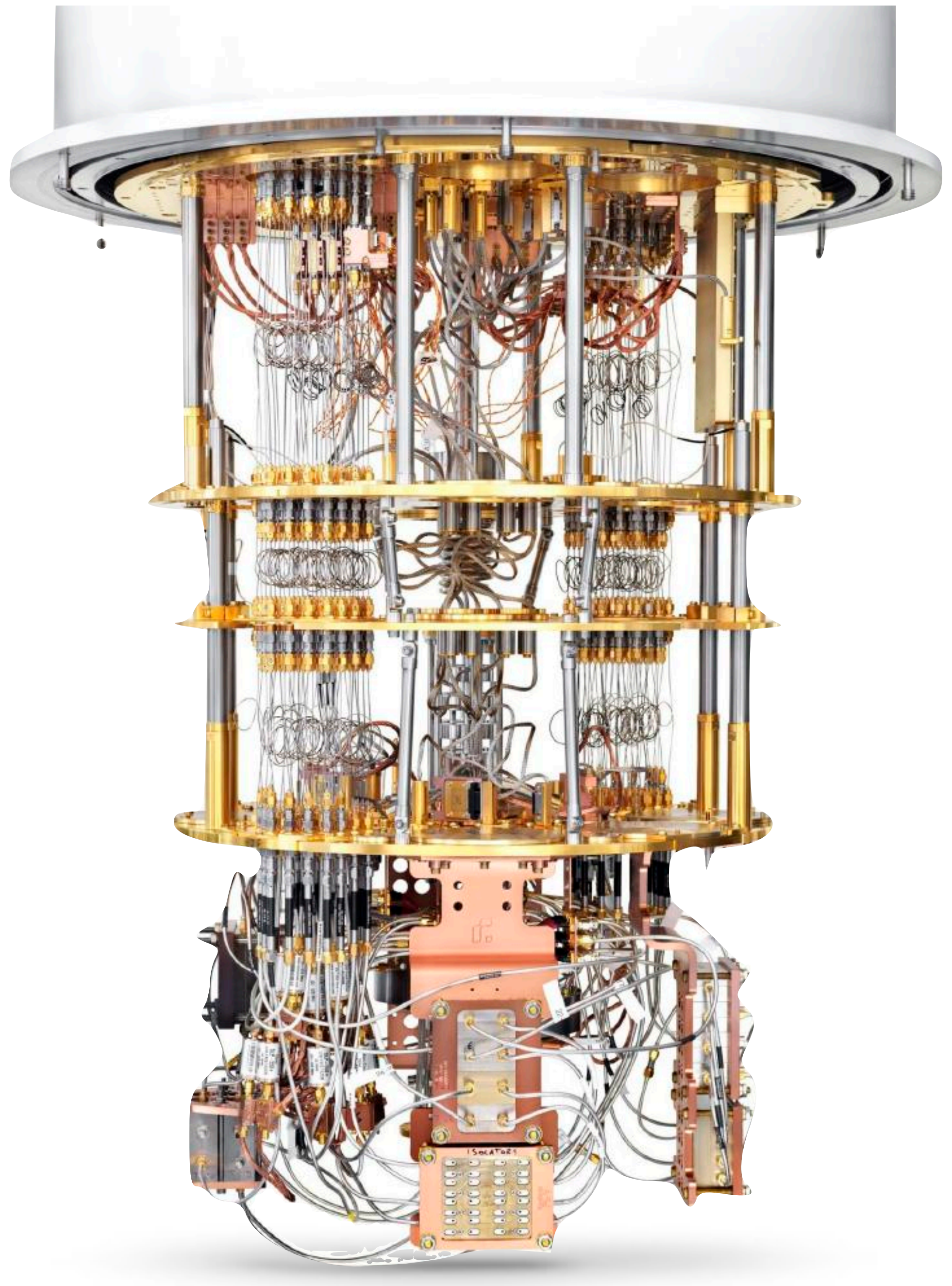


Emerging quantum computers are "NISQ" devices.

(NISQ : Noisy Intermediate-Scale Quantum)



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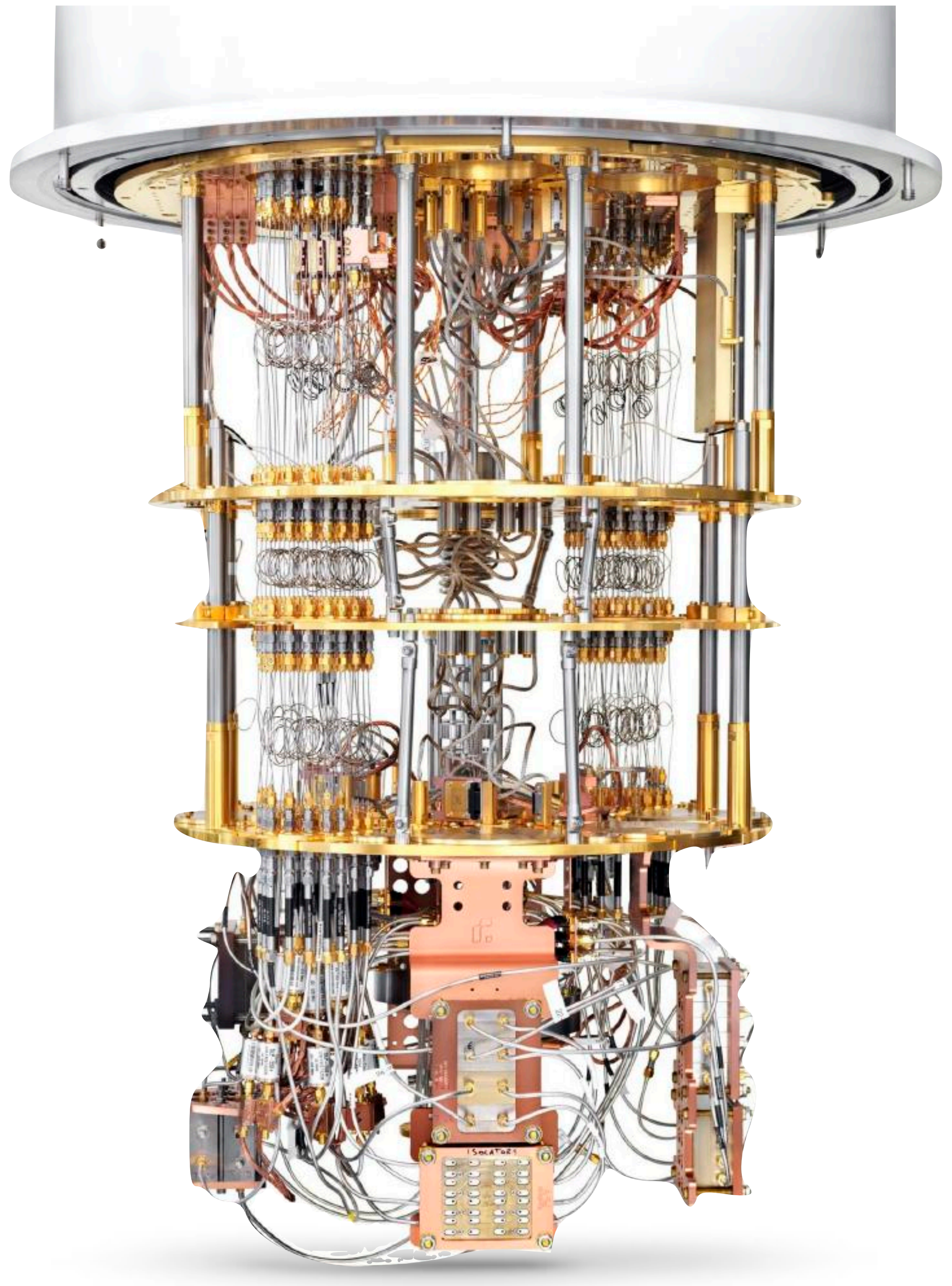
Quantum decoherence

(**qubits = open quantum system**).

I) Introduction to quantum computing



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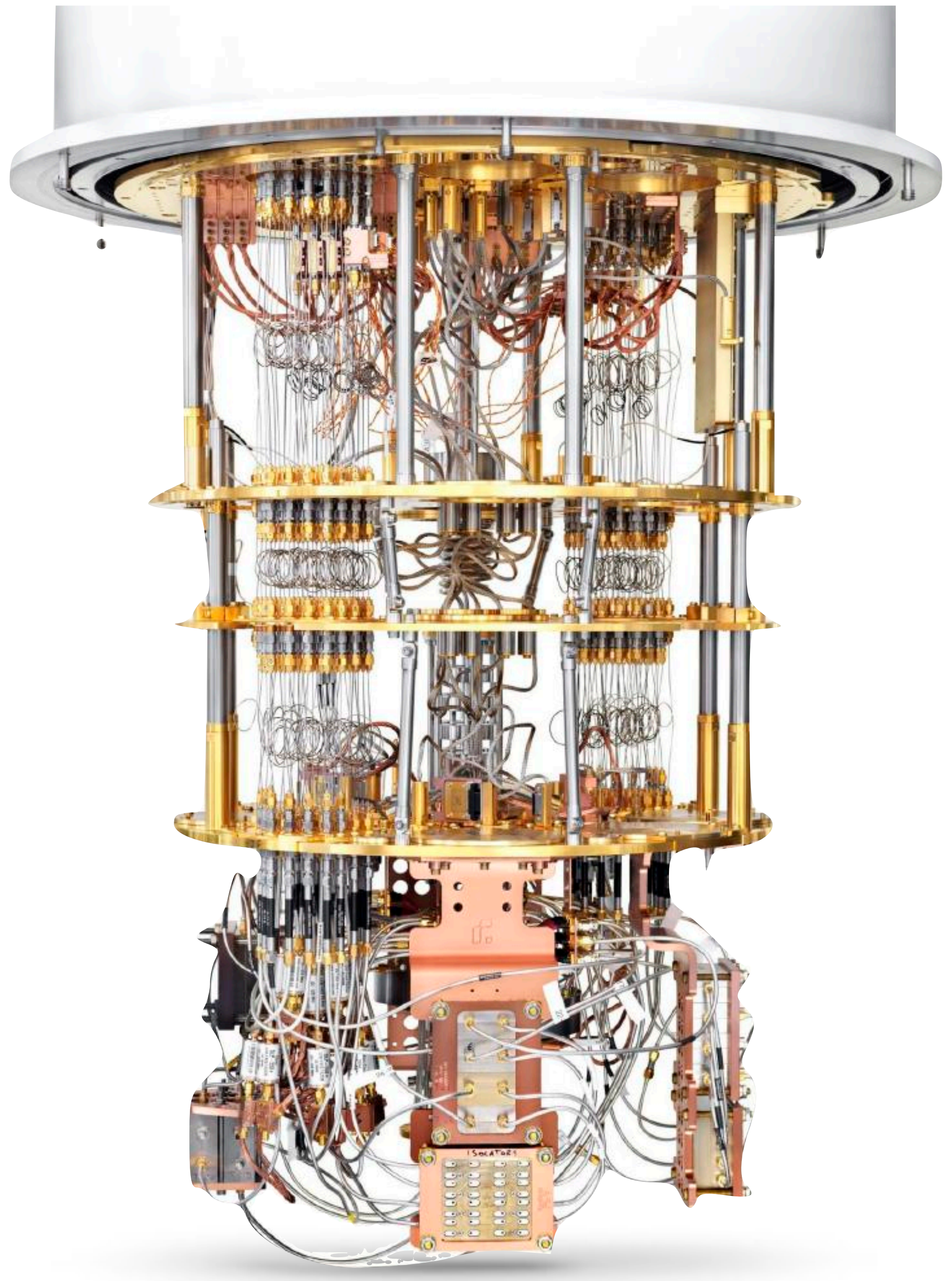
Only **a few qubits** accessible

$N_{qubits} \sim 10$



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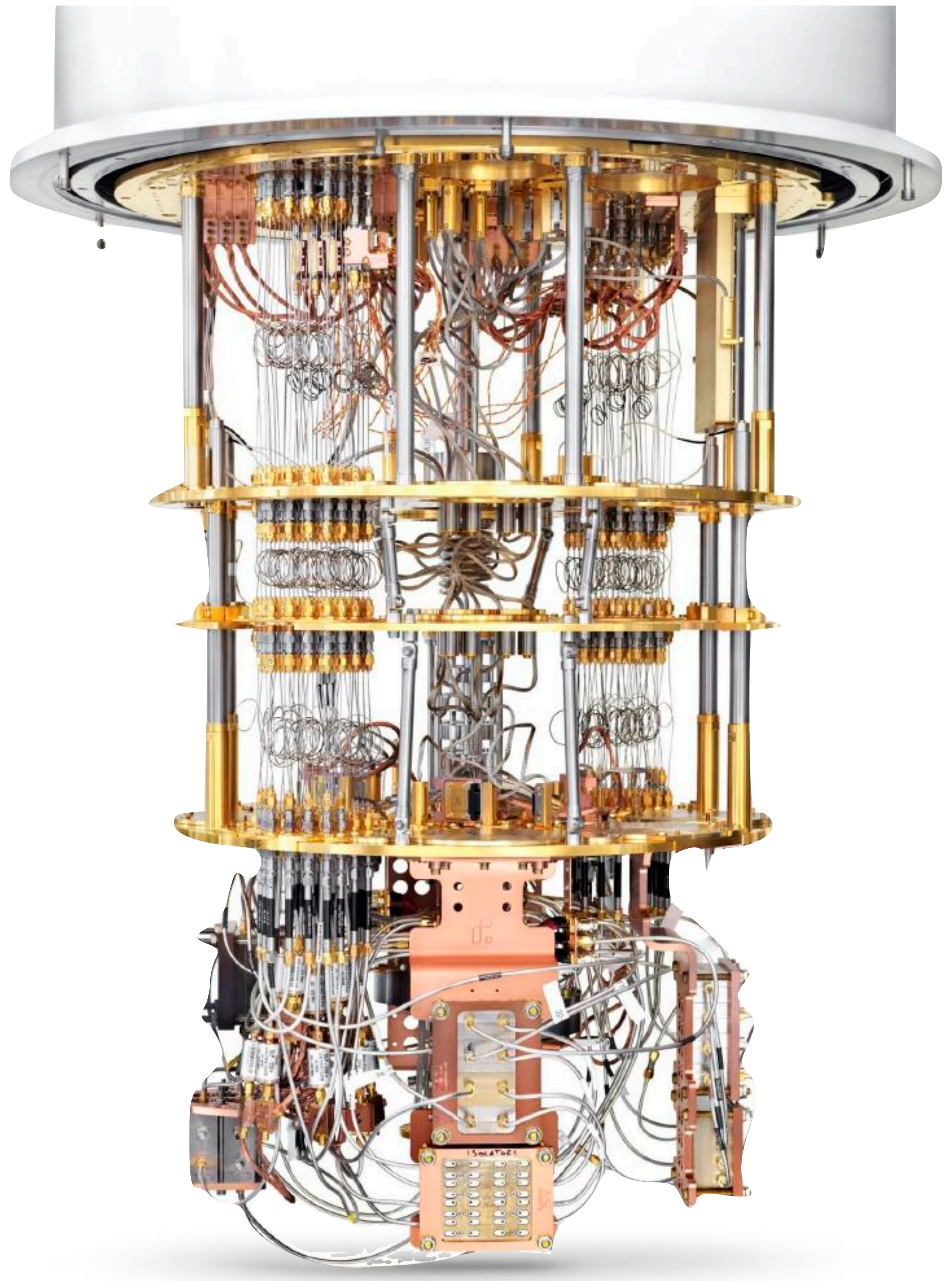
NISQ algorithms

I) Introduction to quantum computing



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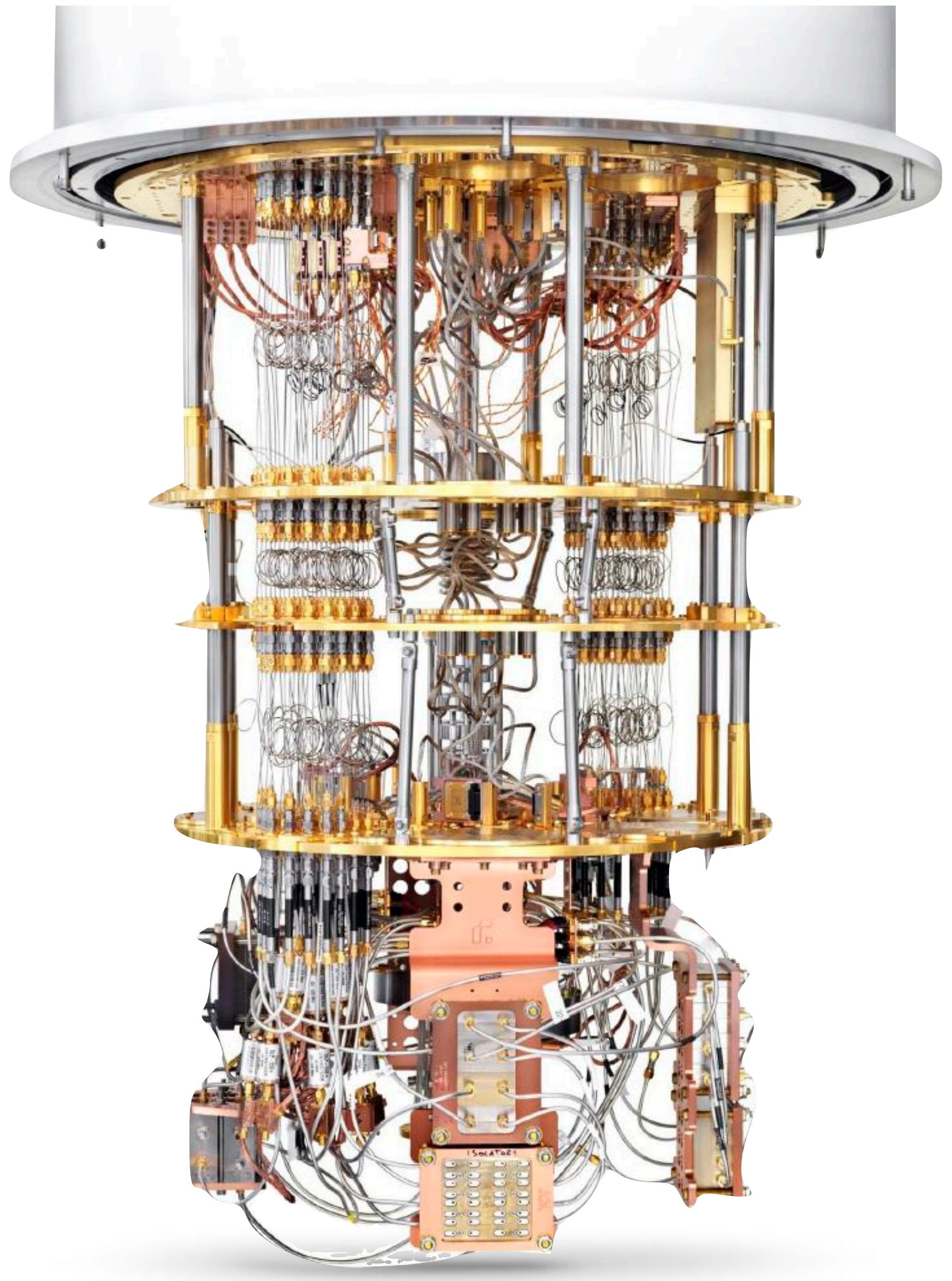
NISQ algorithms

- ***Exponentially*** **fewer resources to store information**



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Quantum decoherence (**qubits = open quantum system**).

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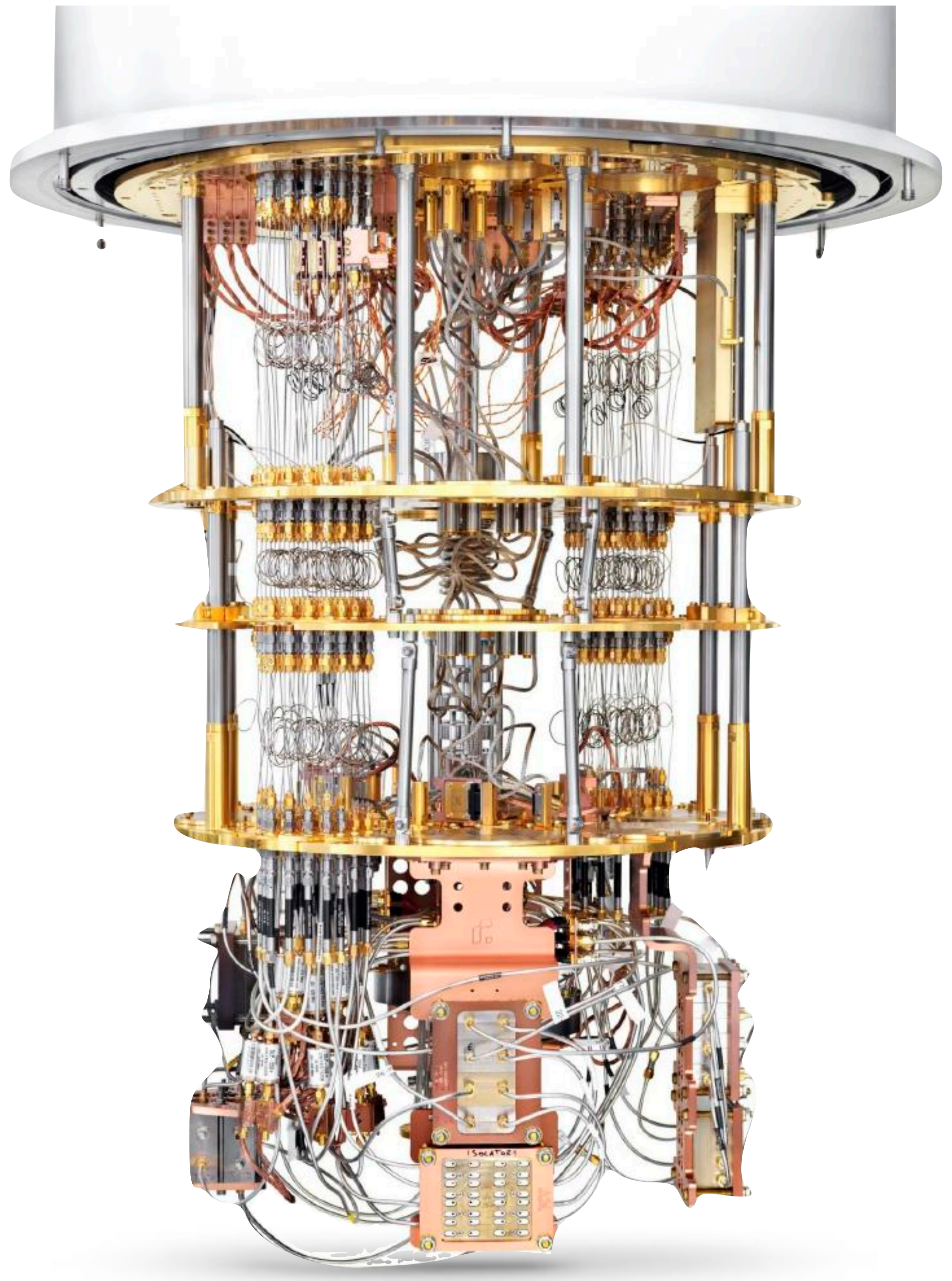
NISQ algorithms

- ***Exponentially* fewer resources to store information**
- Based on **a few qubits and quantum gates.**

I) Introduction to quantum computing



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Quantum decoherence
(**qubits = open quantum system**).

Only **a few qubits** accessible
$N_{qubits} \sim 10$

NISQ algorithms

- ***Exponentially* fewer resources to store information**
- Based on **a few qubits and quantum gates.**
- Pretty resistant to the **noise effects**.

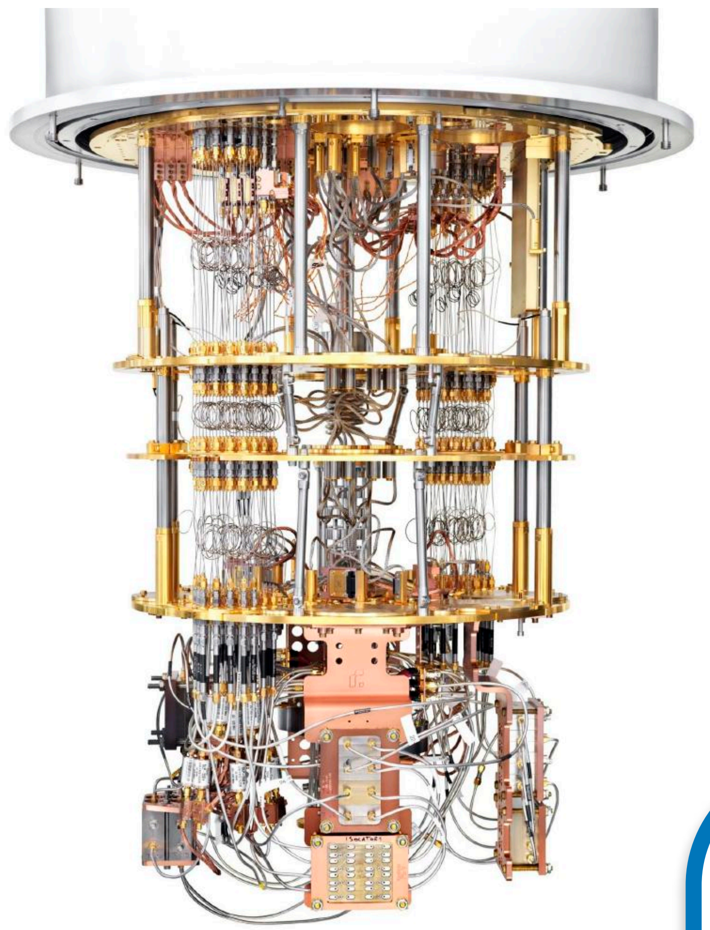
I) Introduction to quantum computing

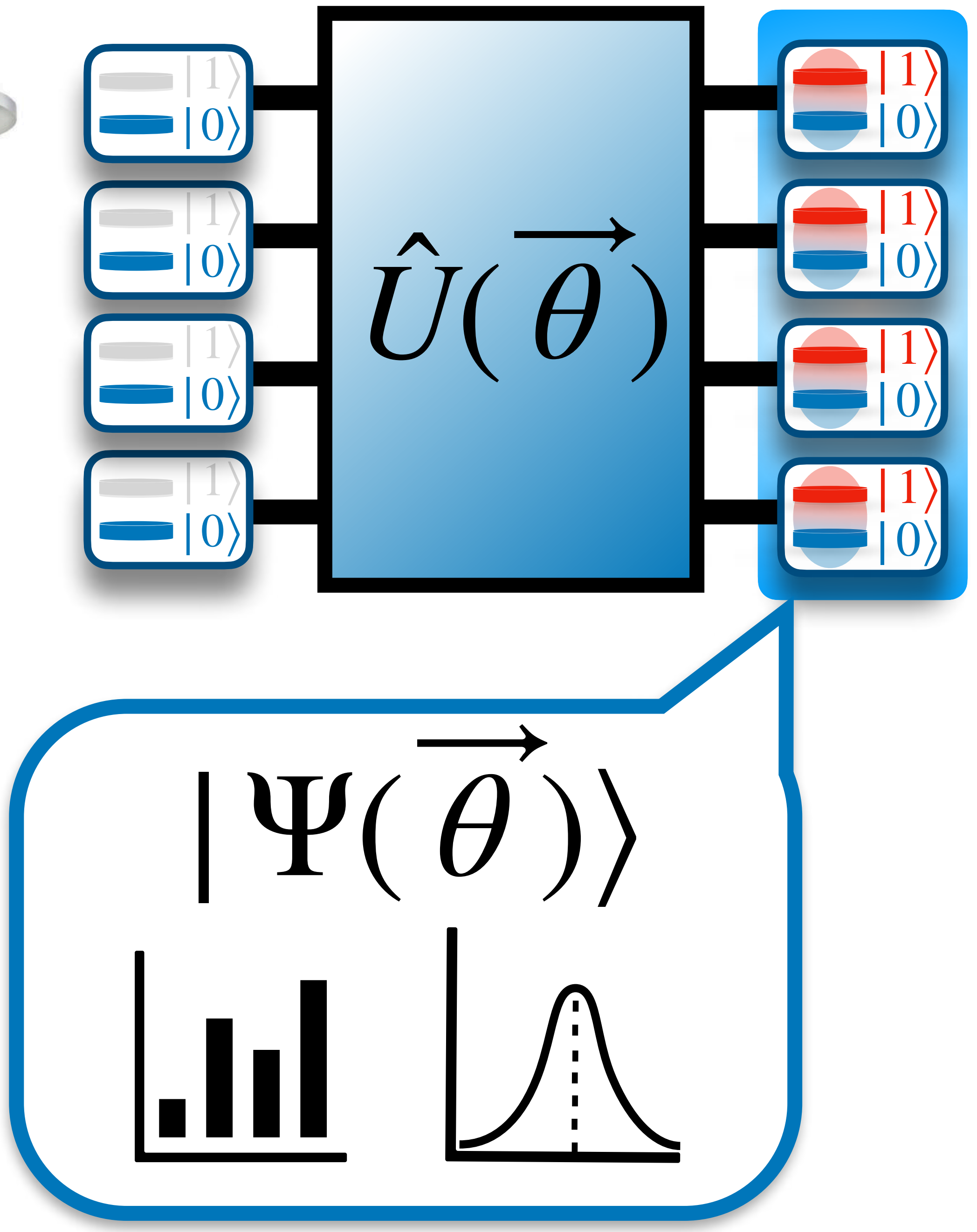
NISQ algorithm: Hybrid Quantum/Classical methods

I) Introduction to quantum computing

NISQ algorithm: Hybrid Quantum/Classical methods

Quantum Computer





I) Introduction to quantum computing

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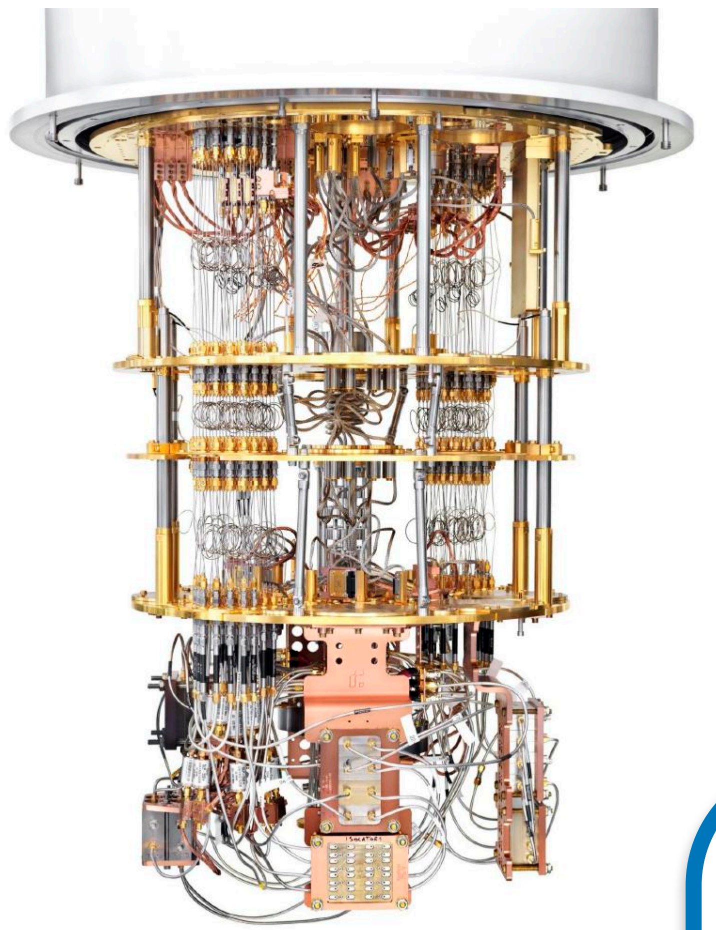
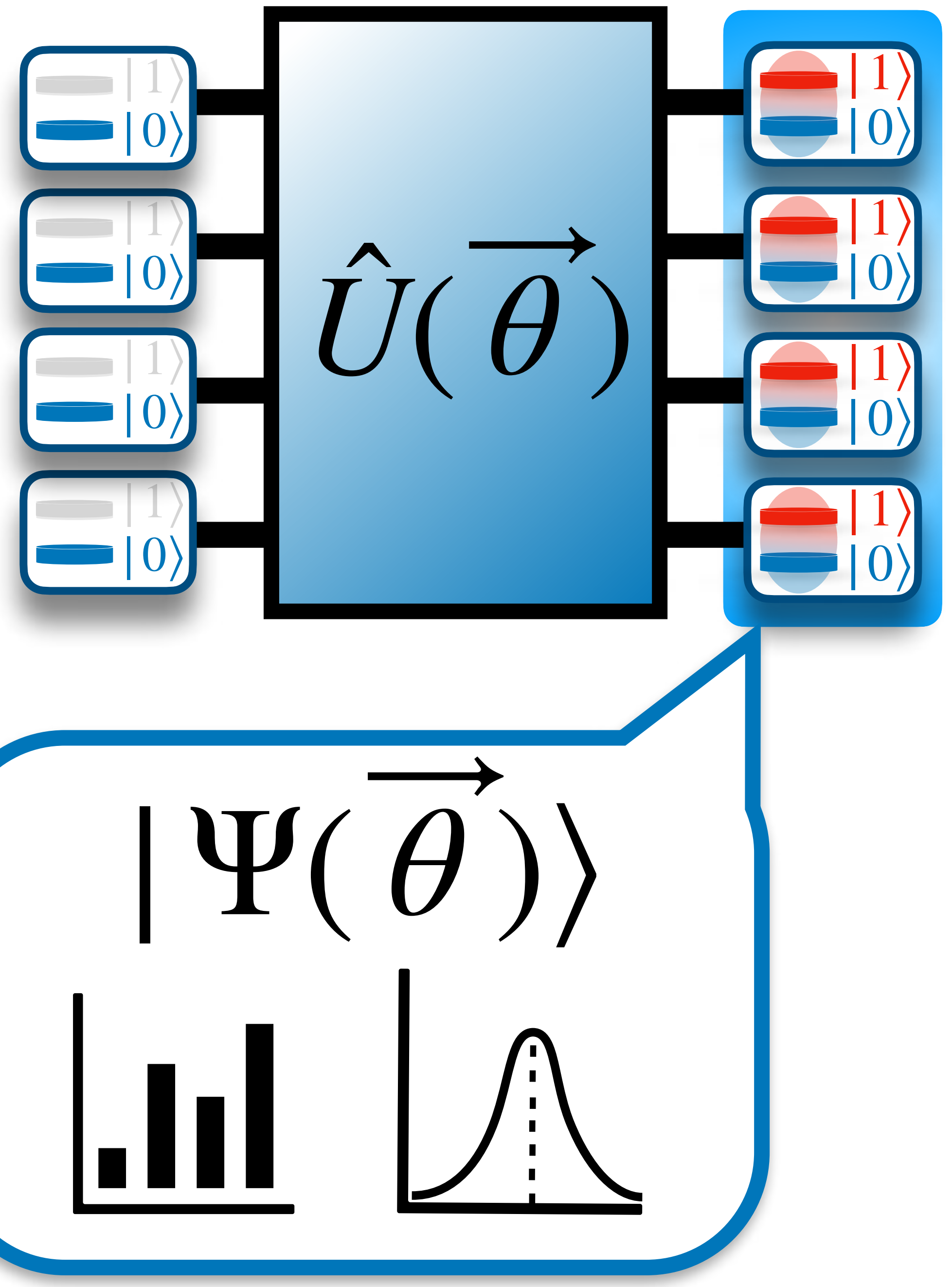
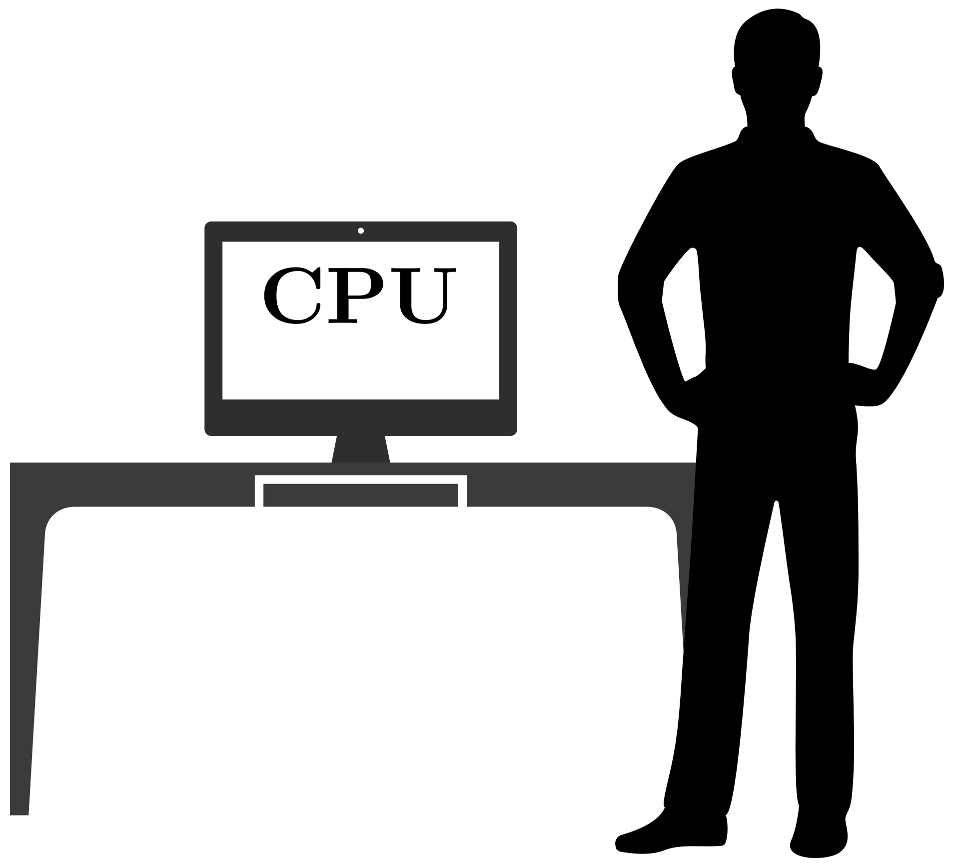




Classical Computer



Classical
Optimization of $\vec{\theta}$

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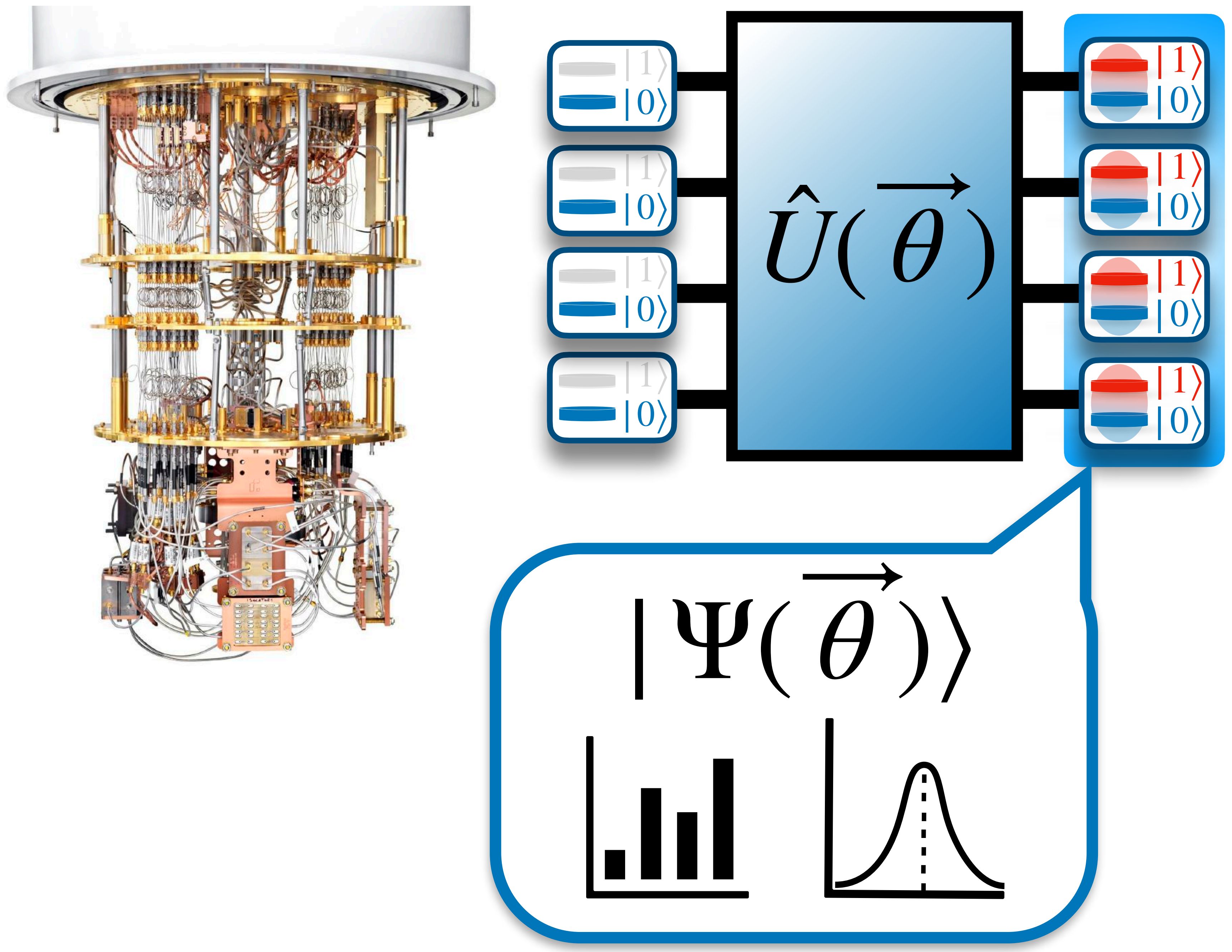
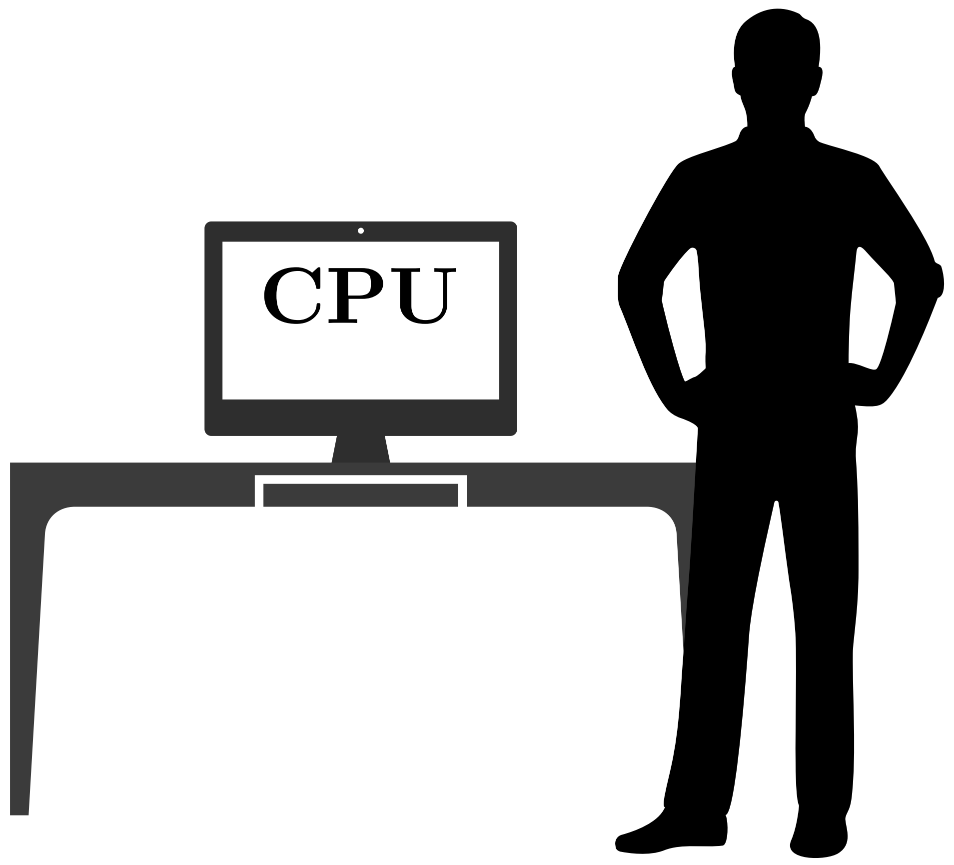


Measure

$$\langle \hat{O}_{\Psi(\vec{\theta})} \rangle = \langle \Psi(\vec{\theta}) | \hat{O} | \Psi(\vec{\theta}) \rangle$$

Classical Computer



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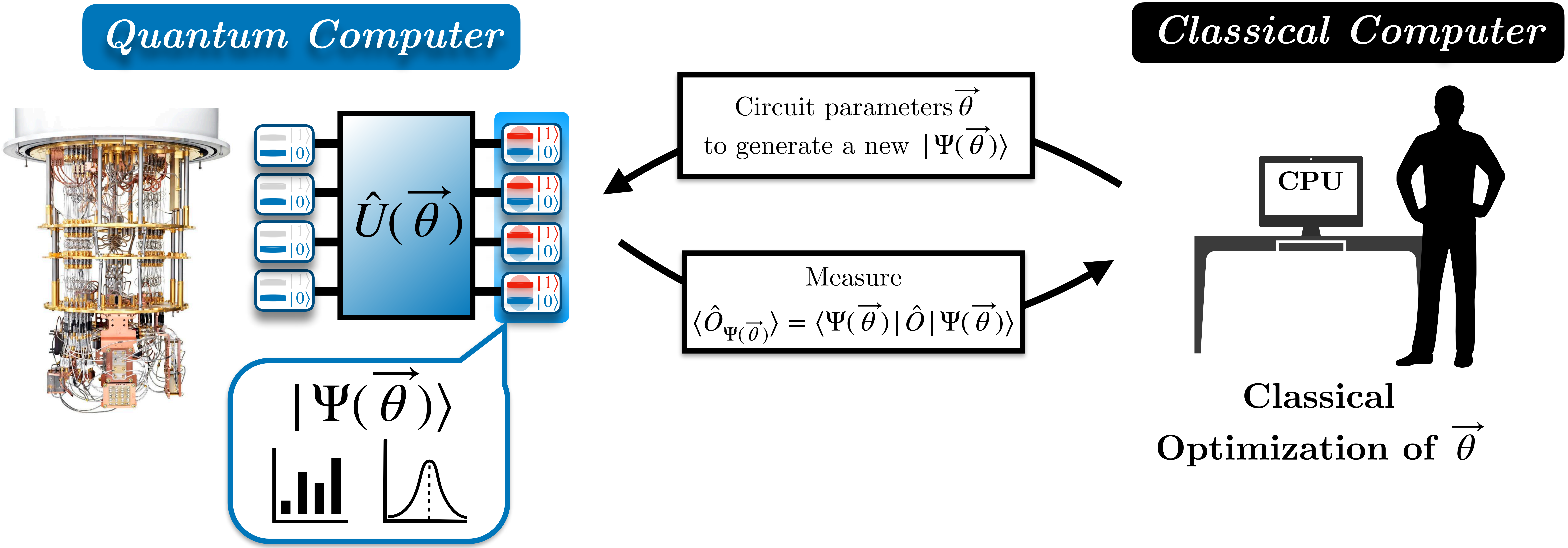

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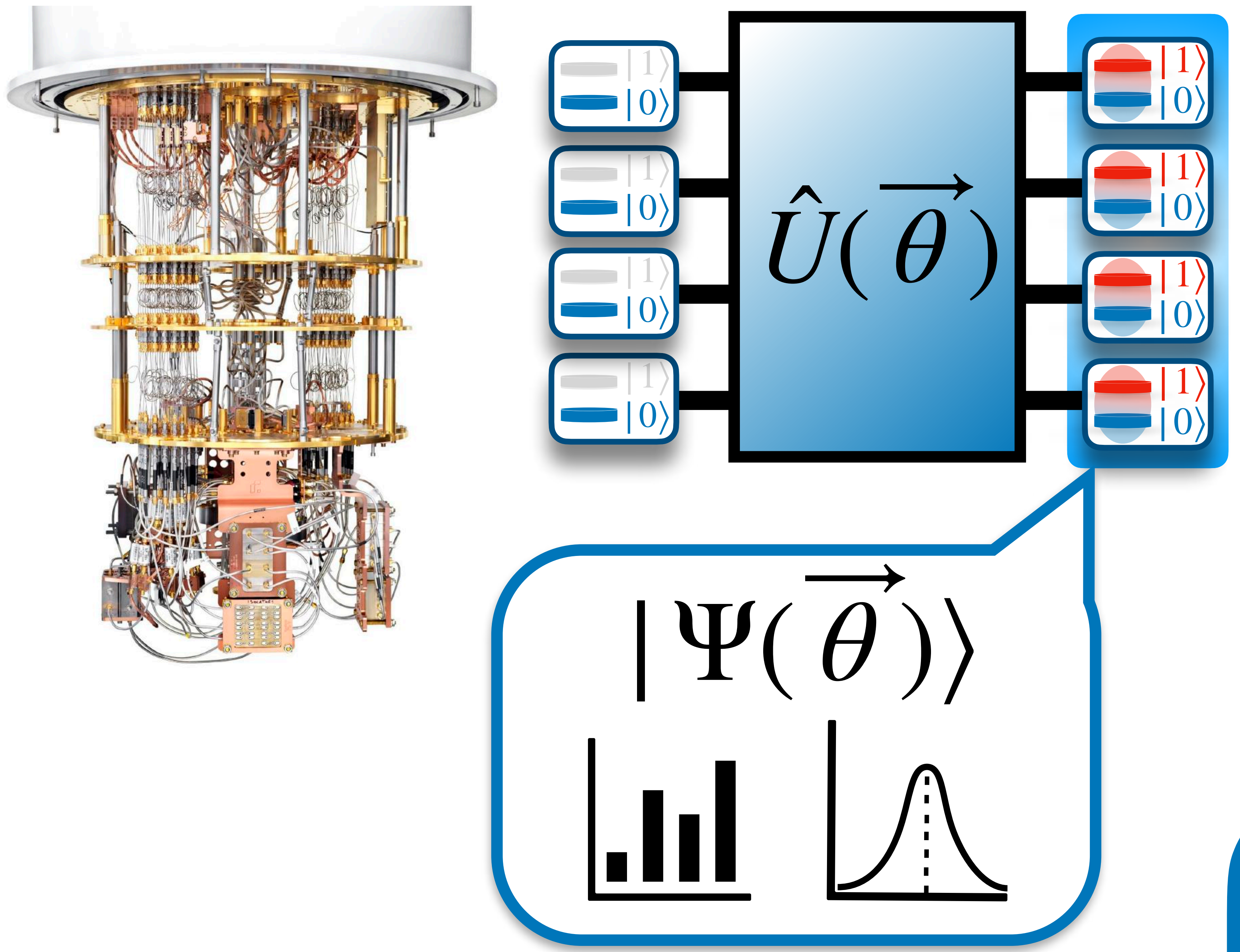
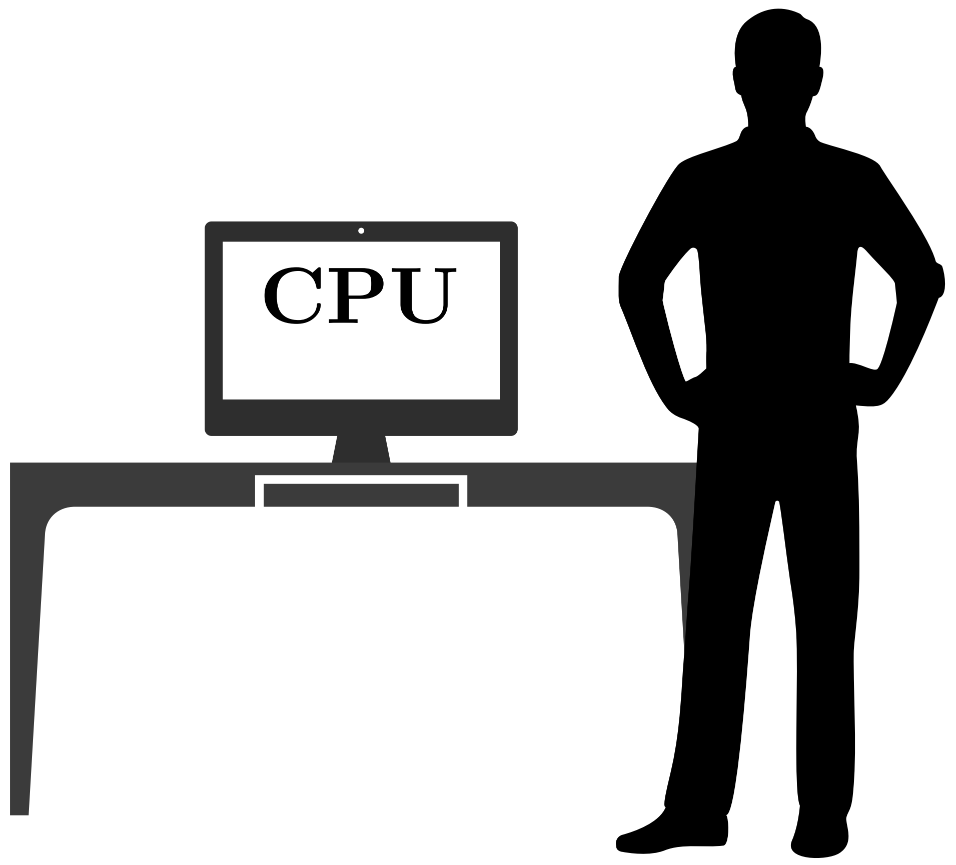


Circuit parameters $\vec{\theta}$ to generate a new $|\Psi(\vec{\theta})\rangle$

Measure $\langle \hat{O}_{\Psi(\vec{\theta})}\rangle = \langle \Psi(\vec{\theta})|\hat{O}|\Psi(\vec{\theta})\rangle$

Classical Computer



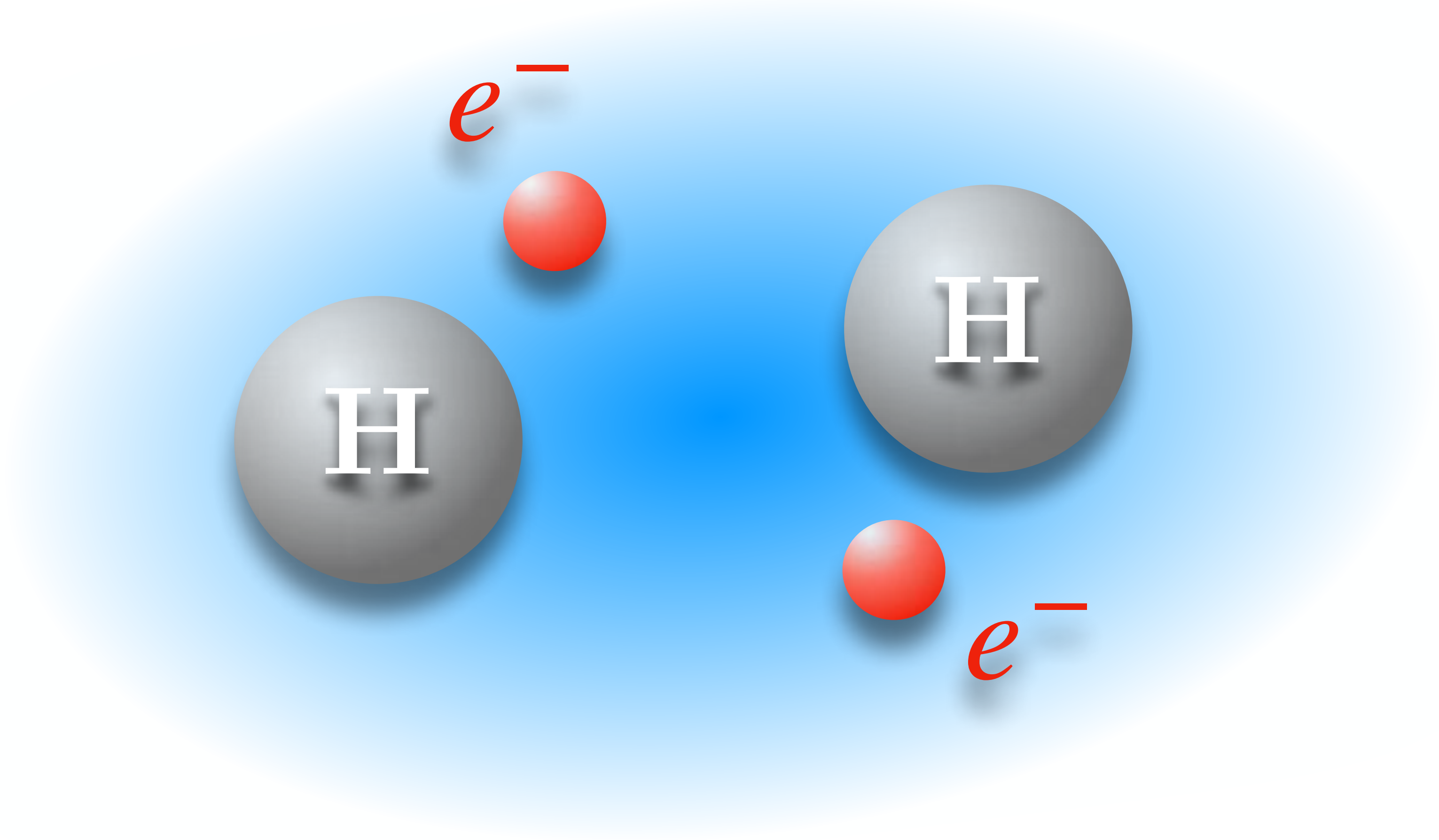
Classical Optimization of $\vec{\theta}$

Applications

- **Quantum machine learning**
- **Quantum Chemistry**

II) From quantum computing to chemistry

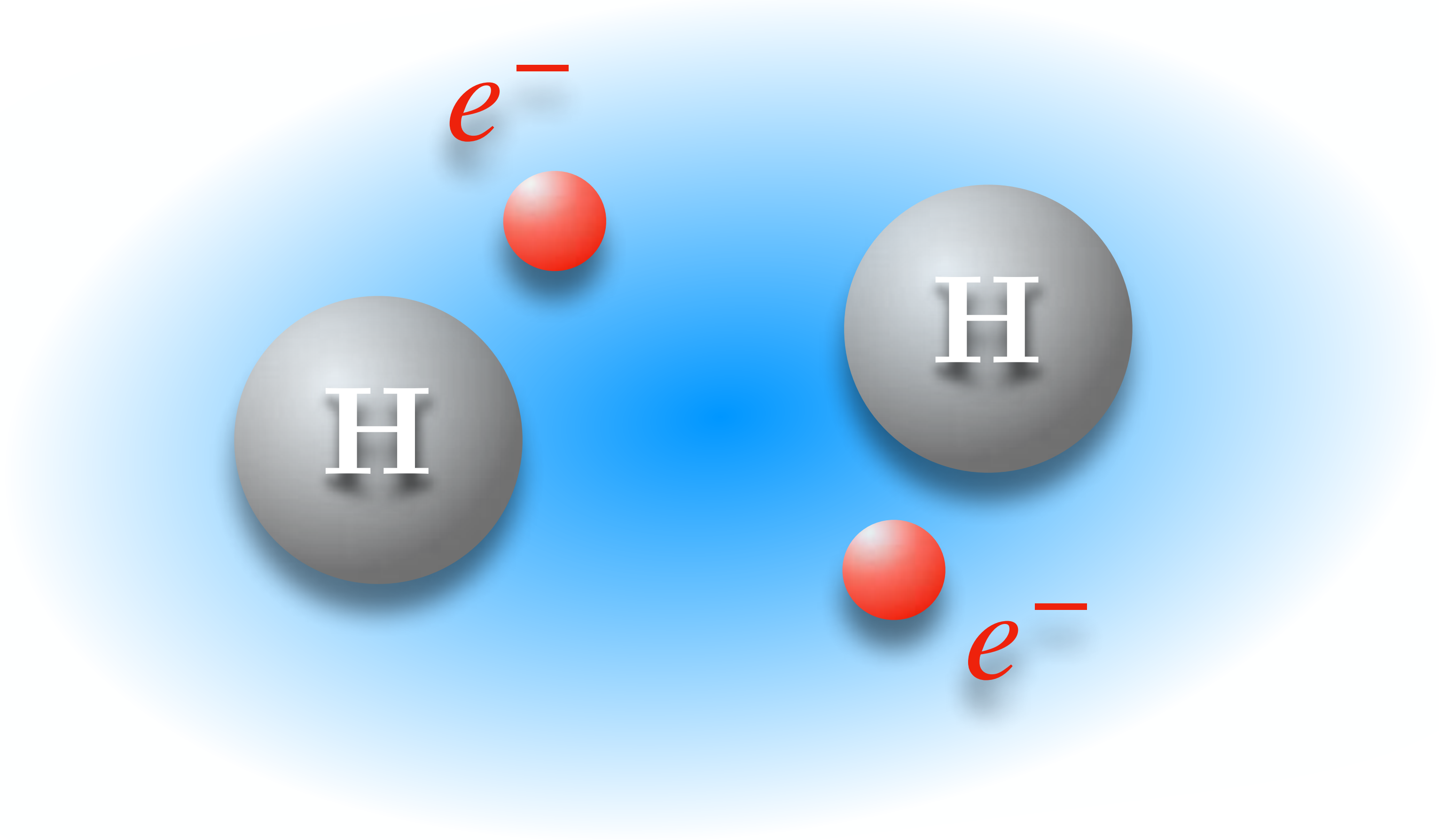
II) From quantum computing to chemistry



Electronic structure Hamiltonian
(Born-Oppenheimer approximation)

$$H = -\frac{1}{2}\sum_{i=1}^{N_e} \nabla^2_{r_i} - \sum_{i=1}^{N_e}\sum_{A=1}^{N_a} \frac{Z_A}{|r_i - R_A|} + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{1}{|r_j - r_j|}$$

II) From quantum computing to chemistry



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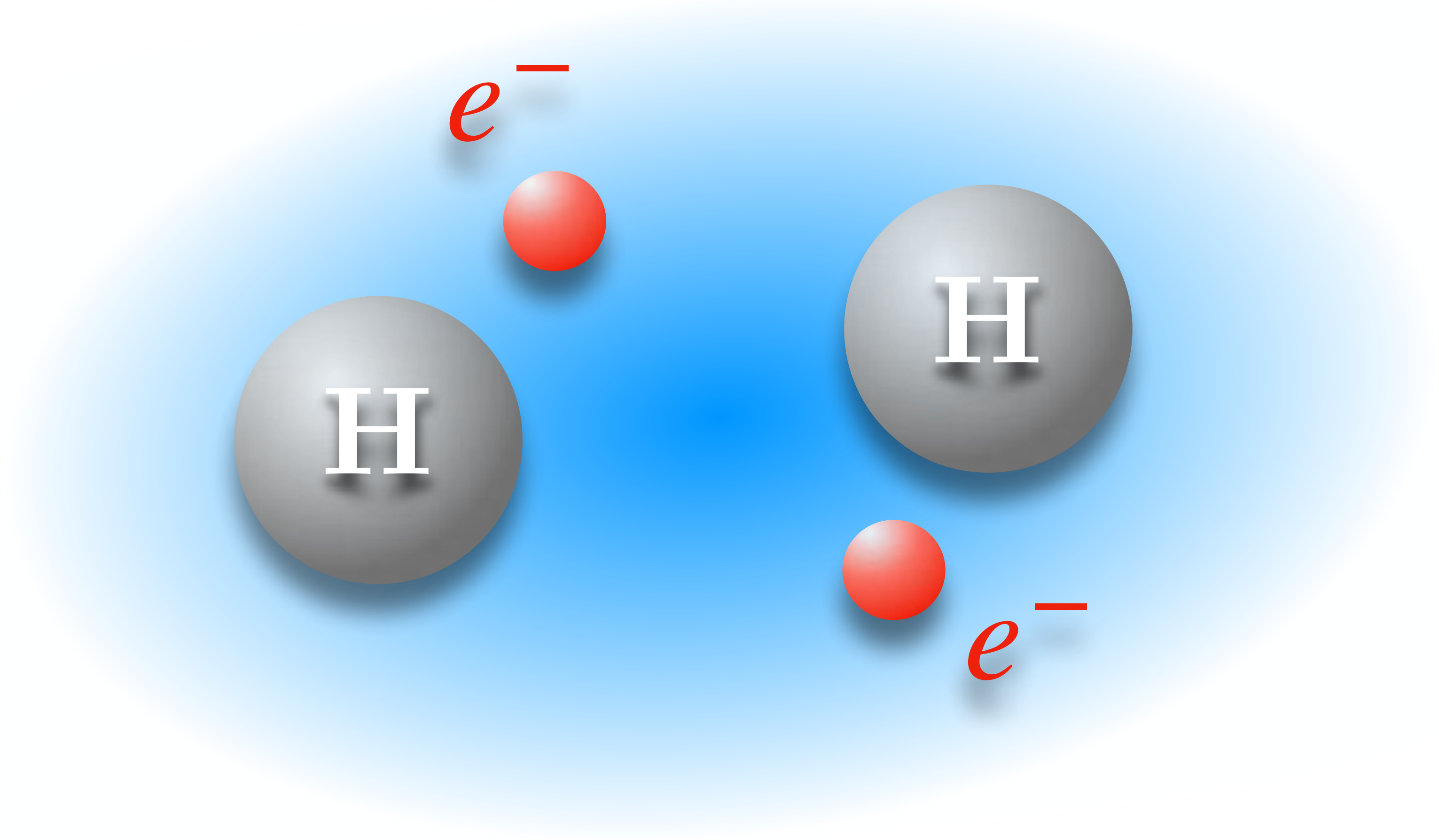
Finding Ground State

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

II) From quantum computing to chemistry



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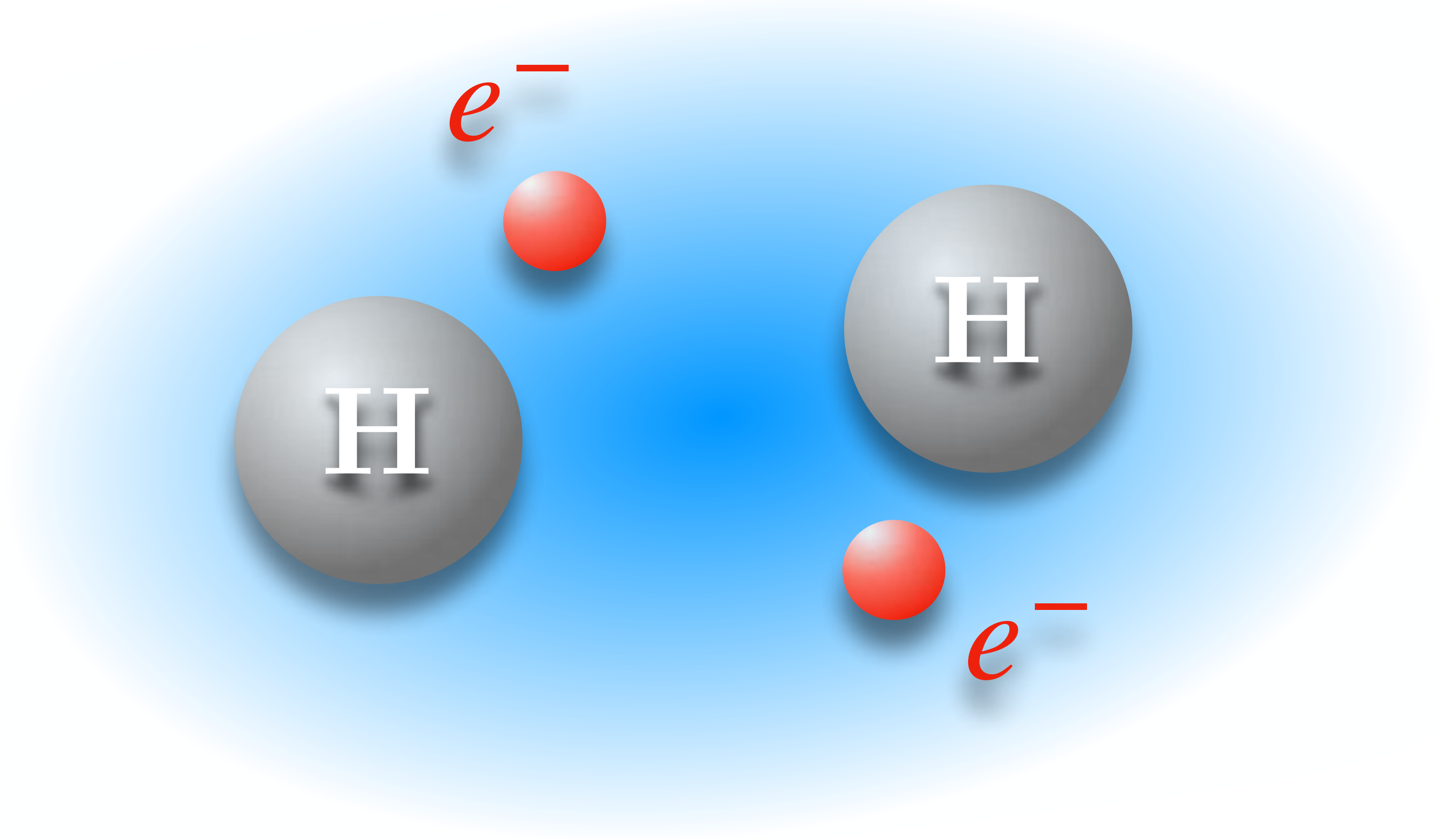
Mean-Field Approach
(Hartree-Fock)

Single Configuration Approximation

$$|\Psi_0\rangle \approx |\Phi_{HF}\rangle$$

II) From quantum computing to chemistry



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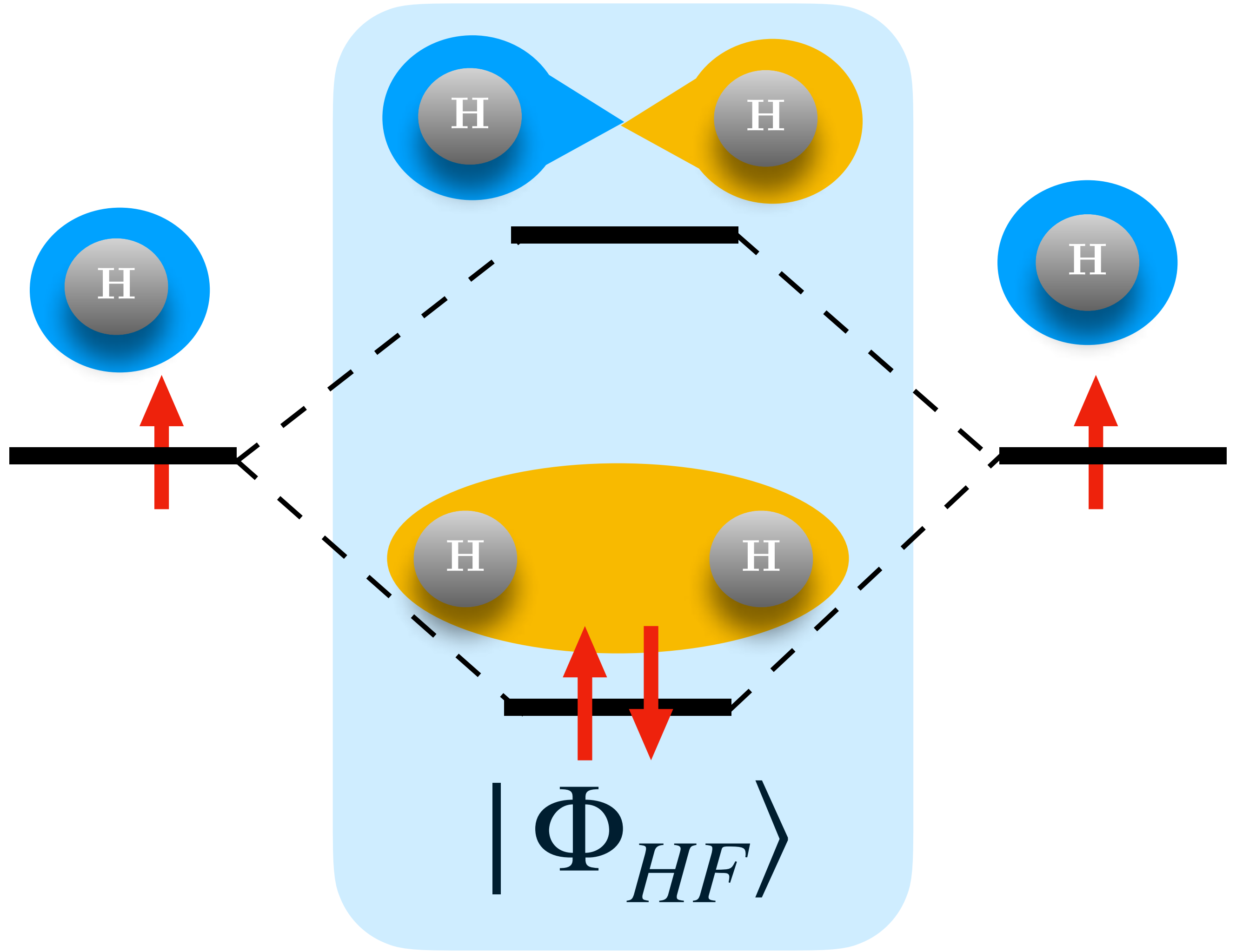
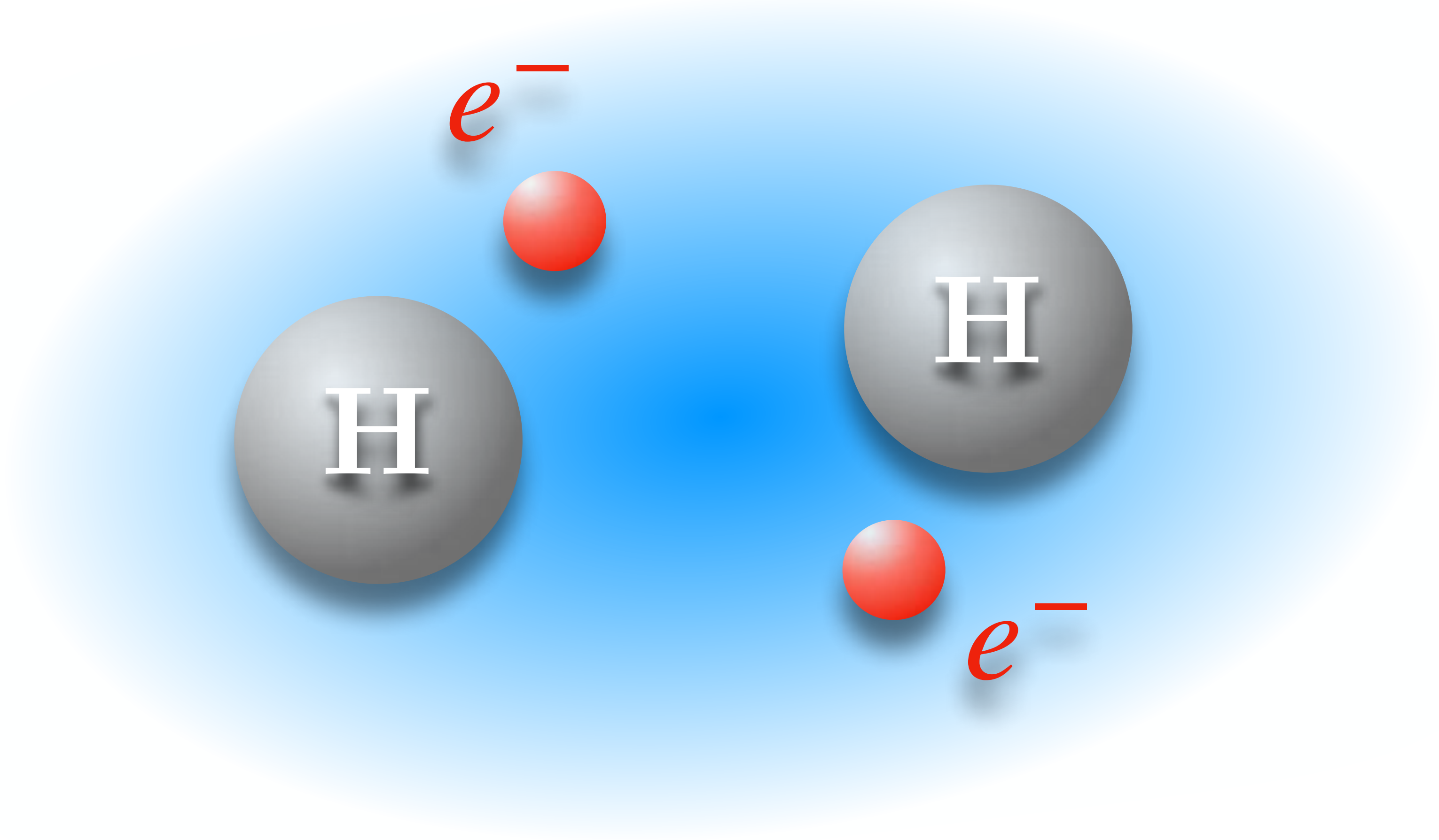
Molecular Orbitals



II) From quantum computing to chemistry



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Finding Ground State → $H|\Psi_0\rangle = E_0|\Psi_0\rangle$

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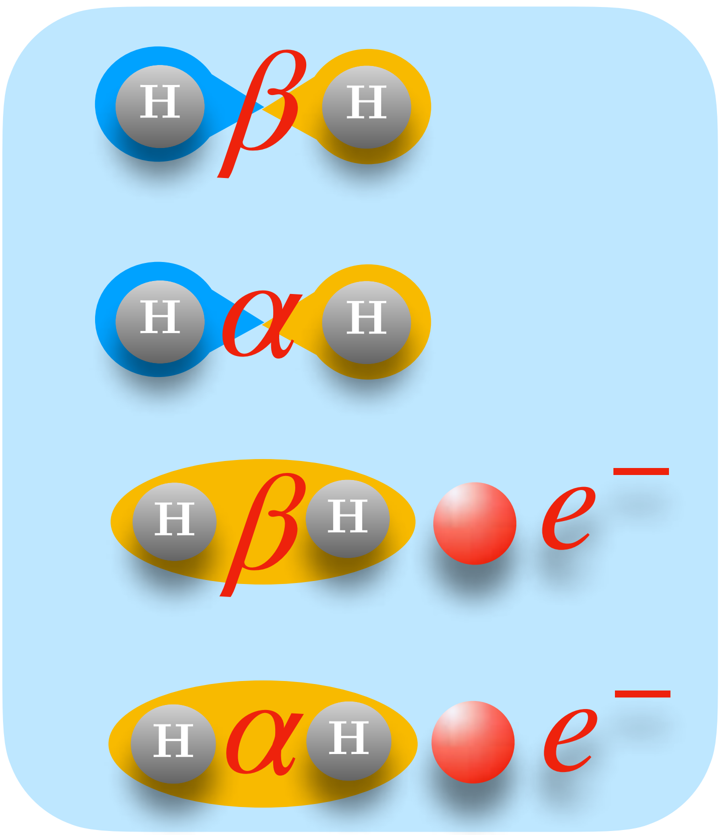
Spin-Orbitals

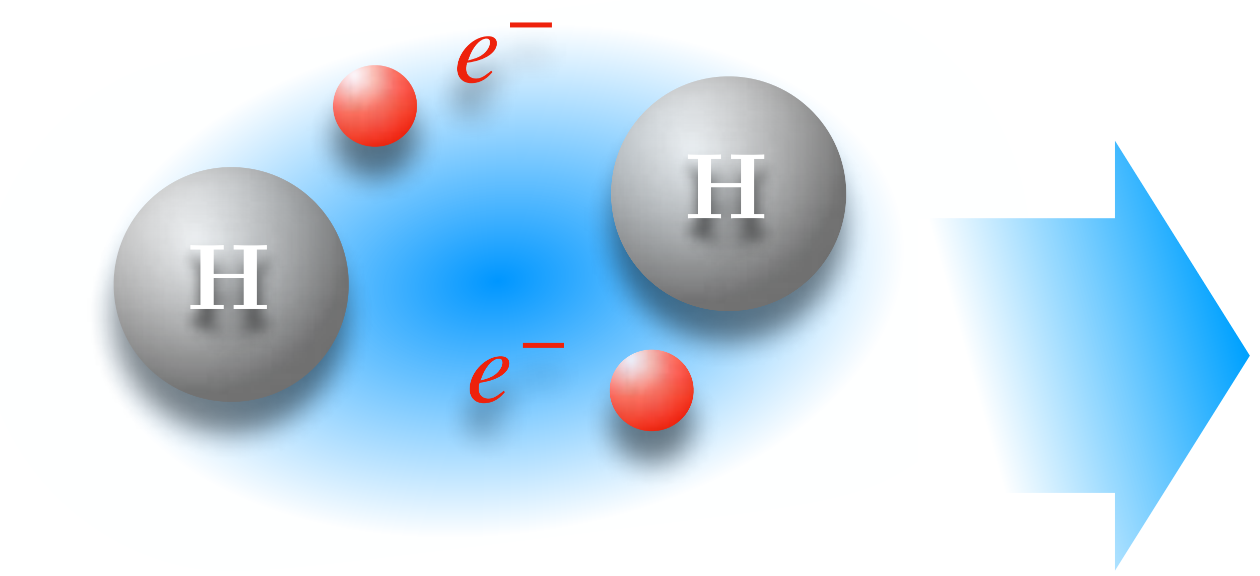


0
0
1
1

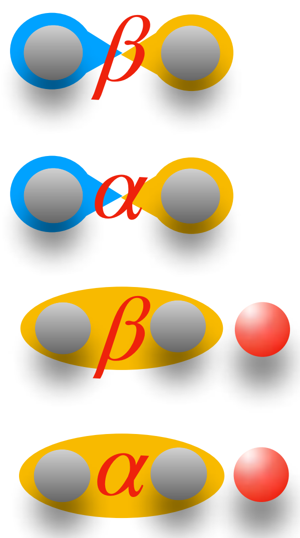
$$|\Phi_{HF}\rangle = |1100\rangle$$

II) From quantum computing to chemistry

Beyond Hartree-Fock: Full Configuration Interaction



$$|\Psi_0^{FCI}\rangle =$$



$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$|HF\rangle = |1100\rangle$$

II) From quantum computing to chemistry

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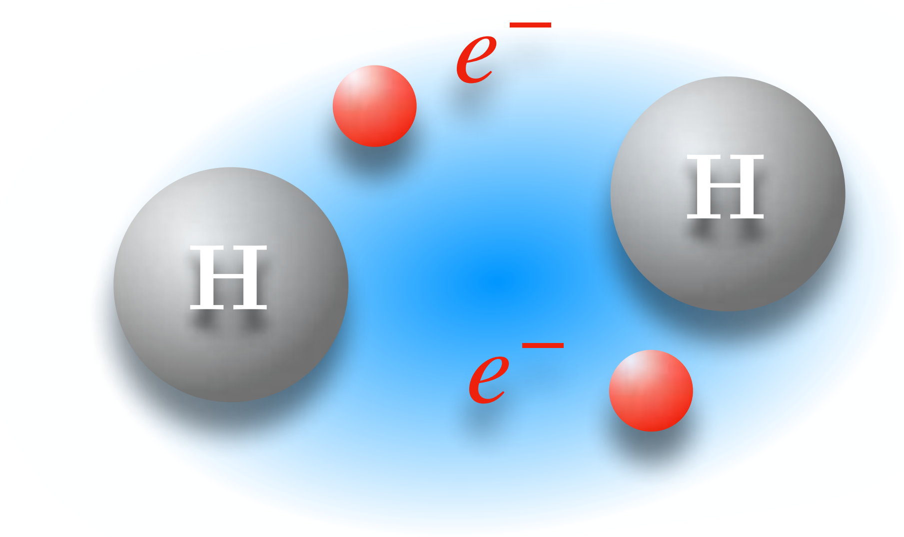
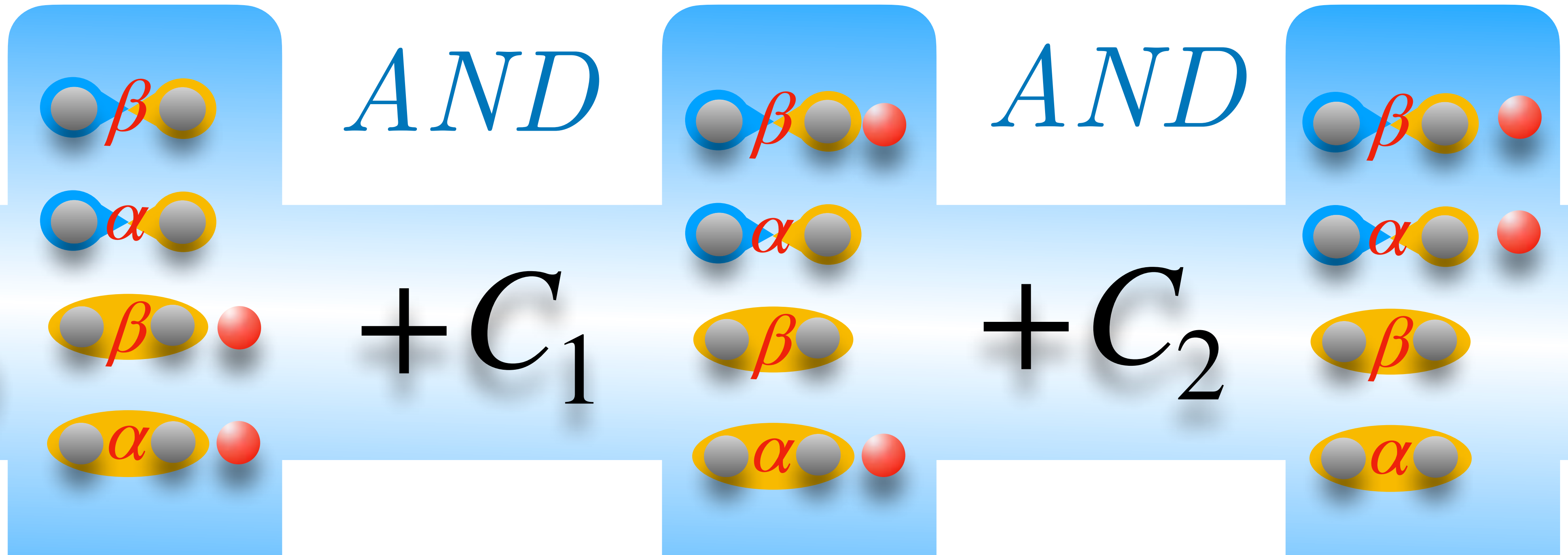


$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$|\Psi_0^{FCI}\rangle = C_0 + C_1 + C_2 \cdots$$



$|HF\rangle = |1100\rangle$

$|1001\rangle$

$|0011\rangle$

II) From quantum computing to chemistry

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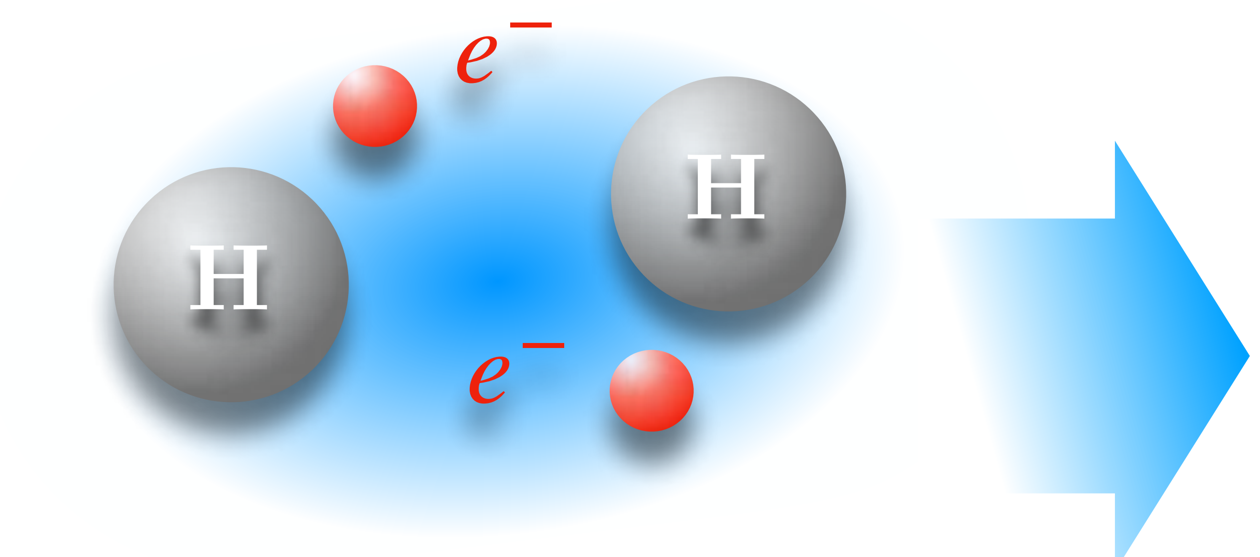

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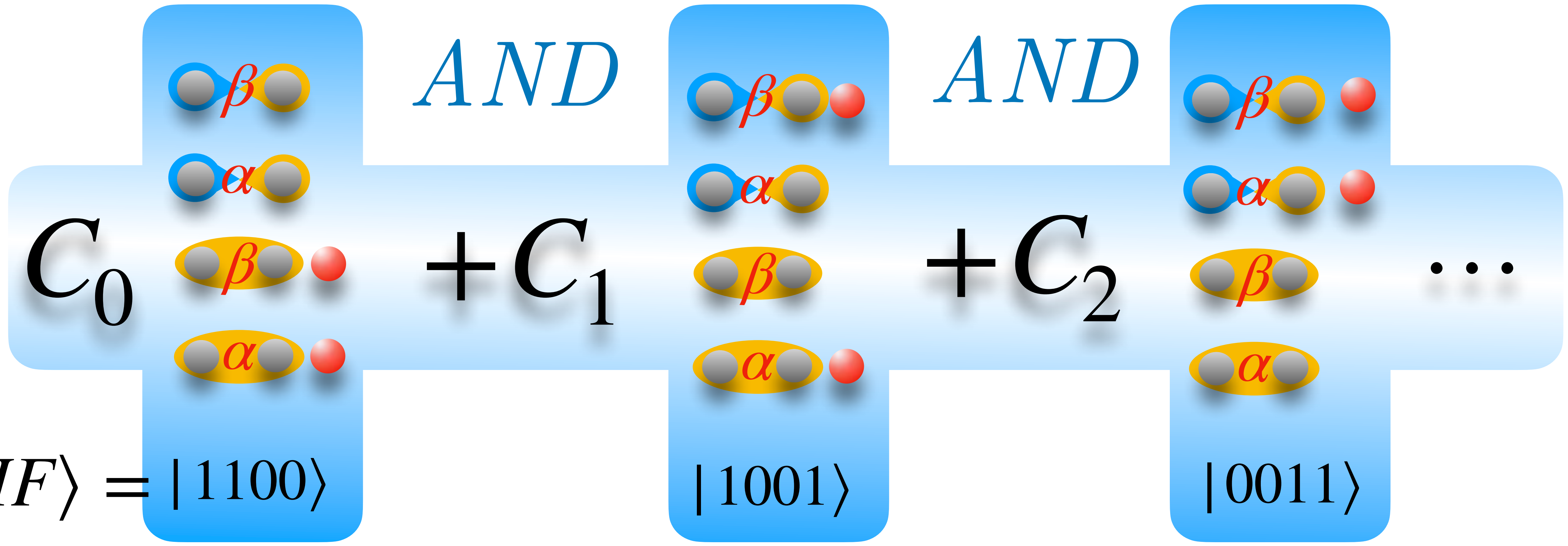
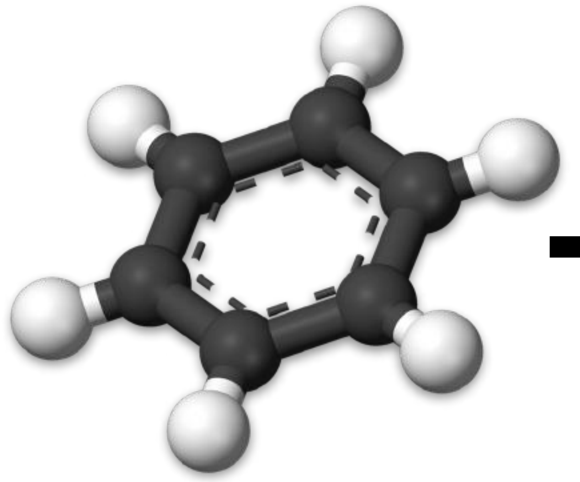


FCI : Ok for very small systems ...
But **it scales dramatically** with larger ones !


Benzene

$\rightarrow N_{CONF} \sim 10^{19}$

II) From quantum computing to chemistry

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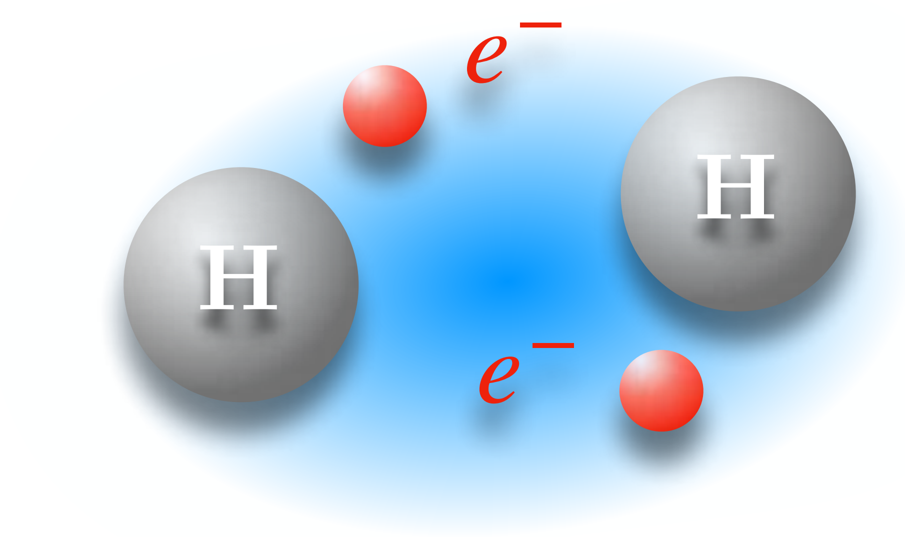

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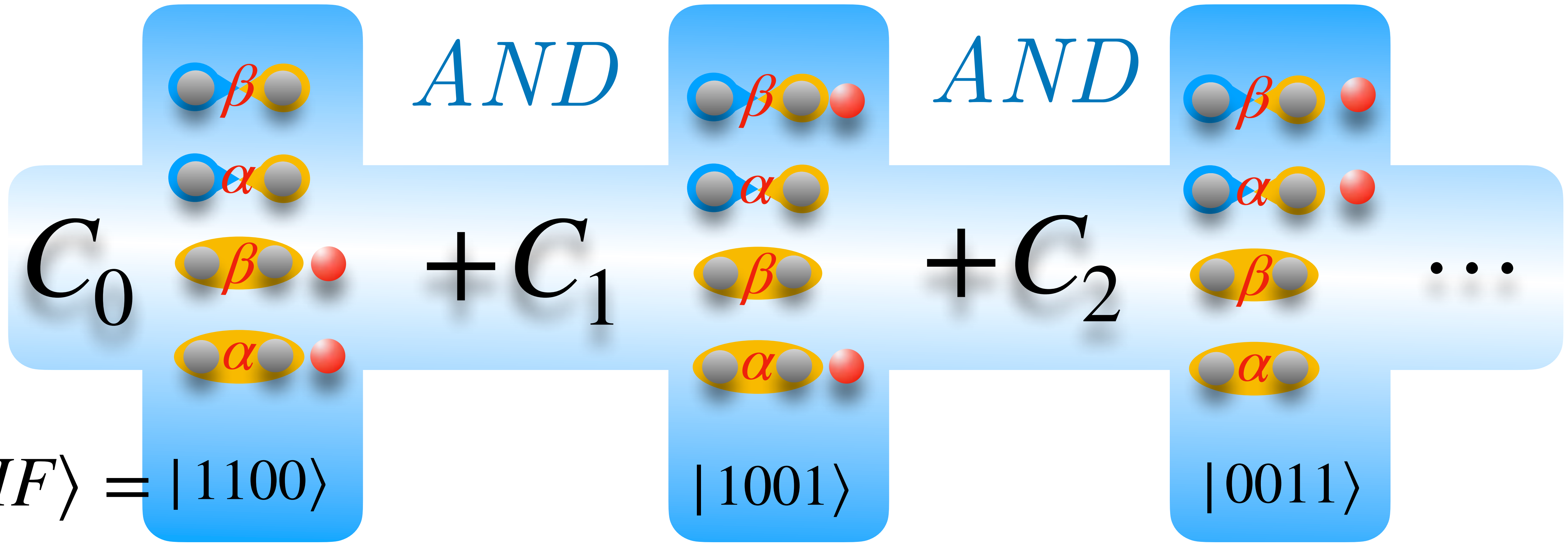

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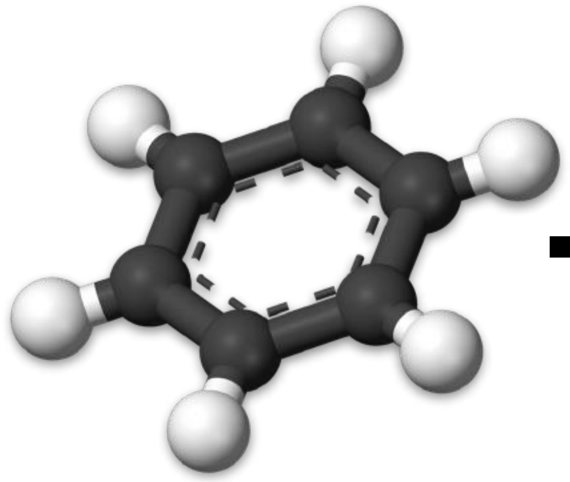

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Quantum computers
can tackle this !

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Richard P. Feynman

We simulate the very complex electronic structure problem **(many electrons in a molecule)** with a quantum computer containing small quantum systems that we master **(qubits)**

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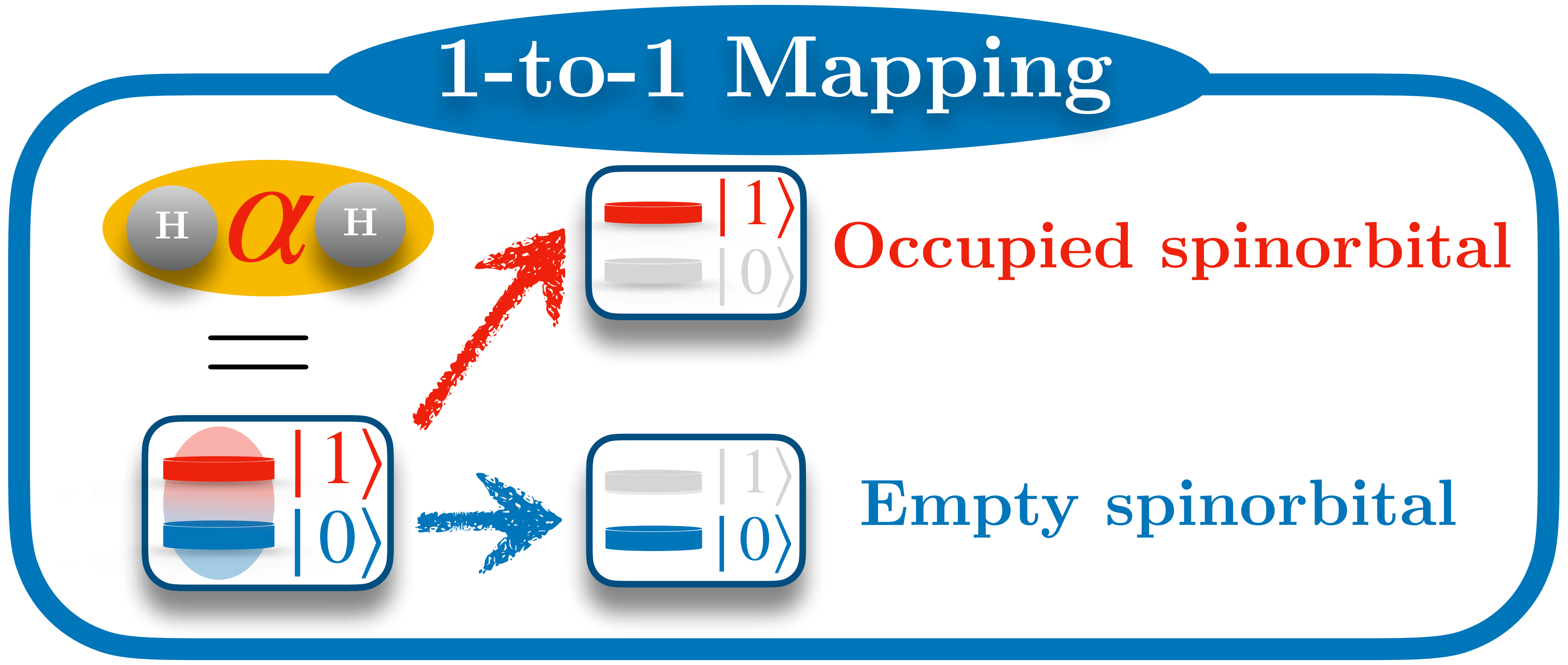

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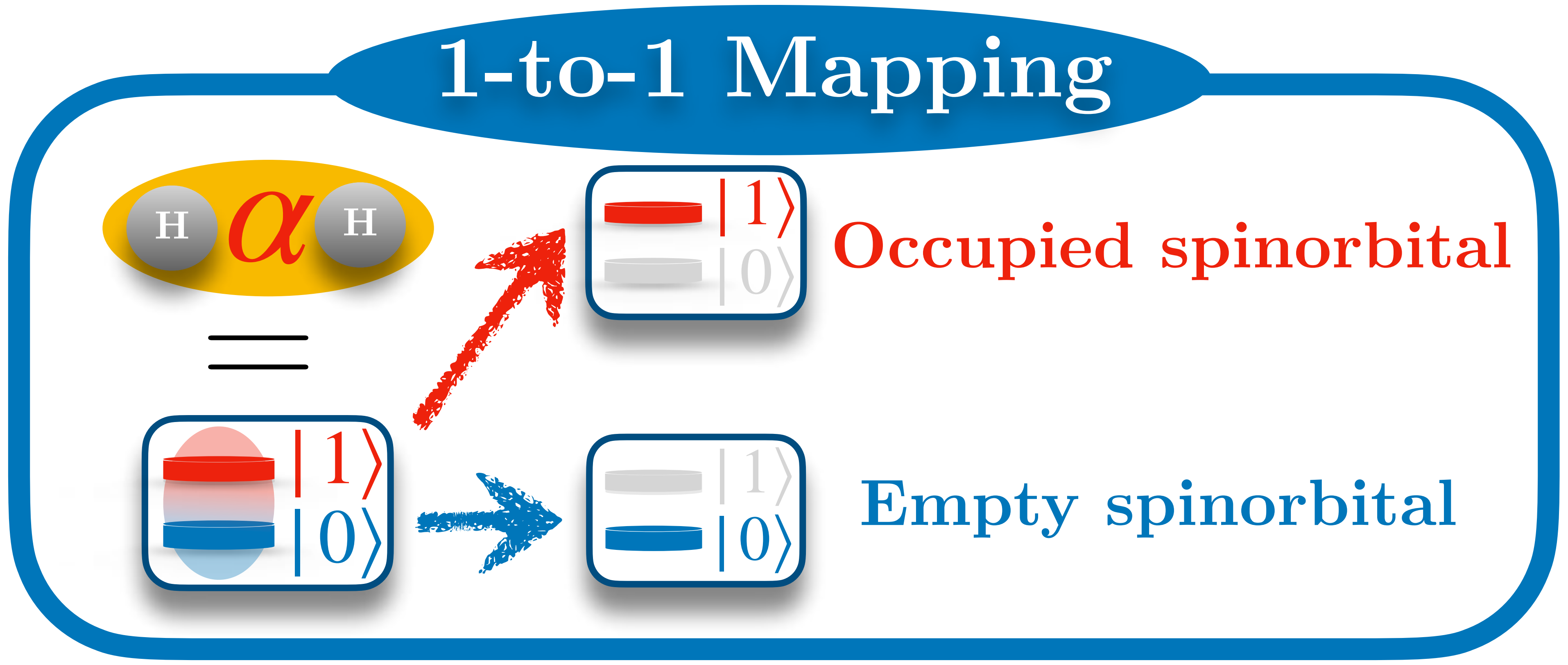

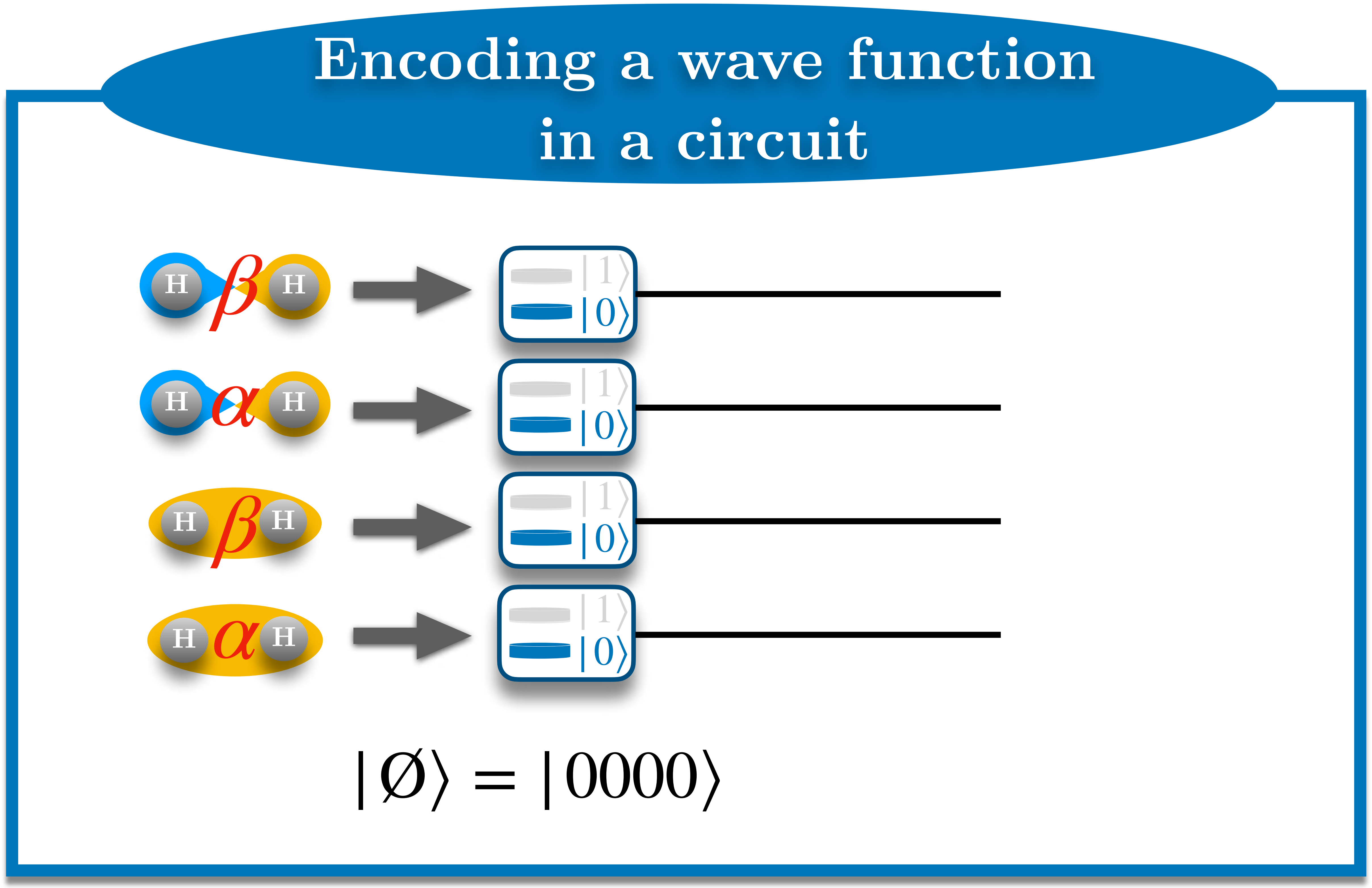

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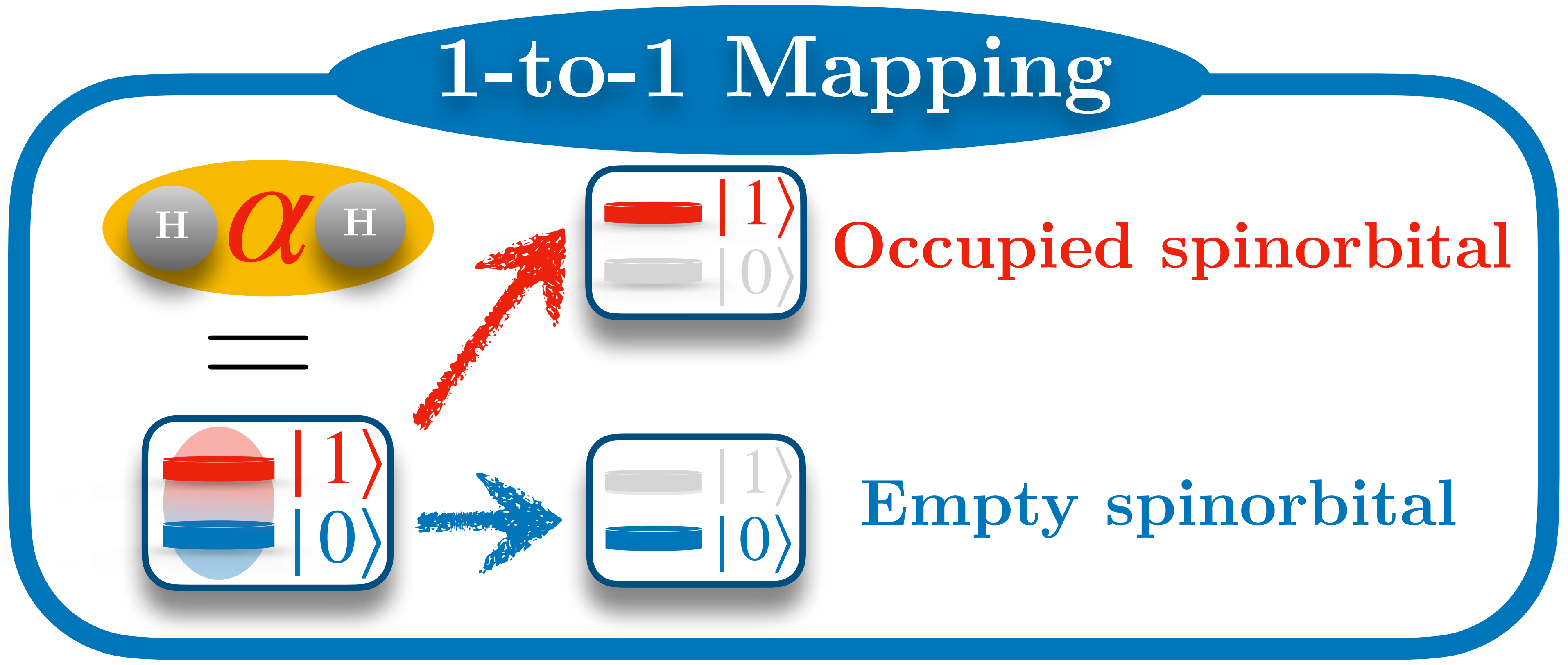

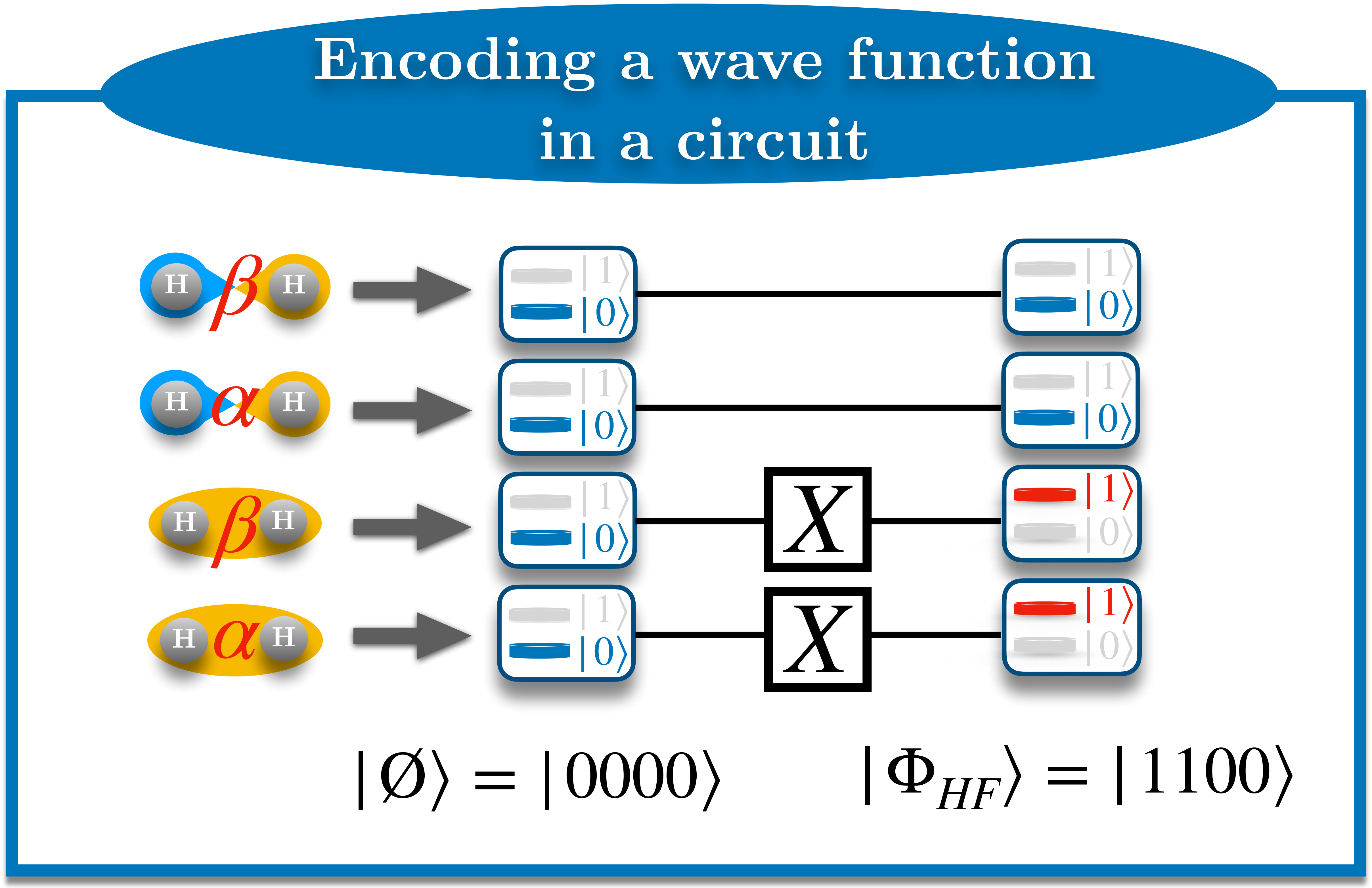

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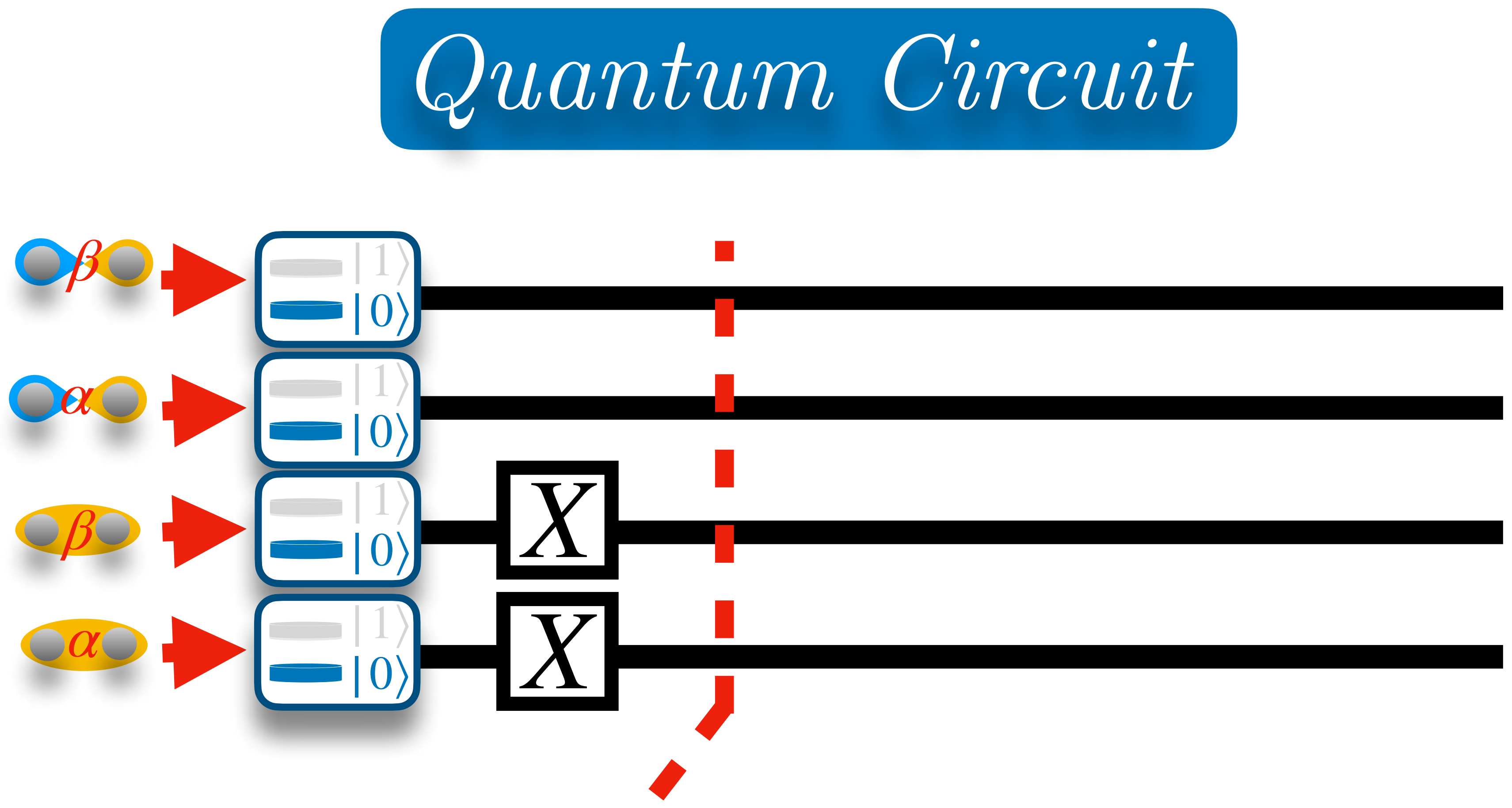

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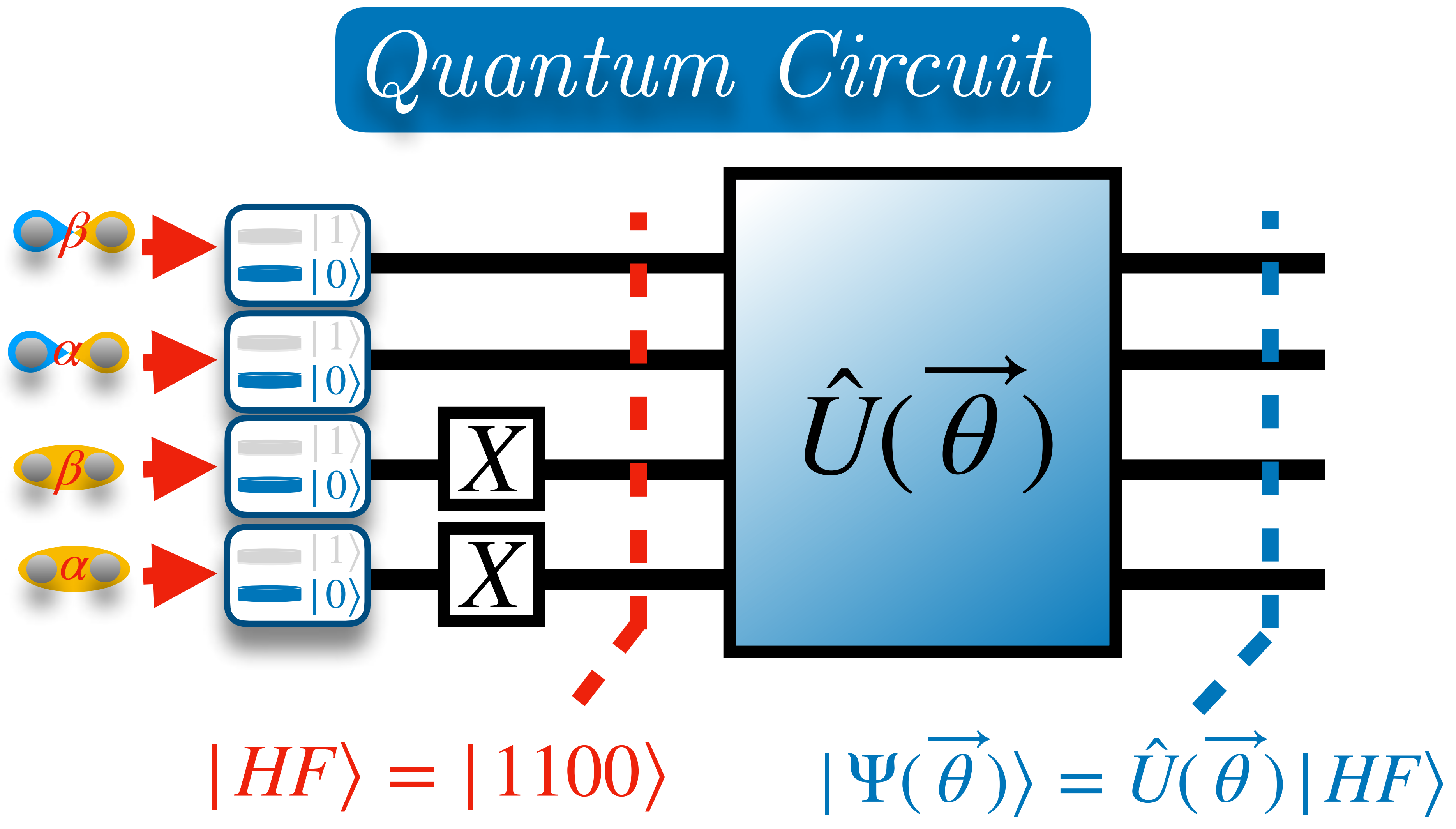
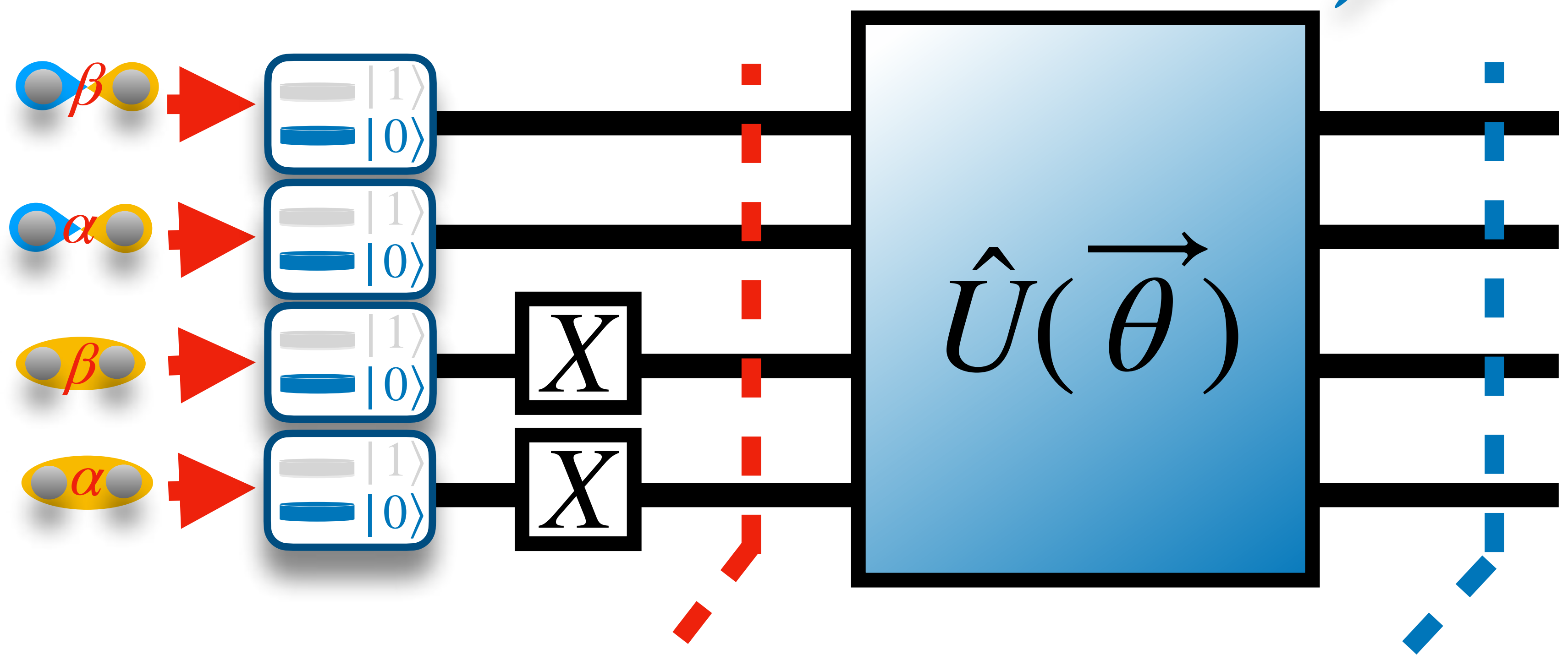
II) From quantum computing to chemistry



II) From quantum computing to chemistry

Quantum Circuit



$|HF\rangle = |1100\rangle$

$|\Psi(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|HF\rangle$

Unitary Coupled Cluster Ansatz

$$\hat{U}(\vec{\theta}) = e^{T(\vec{\theta}) - T(\vec{\theta})^\dagger}$$

II) From quantum computing to chemistry

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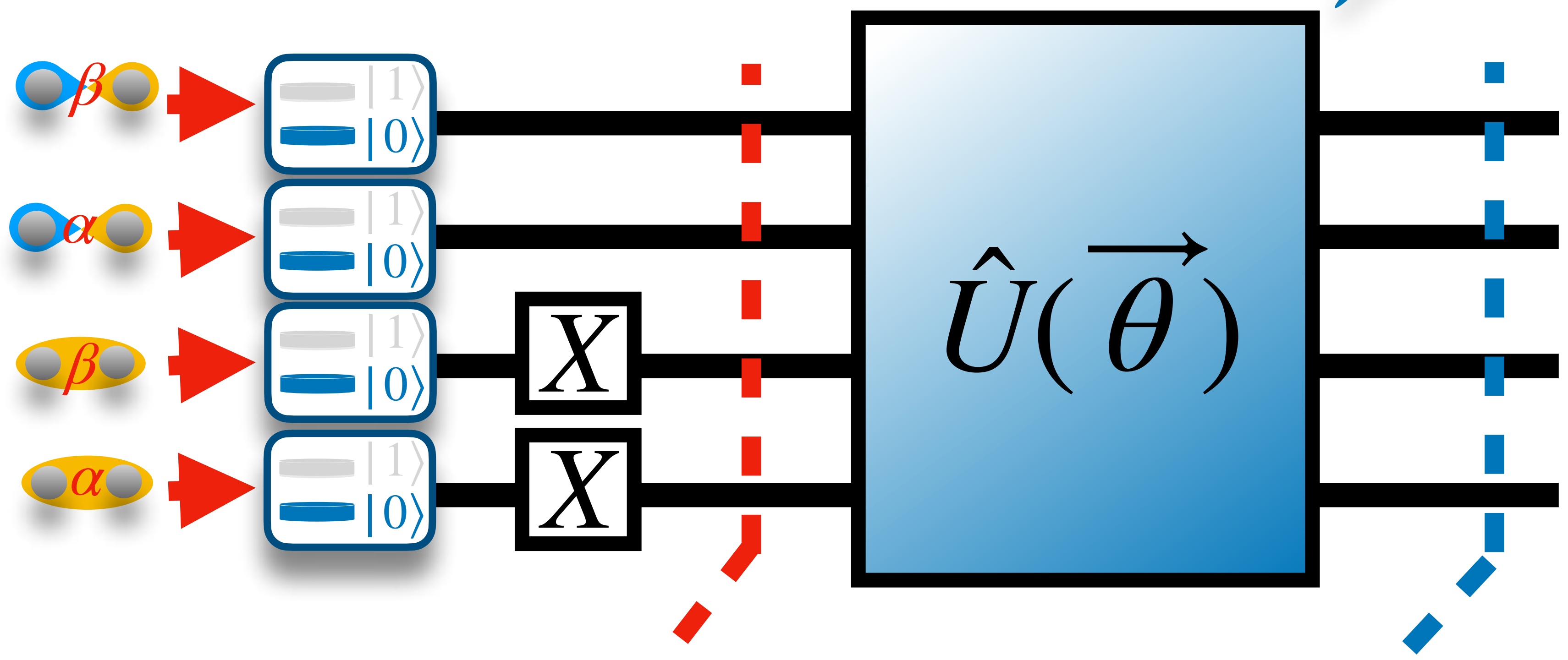

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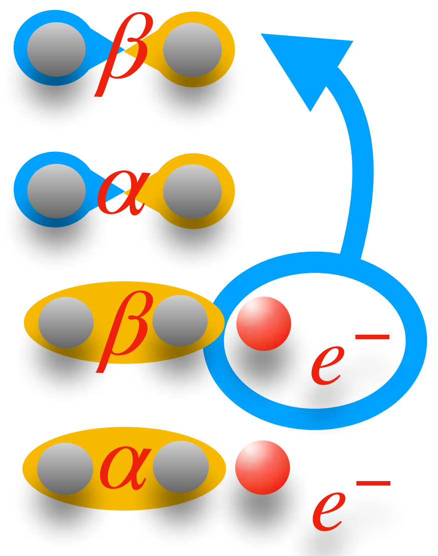

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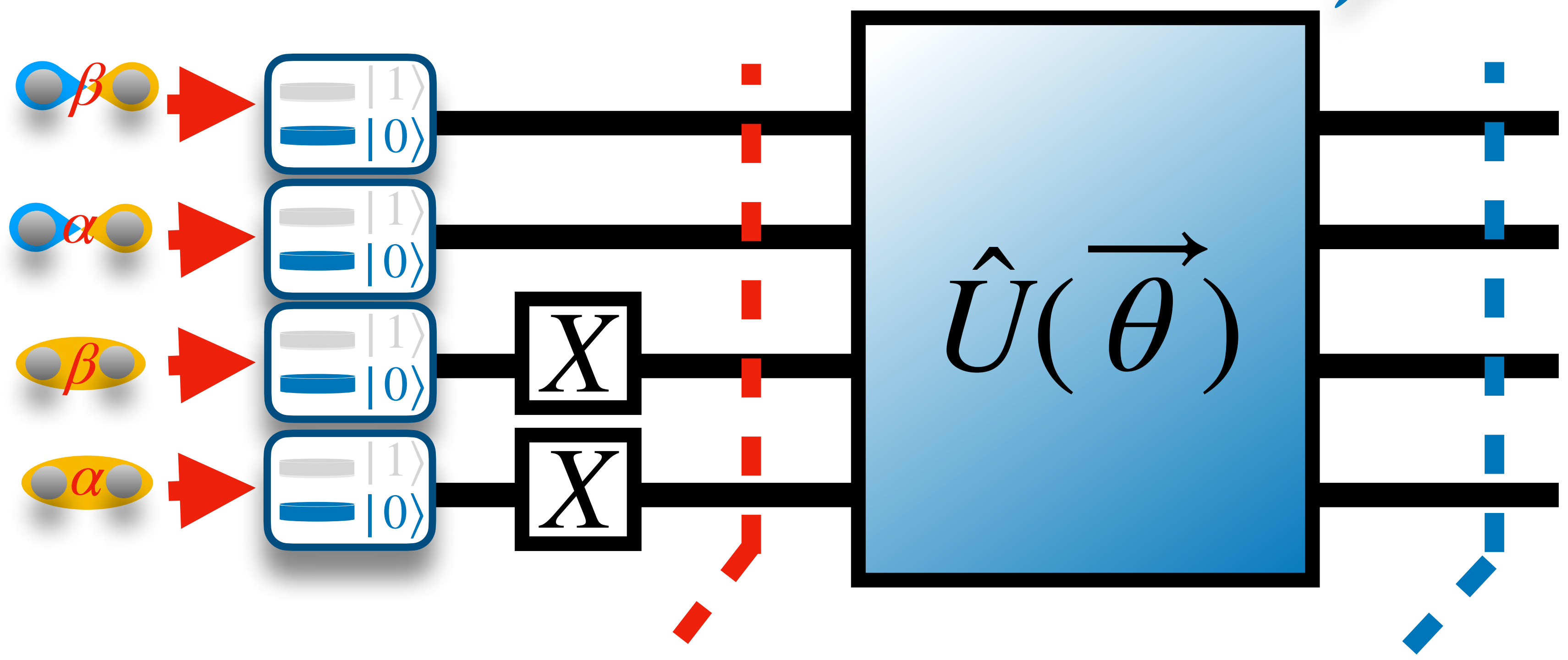

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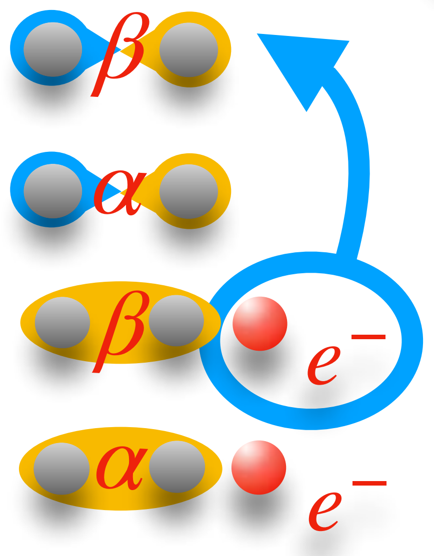
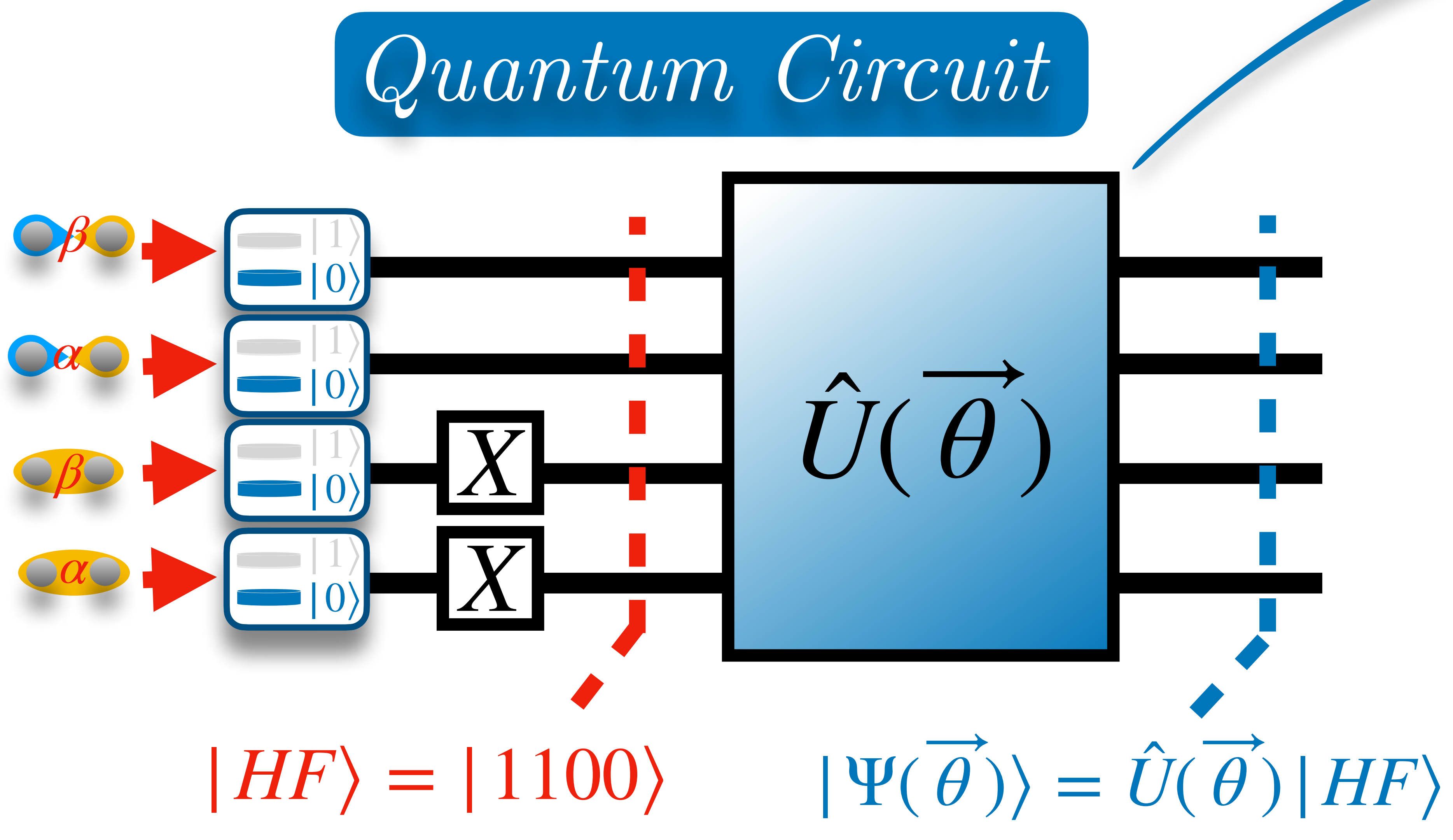


Jordan-Wigner Transformation

$$a_p \xrightarrow{JW} \frac{1}{2}(X_p + iY_p) \bigotimes_{q=0}^{p-1} Z_l$$

II) From quantum computing to chemistry



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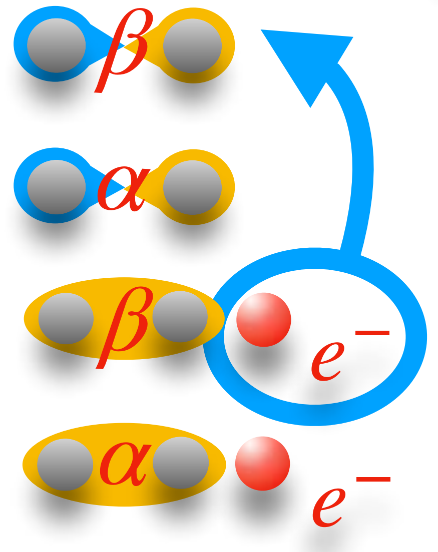

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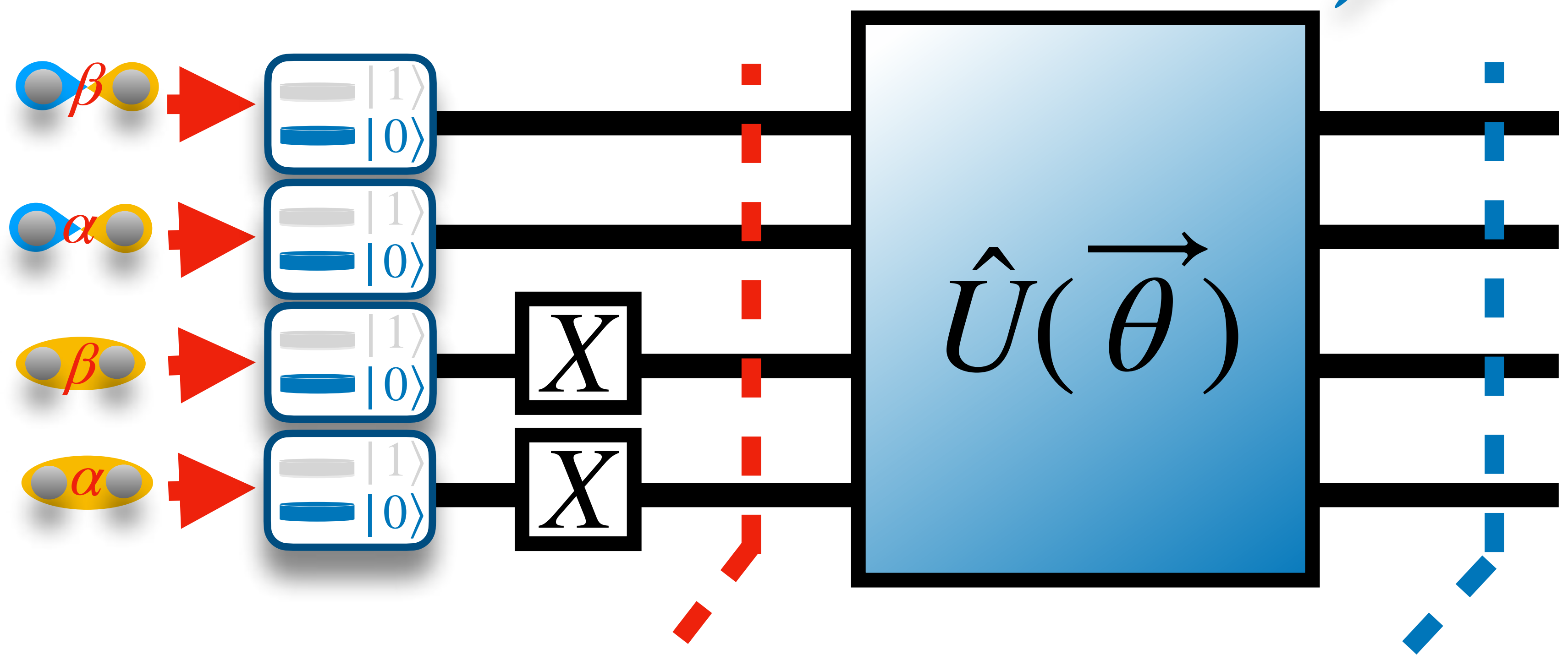
$$\hat{U}(\vec{\theta}) \approx \prod_k e^{-i\theta_k \hat{\mathscr{P}}_k}$$

Where $\hat{\mathscr{P}}_k$ are “Pauli strings”

$$\hat{\mathscr{P}}_k = Z_1 \otimes X_2 \otimes \mathbf{1}_3 \otimes Y_4$$

II) From quantum computing to chemistry

Quantum Circuit



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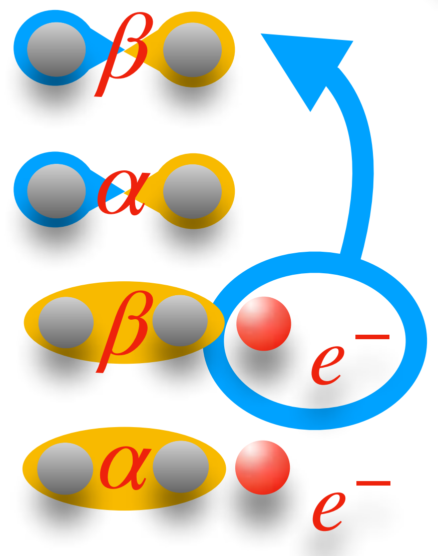

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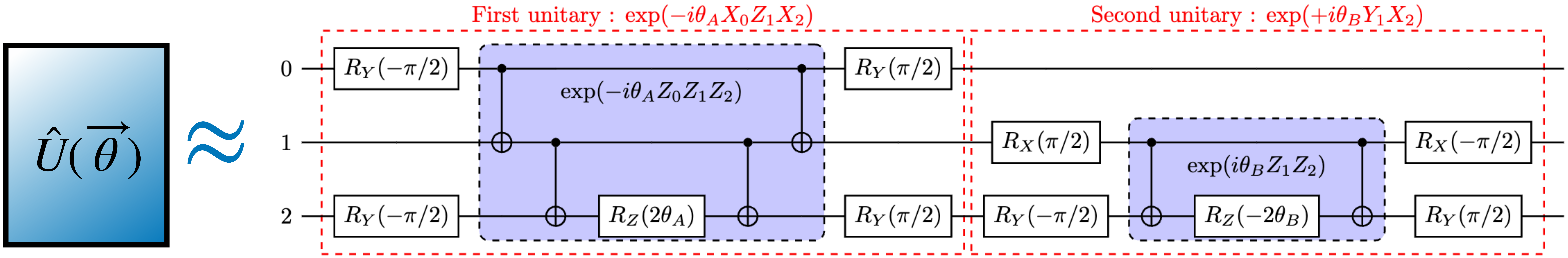
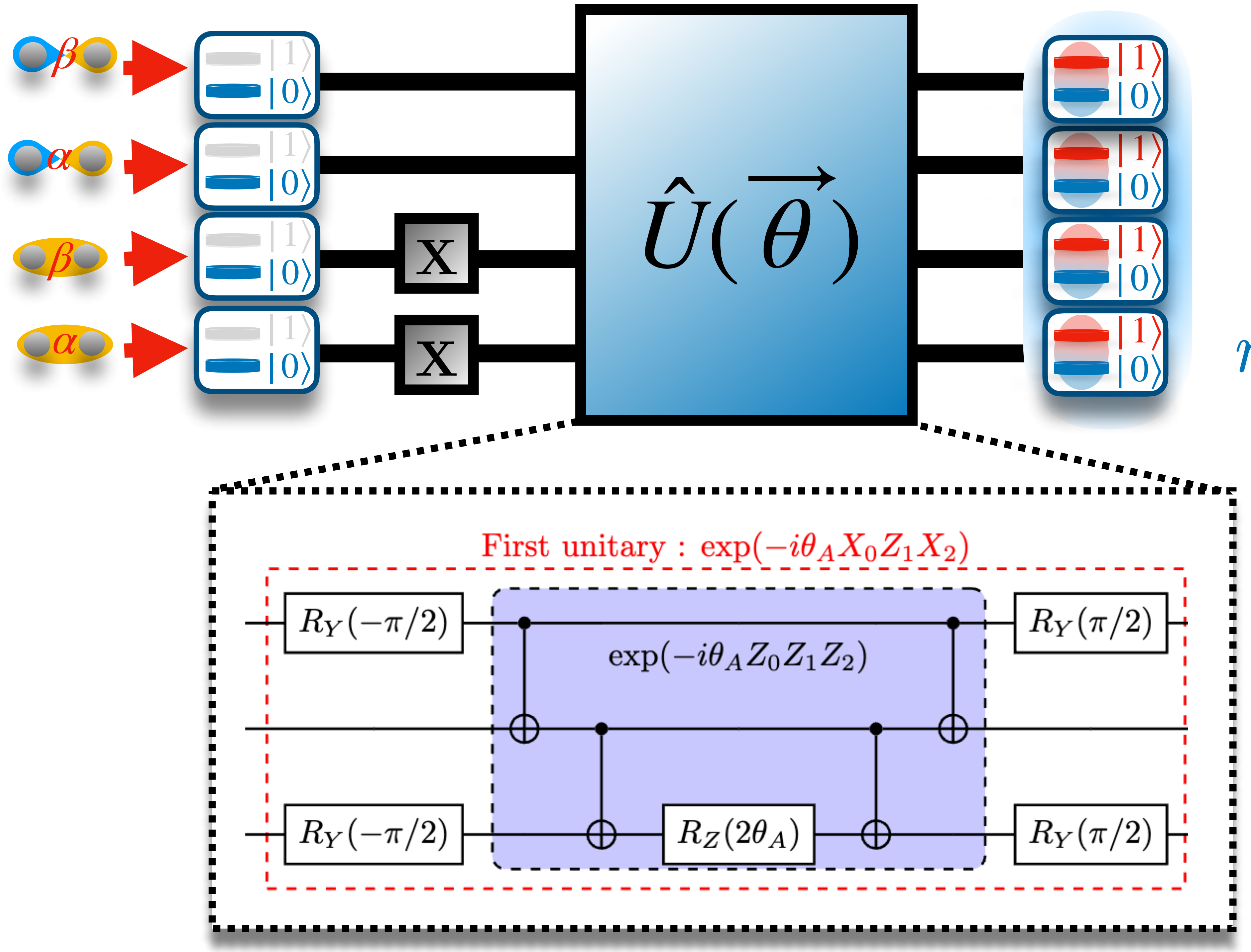


II) From quantum computing to chemistry

VQE : Variational Quantum Eigensolver

Quantum Circuit

$|\Psi(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|HF\rangle$

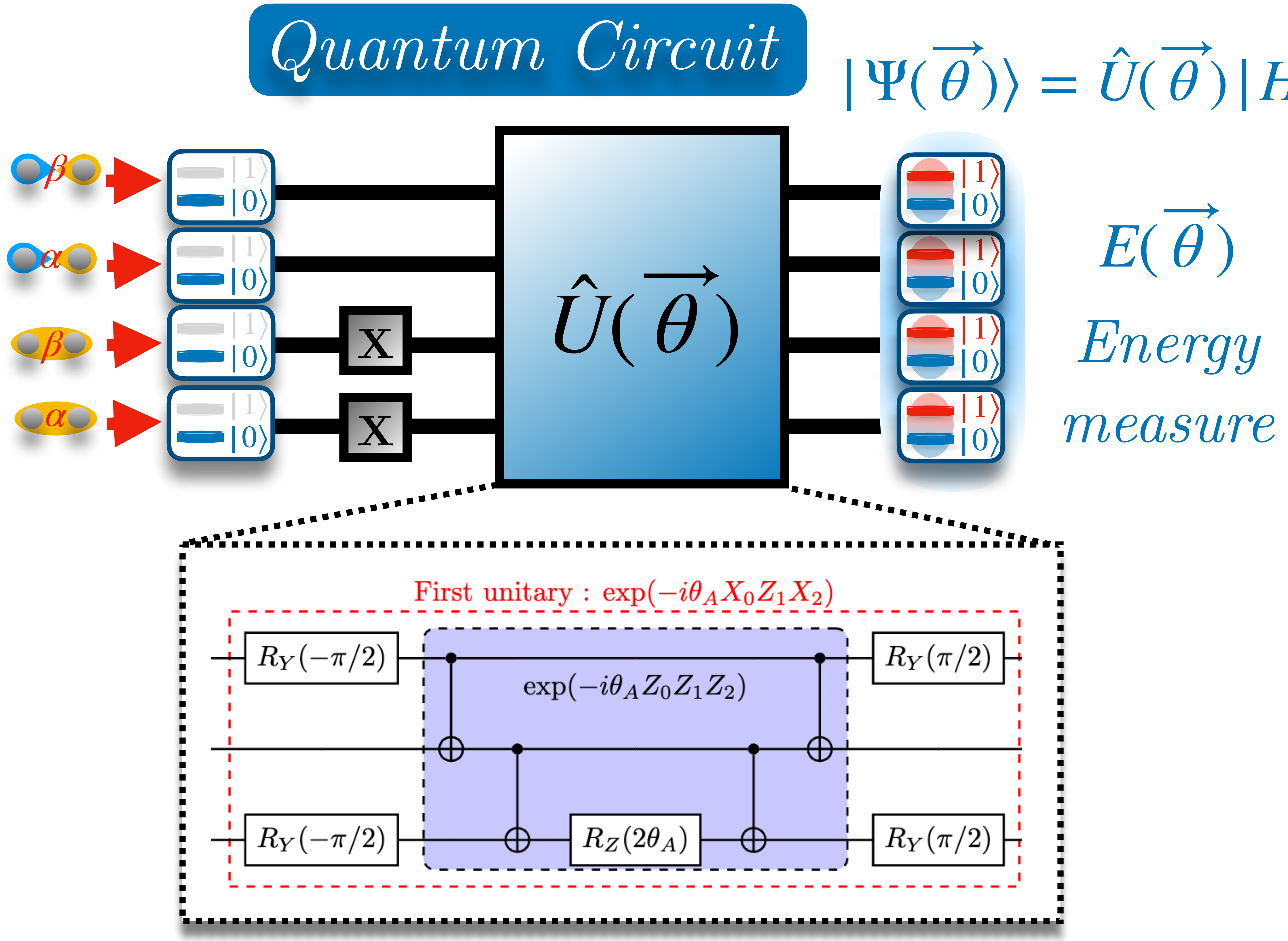


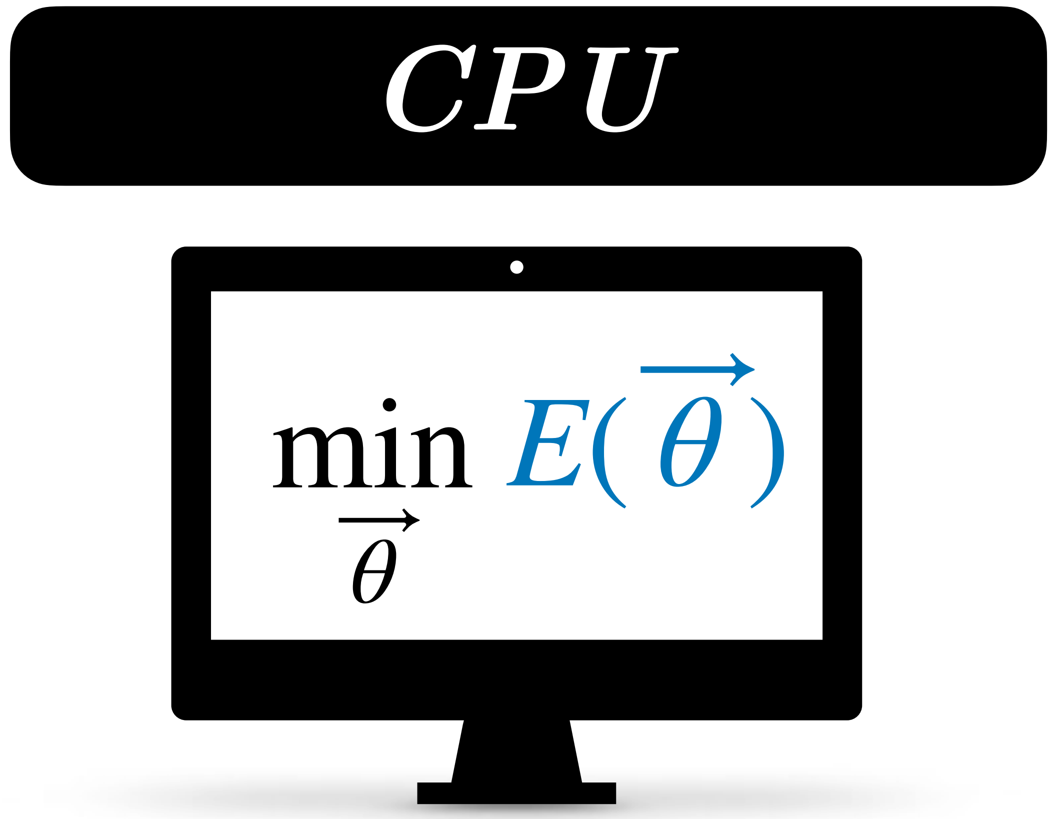
$E(\vec{\theta})$

Energy measure

II) From quantum computing to chemistry

VQE : Variational Quantum Eigensolver





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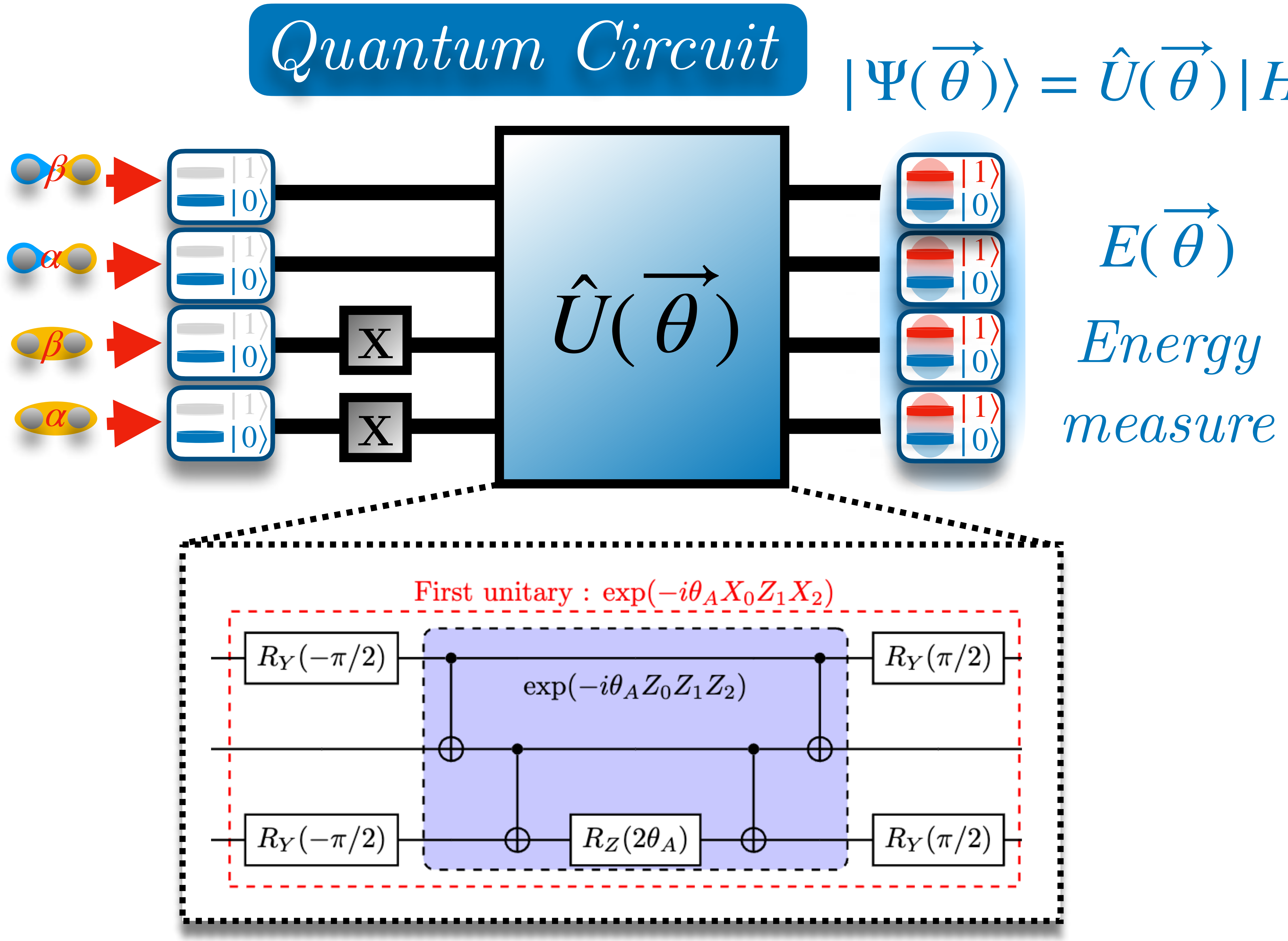
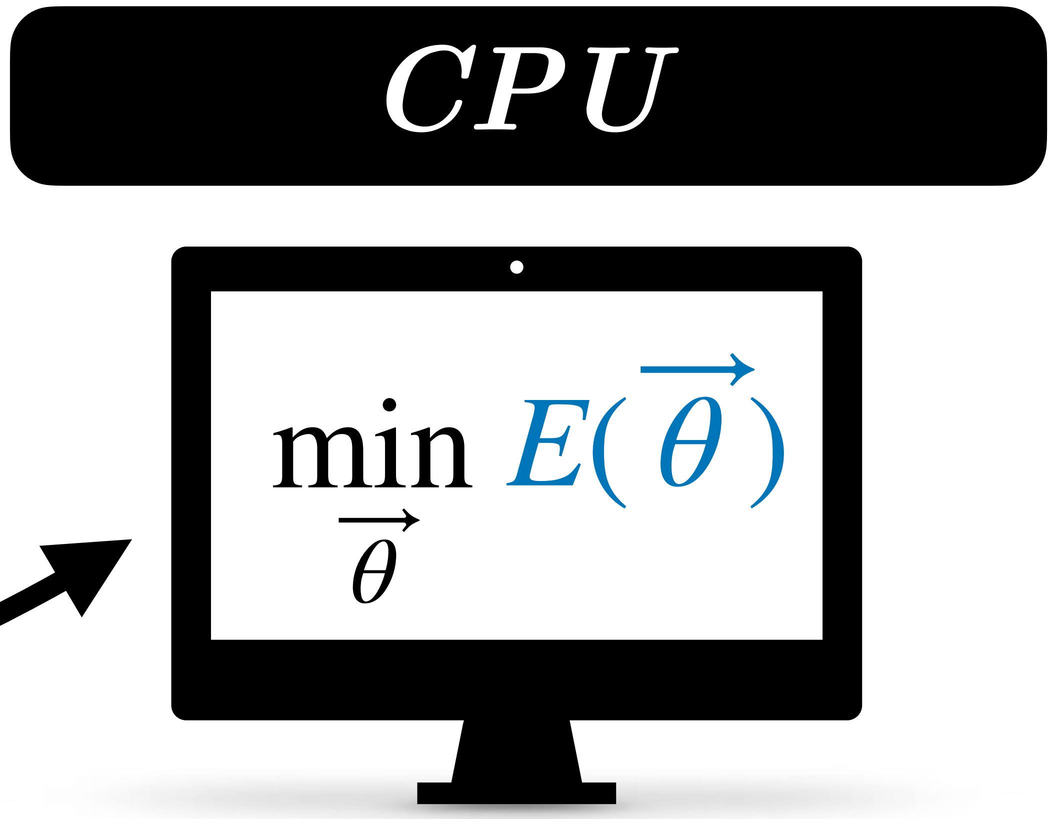


Measures on

$$E(\vec{\theta}) = \langle \Psi(\vec{\theta}) | \hat{H} | \Psi(\vec{\theta}) \rangle$$



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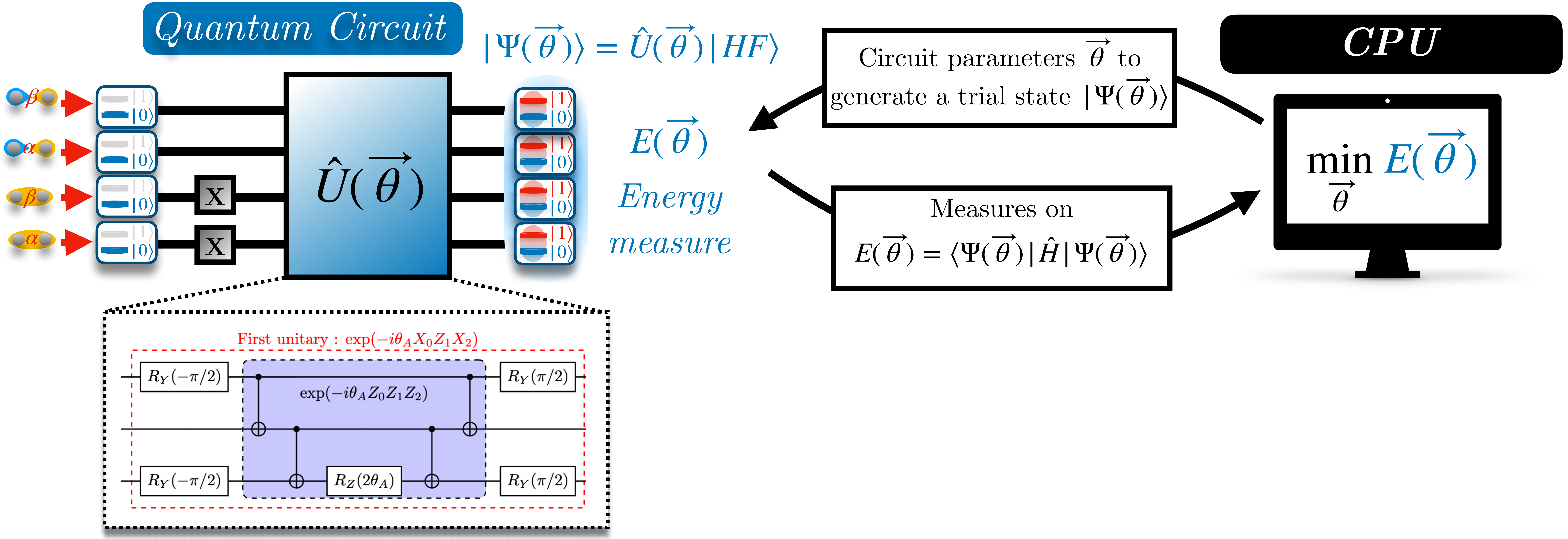

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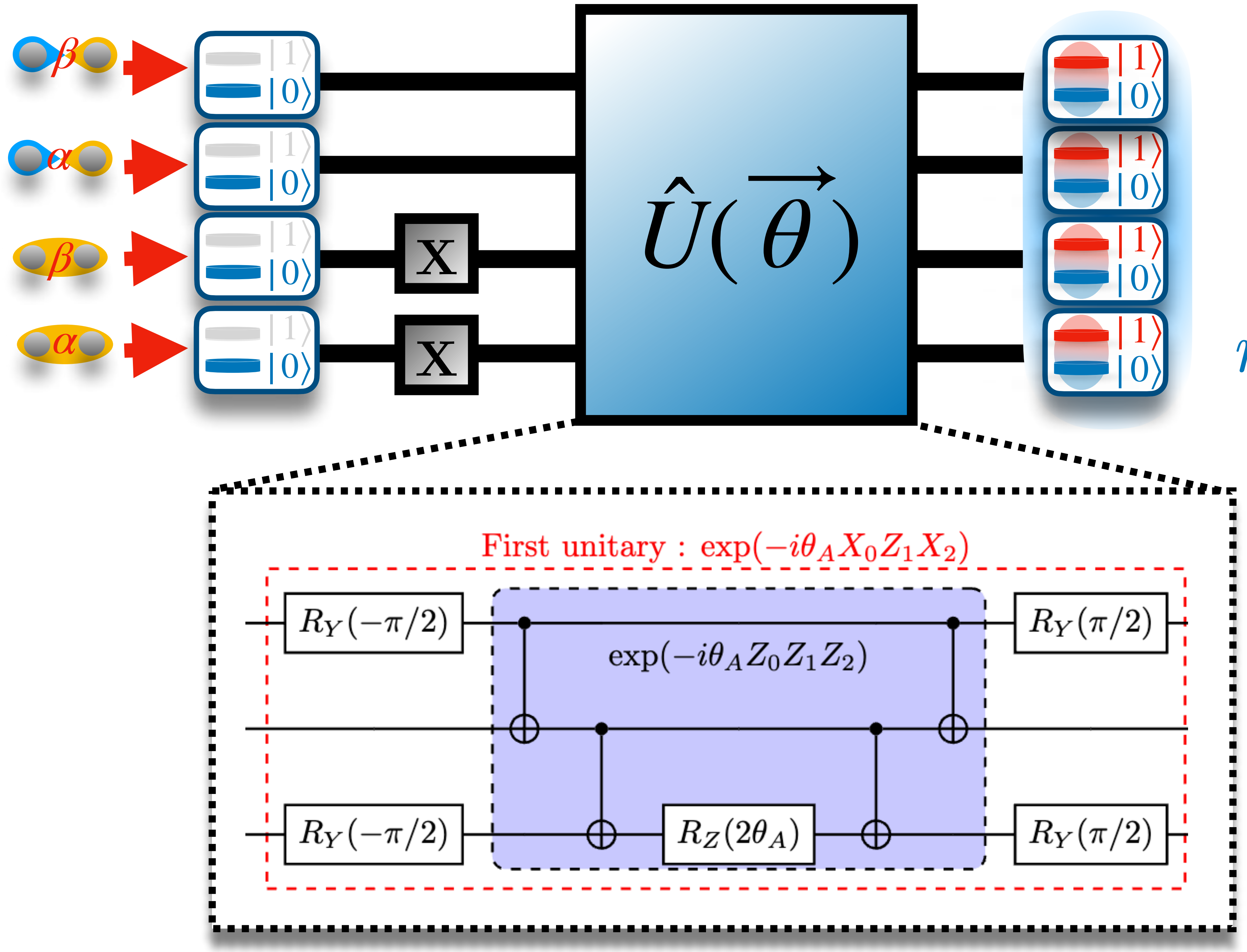
Quantum Circuit

$|\Psi(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|HF\rangle$

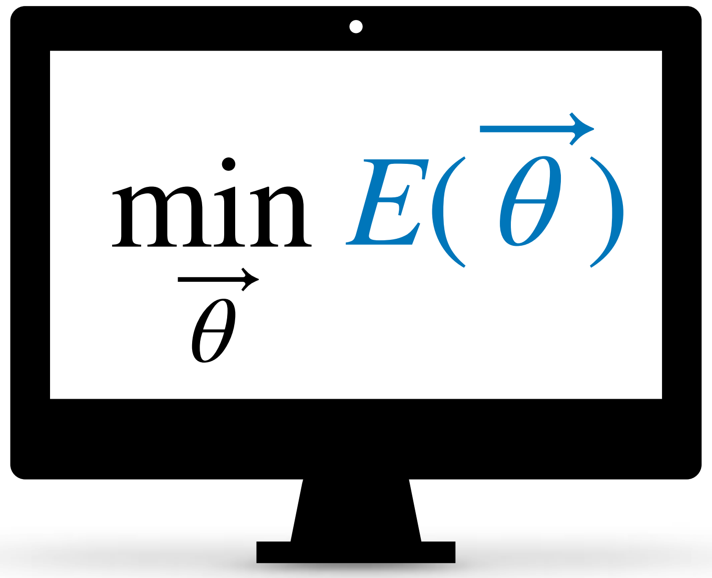


$E(\vec{\theta})$

Energy measure

Circuit parameters $\vec{\theta}$ to generate a trial state $|\Psi(\vec{\theta})\rangle$

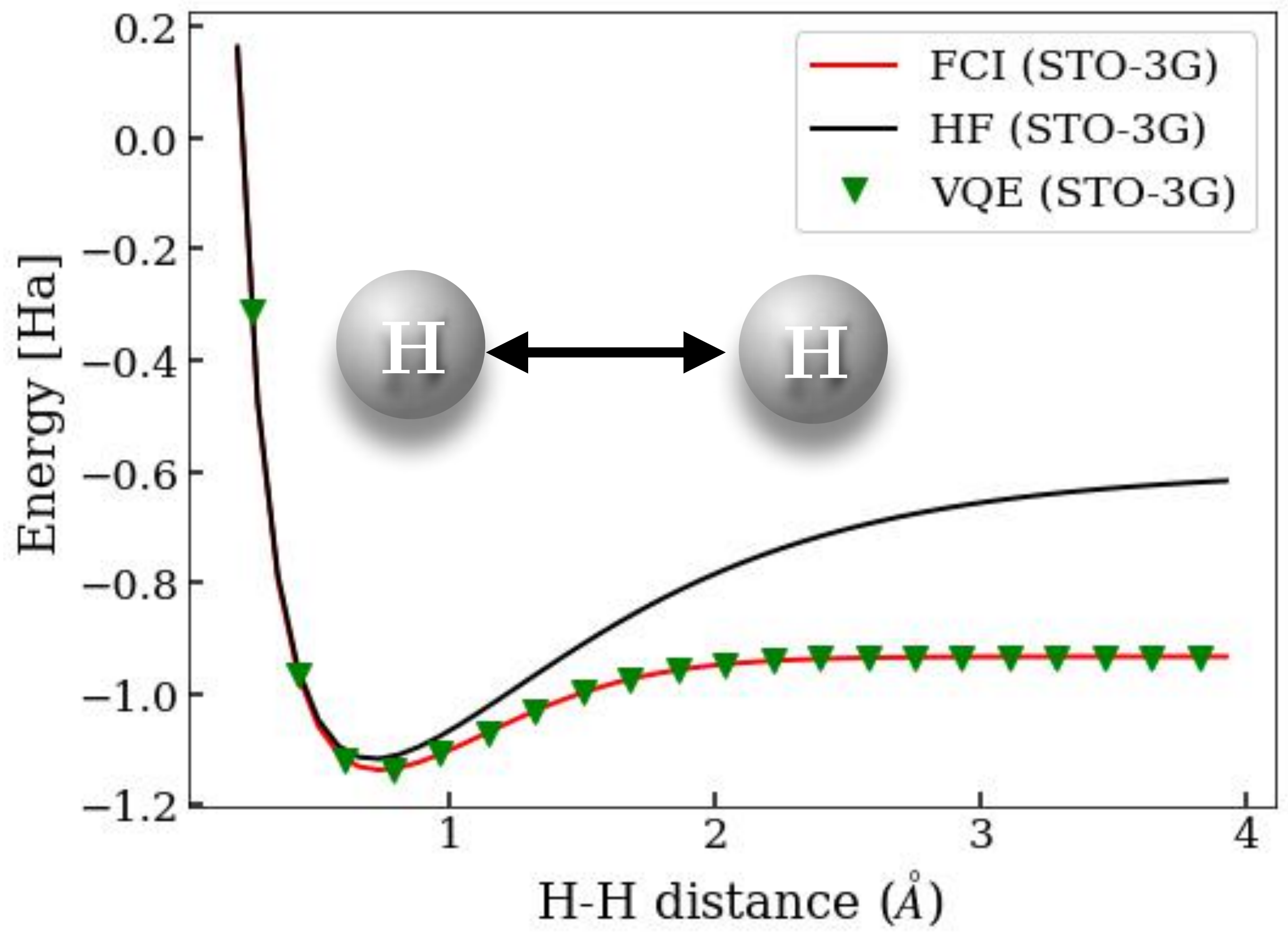
CPU



Measures on

$E(\vec{\theta}) = \langle\Psi(\vec{\theta})|\hat{H}|\Psi(\vec{\theta})\rangle$

VQE Noiseless simulation



III) Quantum algorithm for photochemistry

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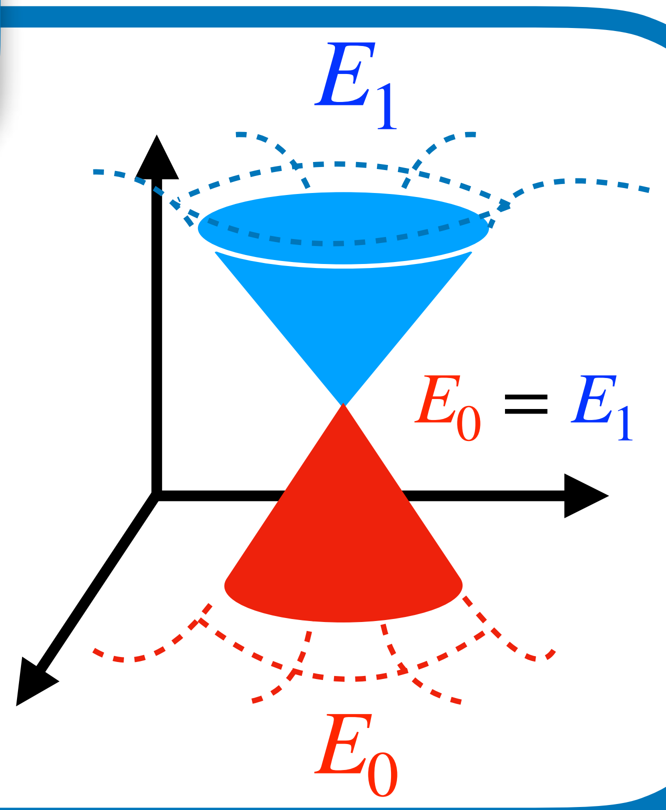
Conical intersection

Singular point of degeneracy connecting two Potential Energy Surfaces



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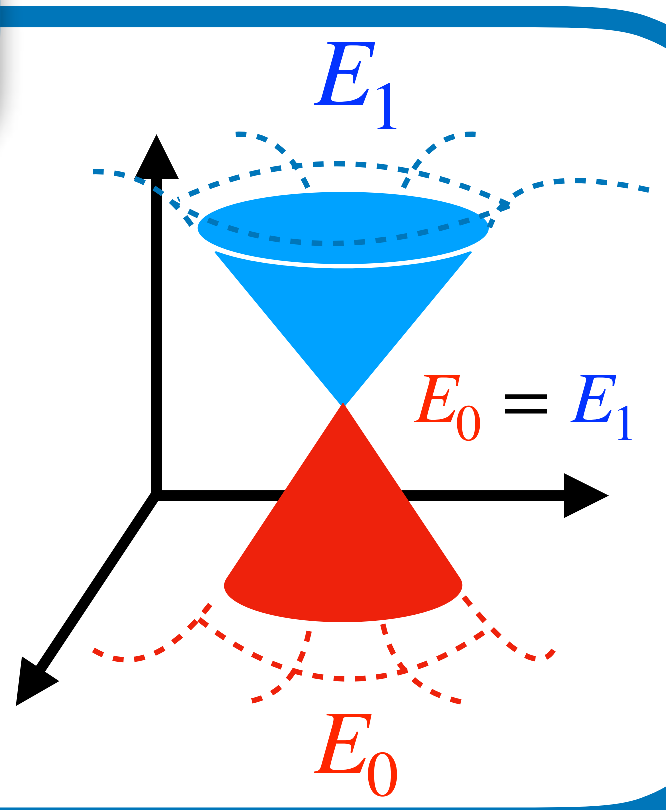

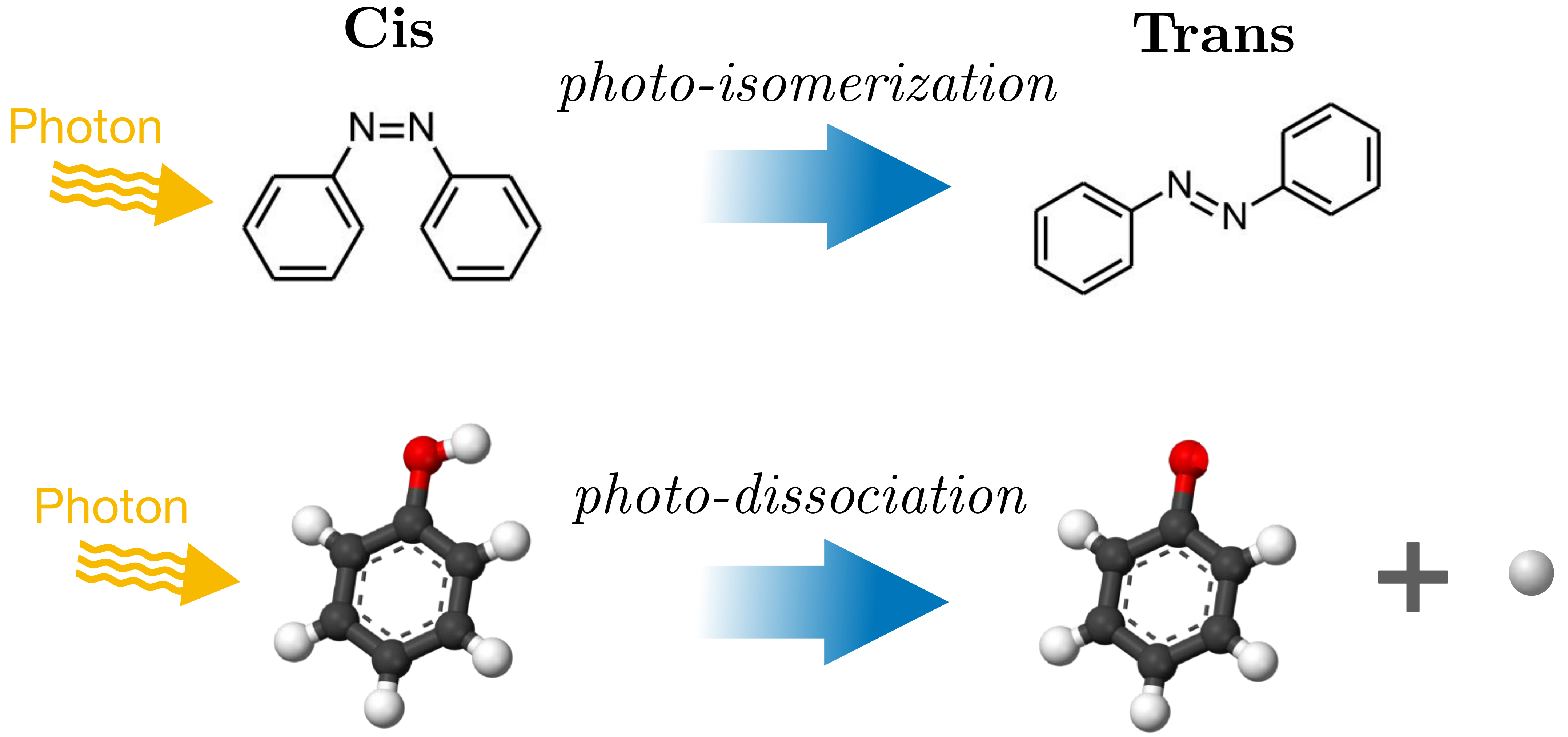

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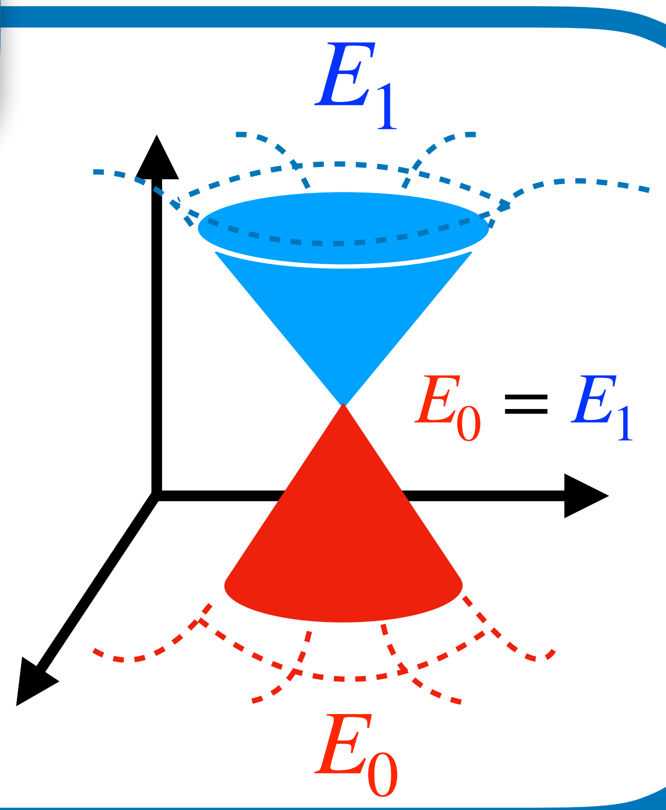

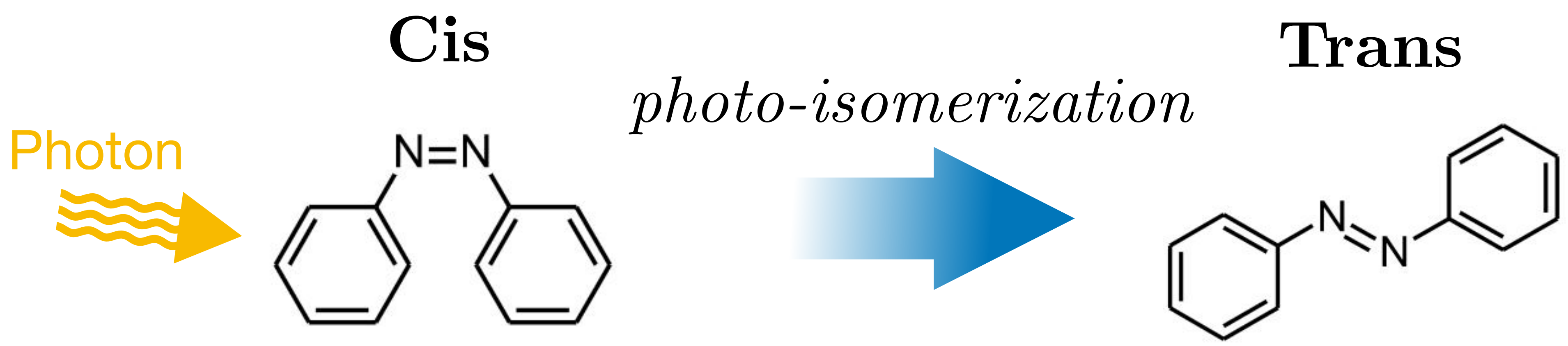

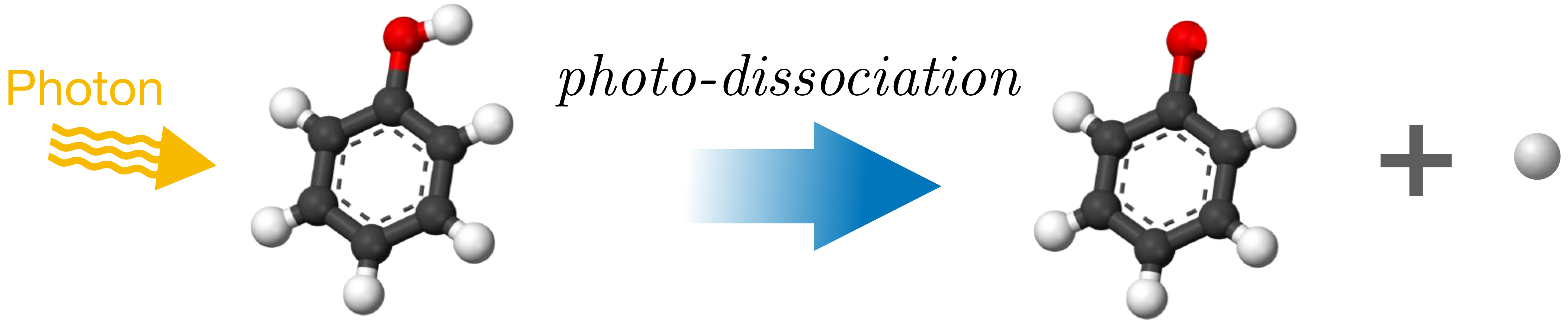

Challenge !

Democratic treatment of
Ground + Excited states

III) Quantum algorithm for photochemistry

Conical intersection

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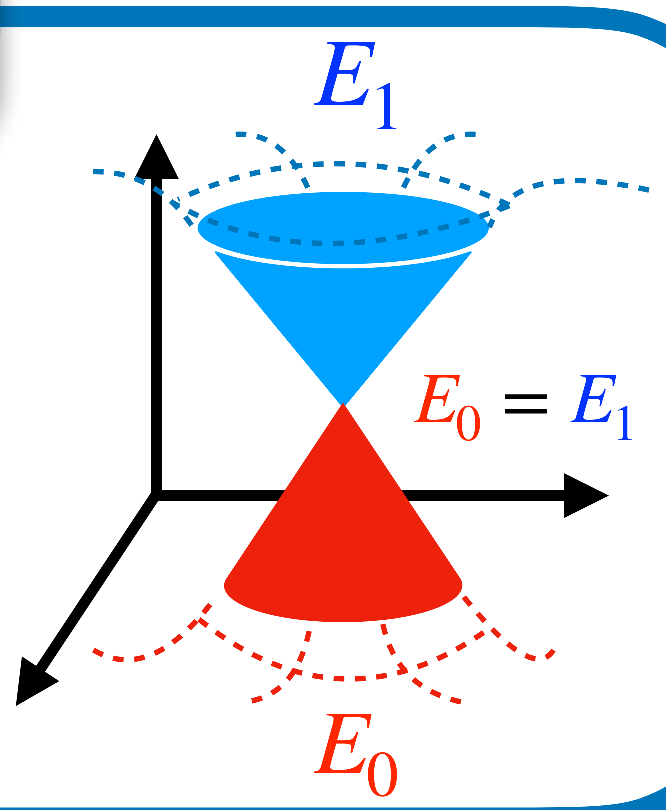
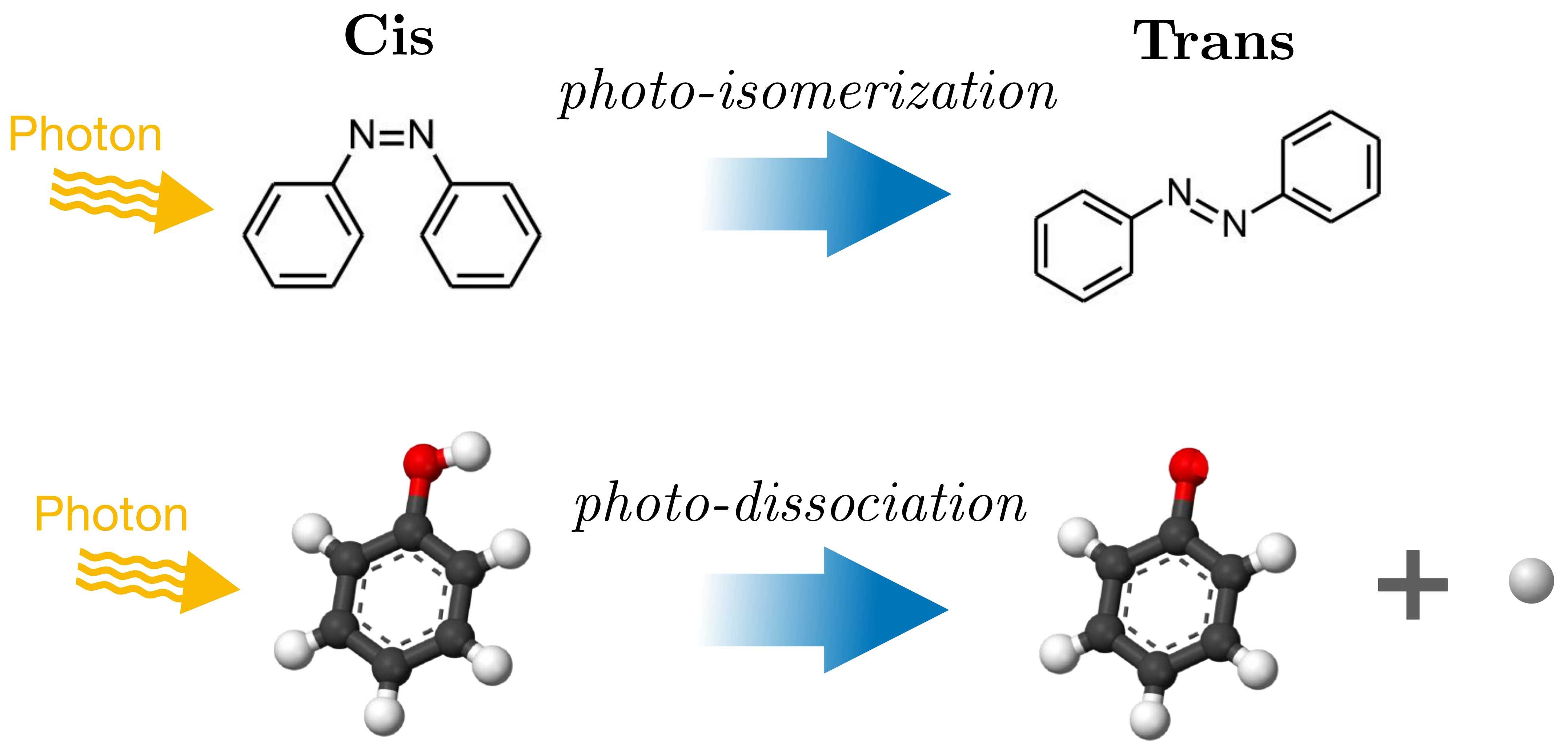




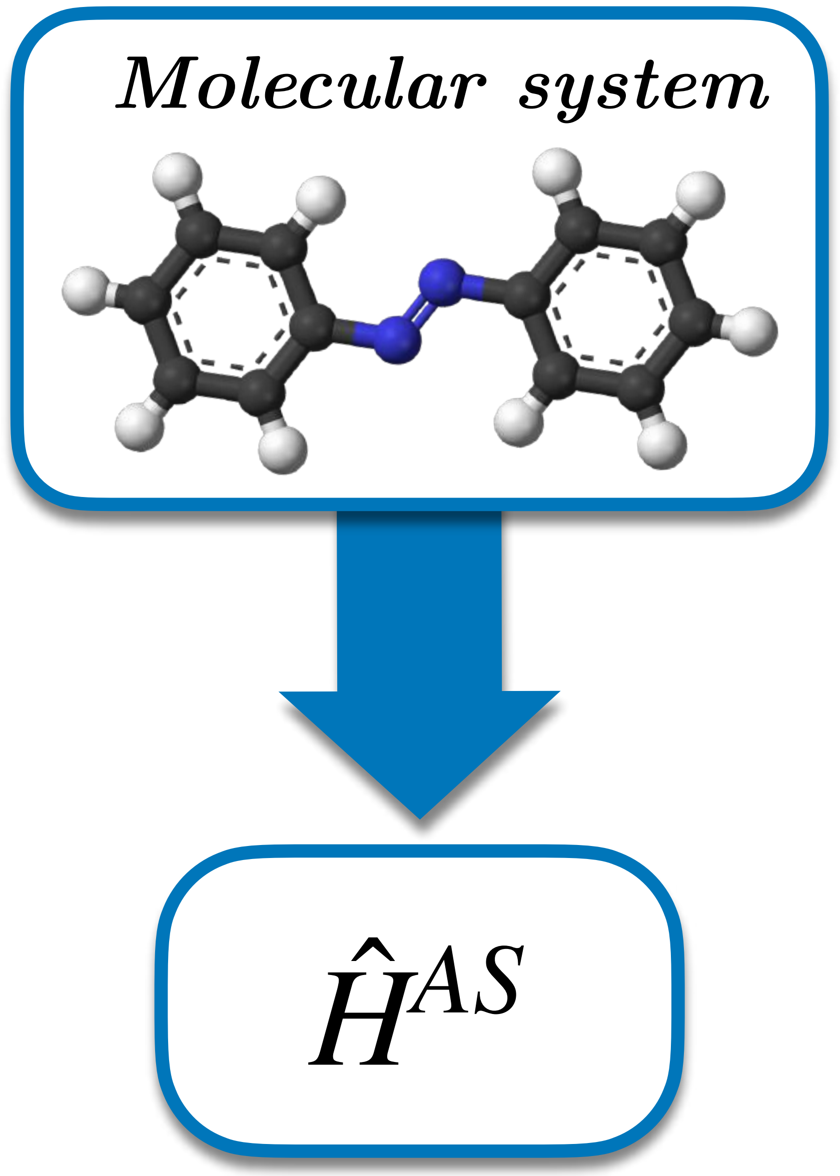
Challenge !

Democratic treatment of Ground + Excited states

SA-OO-VQE: State-Averaged Orbital-Optimized VQE

- Treats on an equal footing ensemble of states
- Provides useful data for photochemistry studies (*e.g.* PES, gradients and NAC)

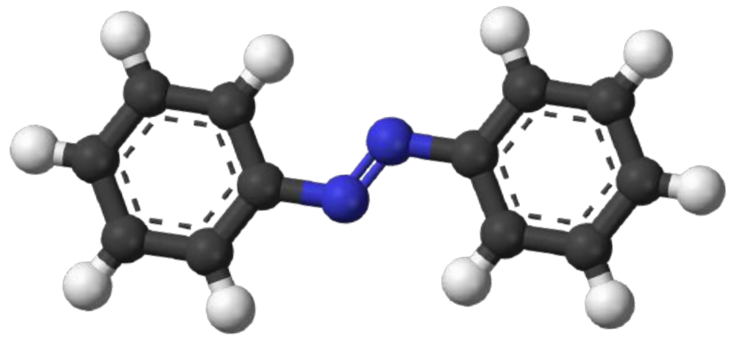
III) Quantum algorithm for photochemistry



III) Quantum algorithm for photochemistry

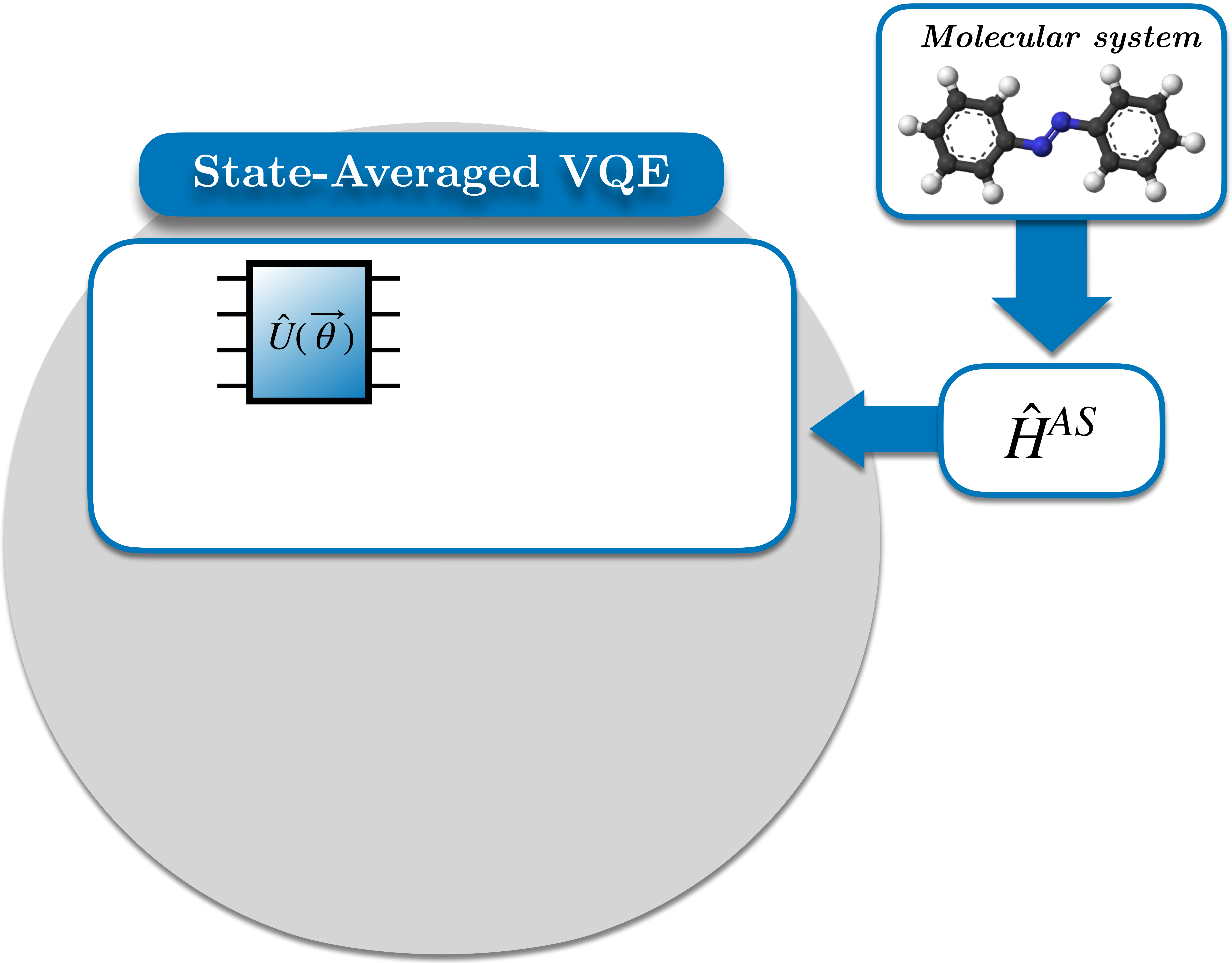
State-Averaged VQE

Molecular system

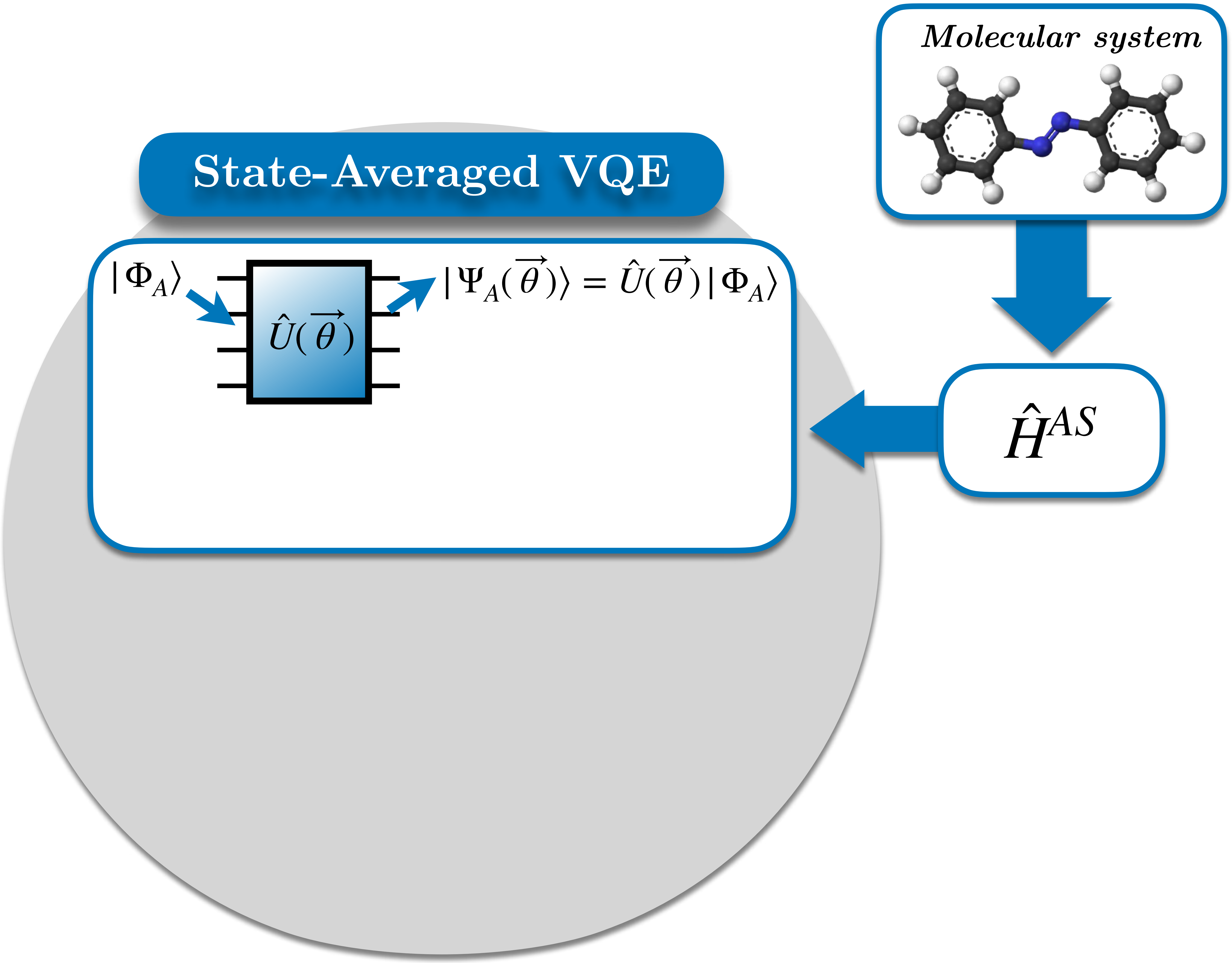


$\hat{H}^{AS}$

III) Quantum algorithm for photochemistry



III) Quantum algorithm for photochemistry



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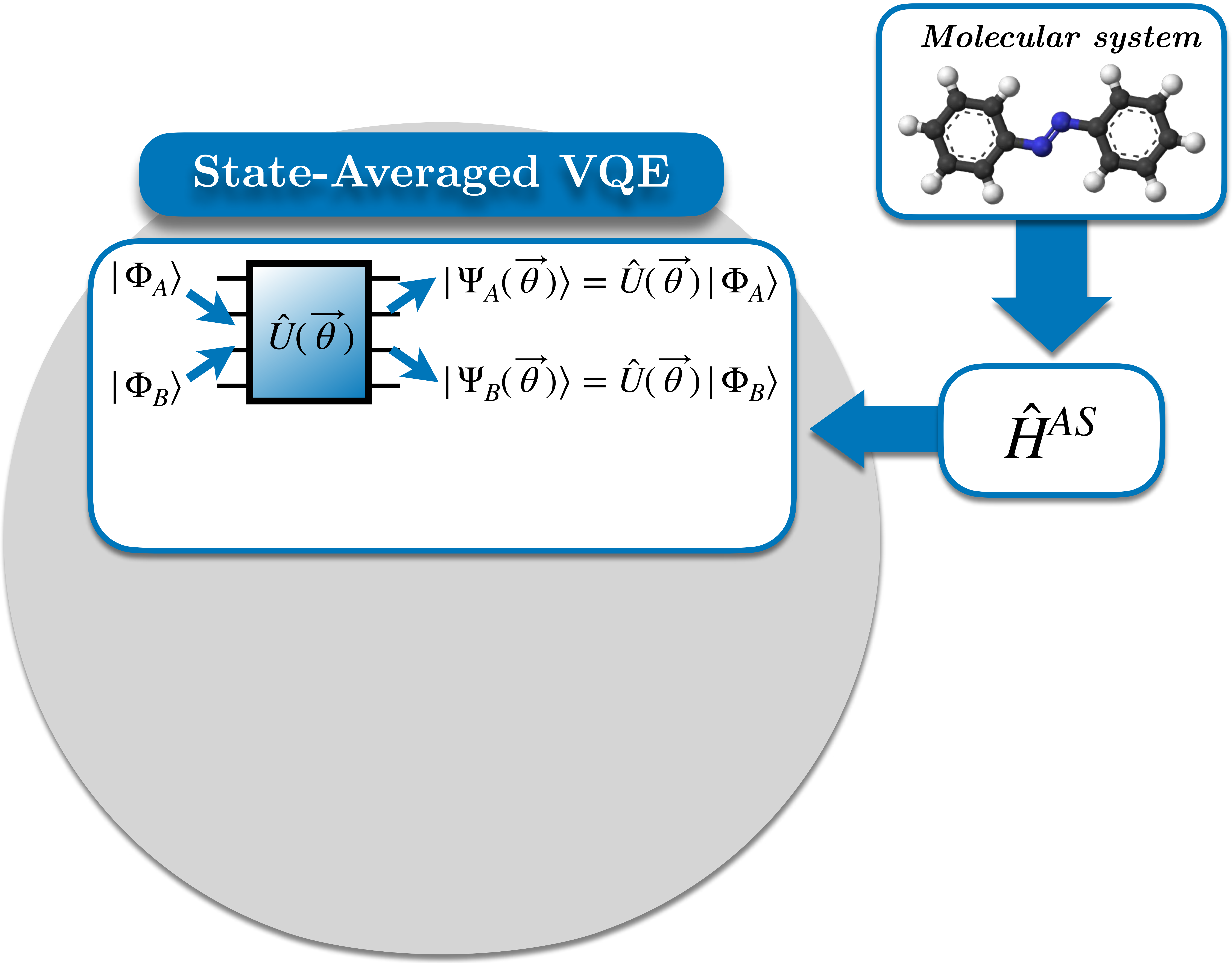

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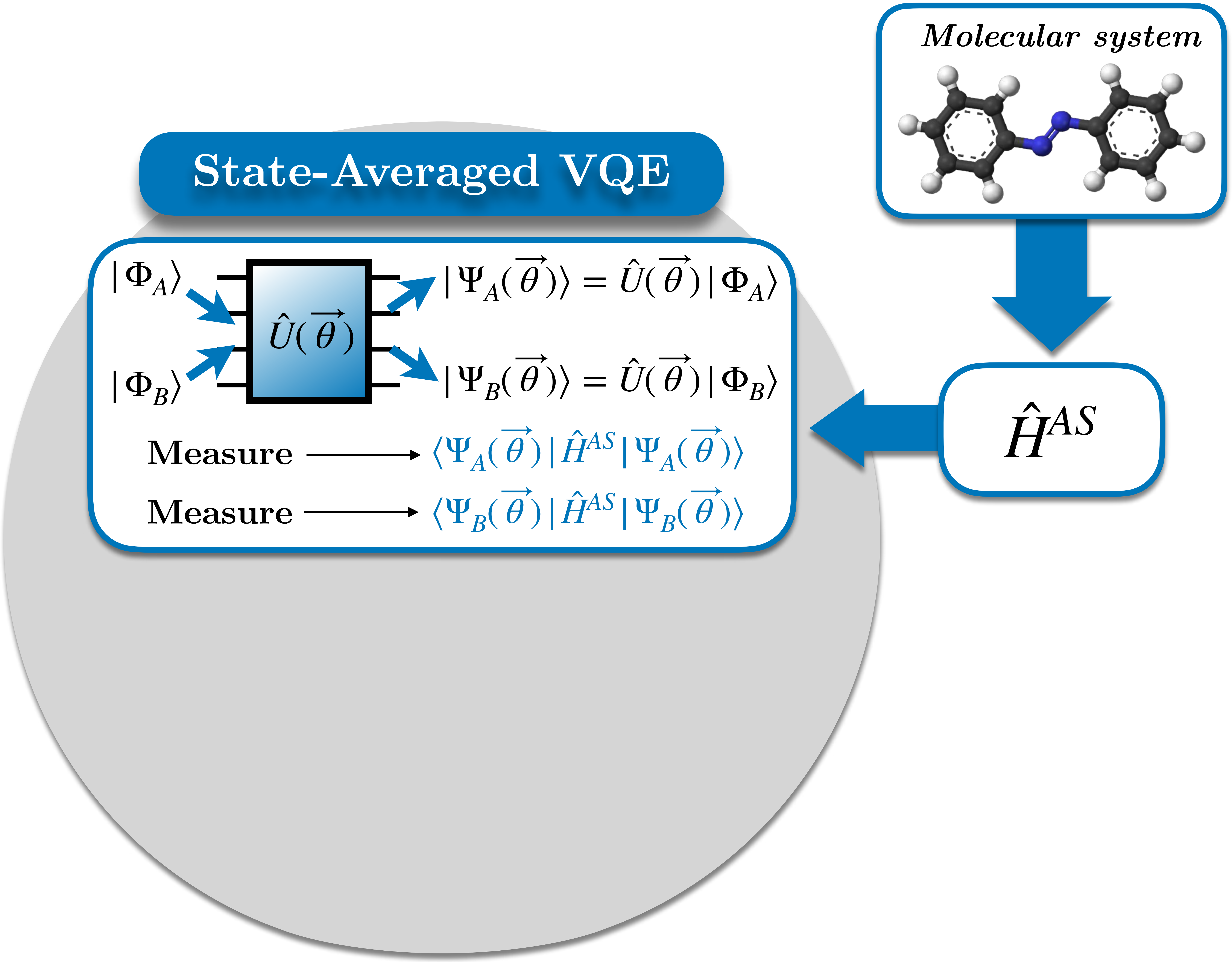

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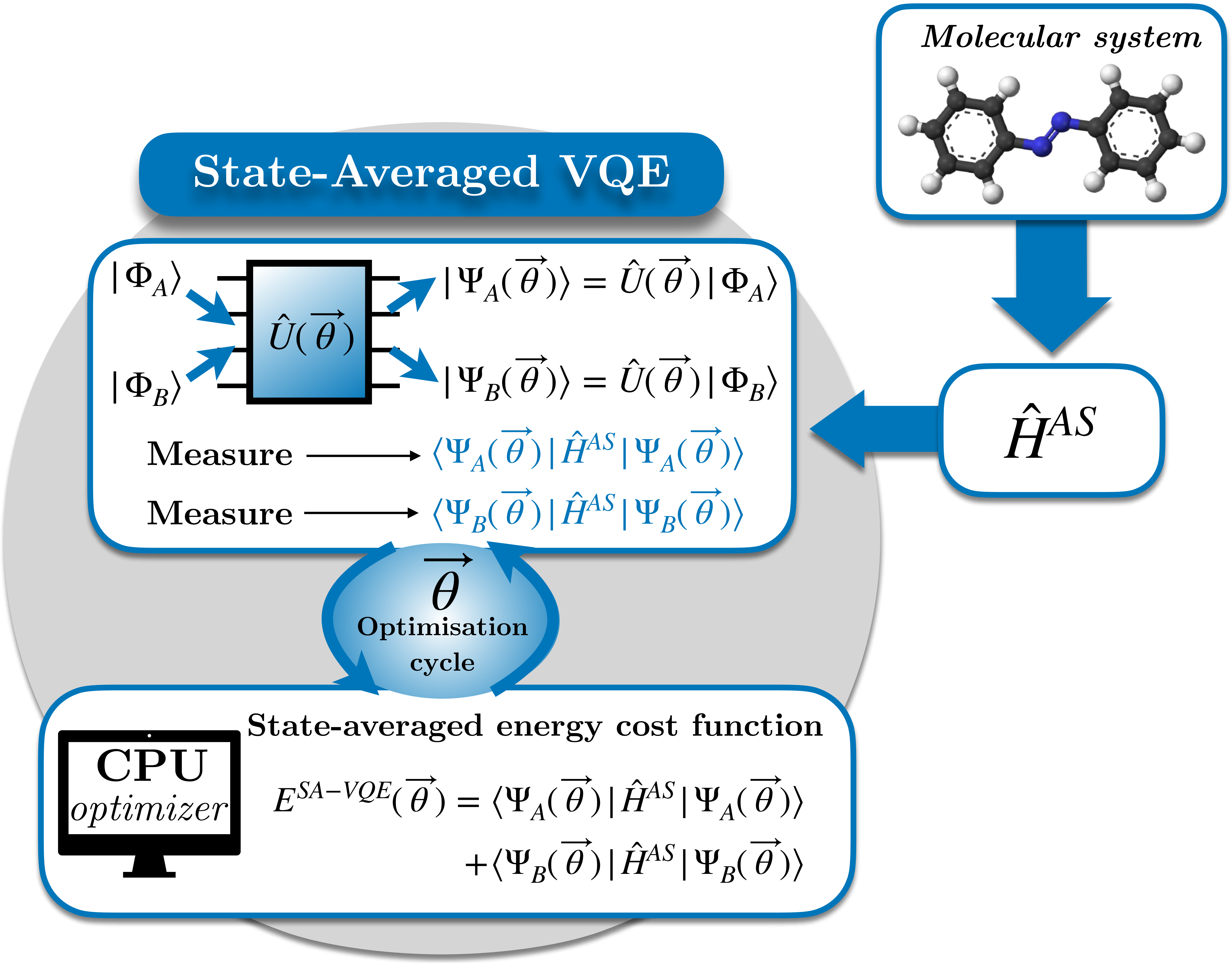

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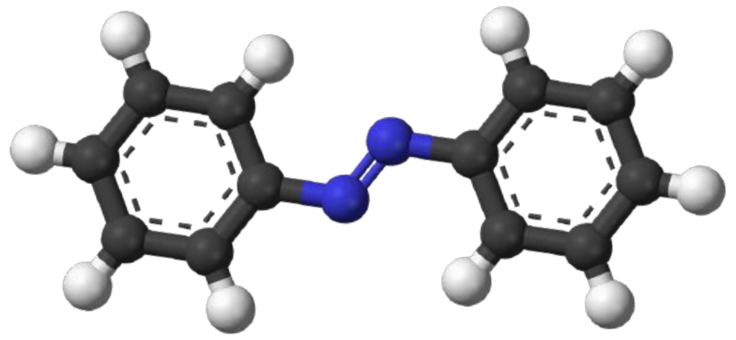

State-Averaged VQE

$|\Phi_A\rangle$, $|\Phi_B\rangle$ → $\hat{U}(\vec{\theta})$

$|\Psi_A(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|\Phi_A\rangle$

$|\Psi_B(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|\Phi_B\rangle$

$\hat{H}^{AS}$

Measure ⟶ $\langle\Psi_A(\vec{\theta})|\hat{H}^{AS}|\Psi_A(\vec{\theta})\rangle$

Measure ⟶ $\langle\Psi_B(\vec{\theta})|\hat{H}^{AS}|\Psi_B(\vec{\theta})\rangle$

$\vec{\theta}$ Optimisation cycle

CPU *optimizer*

State-averaged energy cost function

$$E^{SA-VQE}(\vec{\theta}) = \langle\Psi_A(\vec{\theta})|\hat{H}^{AS}|\Psi_A(\vec{\theta})\rangle + \langle\Psi_B(\vec{\theta})|\hat{H}^{AS}|\Psi_B(\vec{\theta})\rangle$$

Optimized correlated states

$|\Psi_A\rangle, |\Psi_B\rangle$

(1- & 2-RDMs)

State-Averaged Orbital-Optimizer

$\vec{\kappa}$ Orbital Rotation Parameters

Orbital rotated Hamiltonian

$$\hat{H}(\vec{\kappa}) = U_O(\vec{\kappa})^{\dagger}\hat{H}U_O(\vec{\kappa})$$

III) Quantum algorithm for photochemistry

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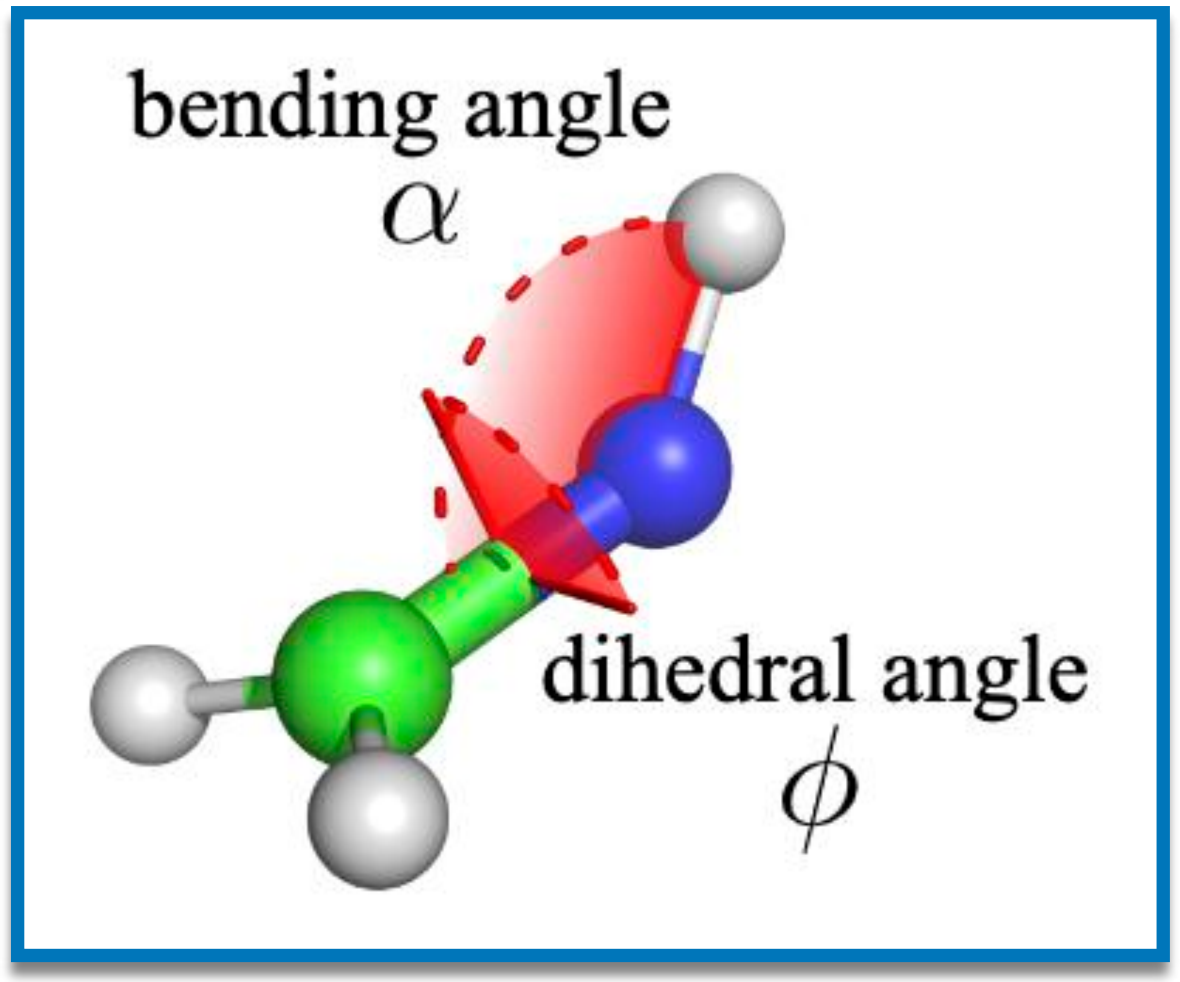
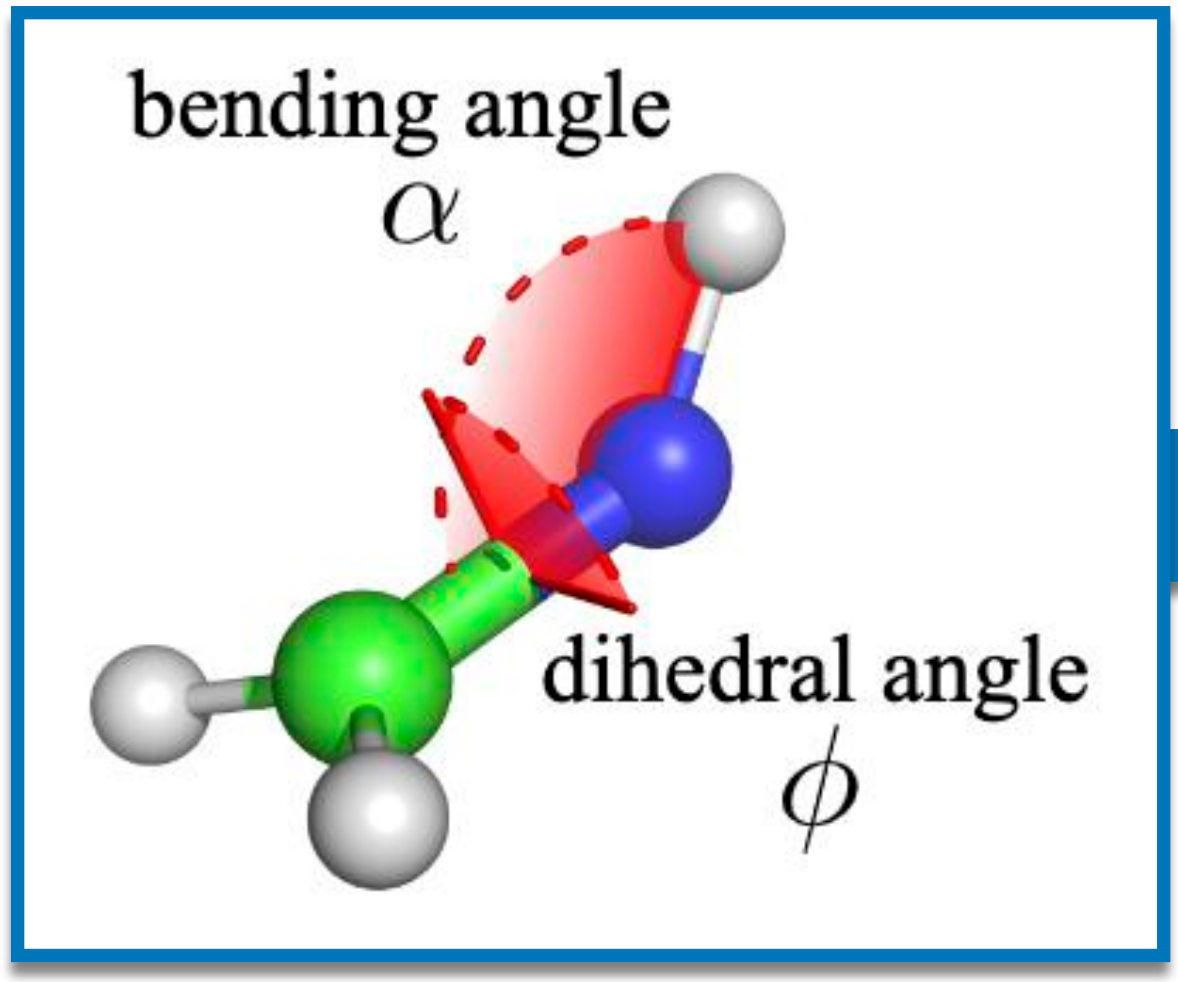


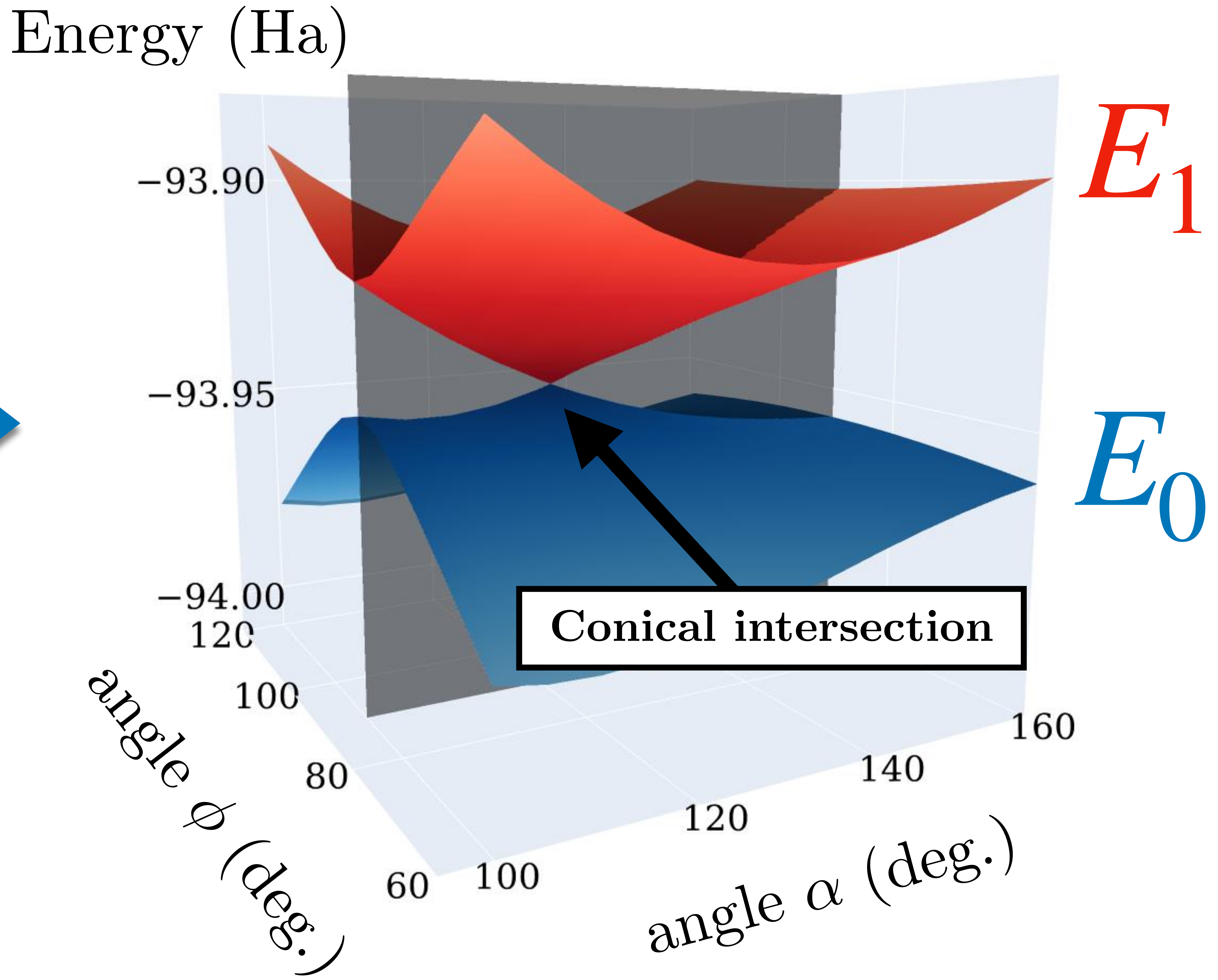
Setup :

- cc-pVDZ basis
- Active space (4 elec. in 3 orb.)
- Optimiser = SLSQP
- Generalised UCCD ansatz

III) Quantum algorithm for photochemistry



SA-OO-VQE
Noiseless
Simulations



Ground and first excited state PESs

Setup :

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- Active space (4 elec. in 3 orb.)
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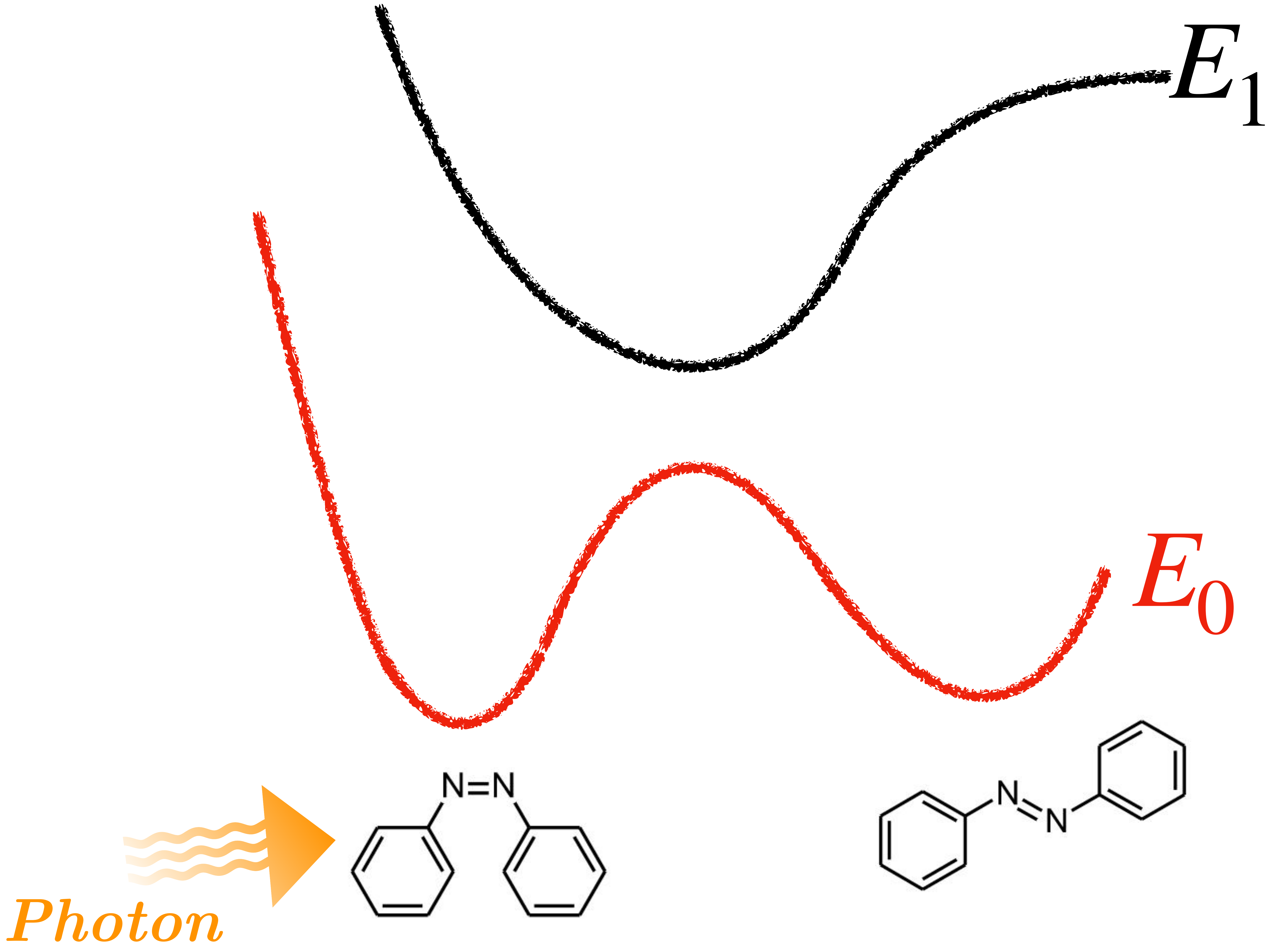
- Generalised UCCD ansatz

III) Quantum algorithm for photochemistry

Ab initio Quantum Dynamics

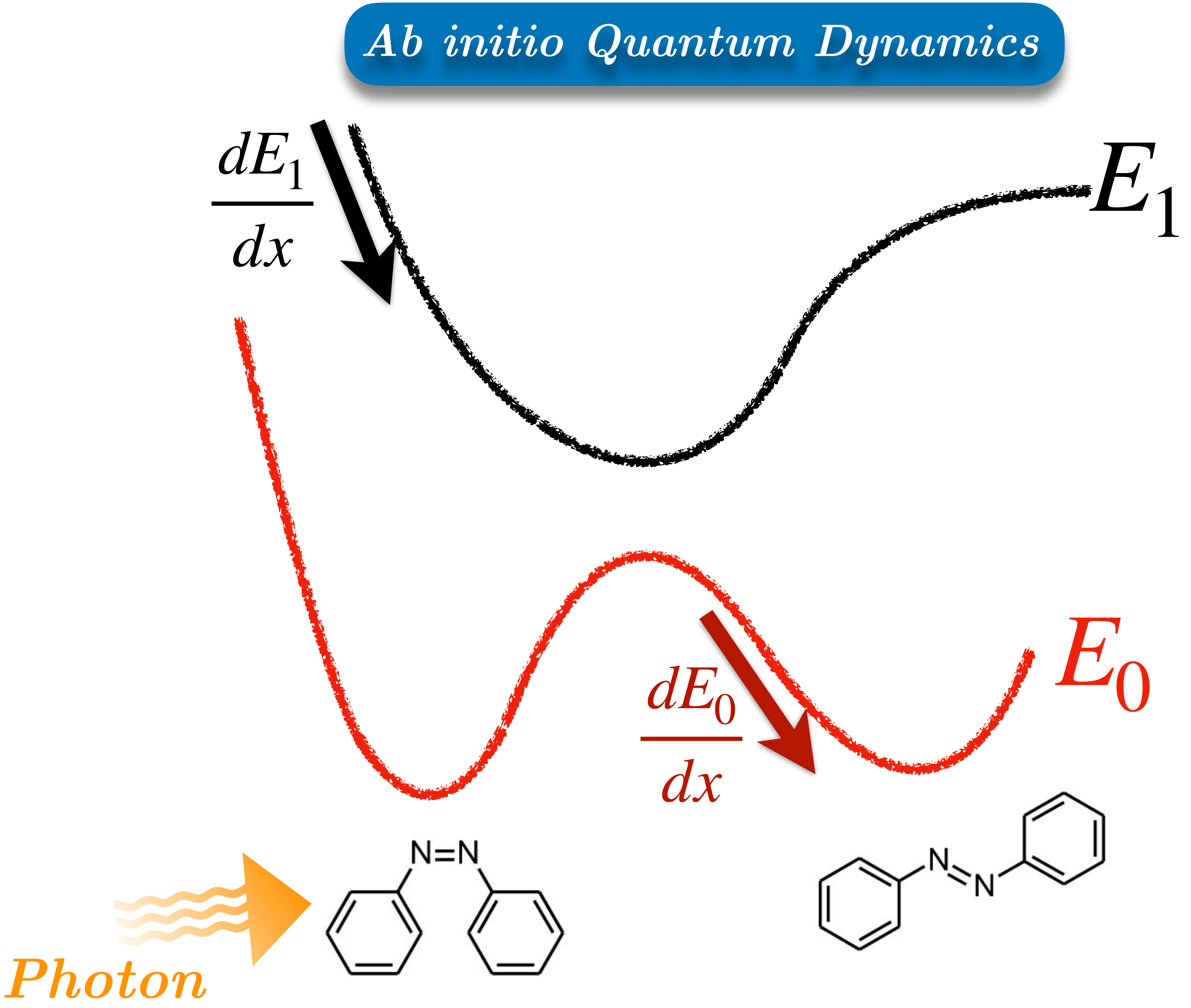


III) Quantum algorithm for photochemistry

Nuclear derivatives

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

Nuclear forces with respect to coordinate " x "



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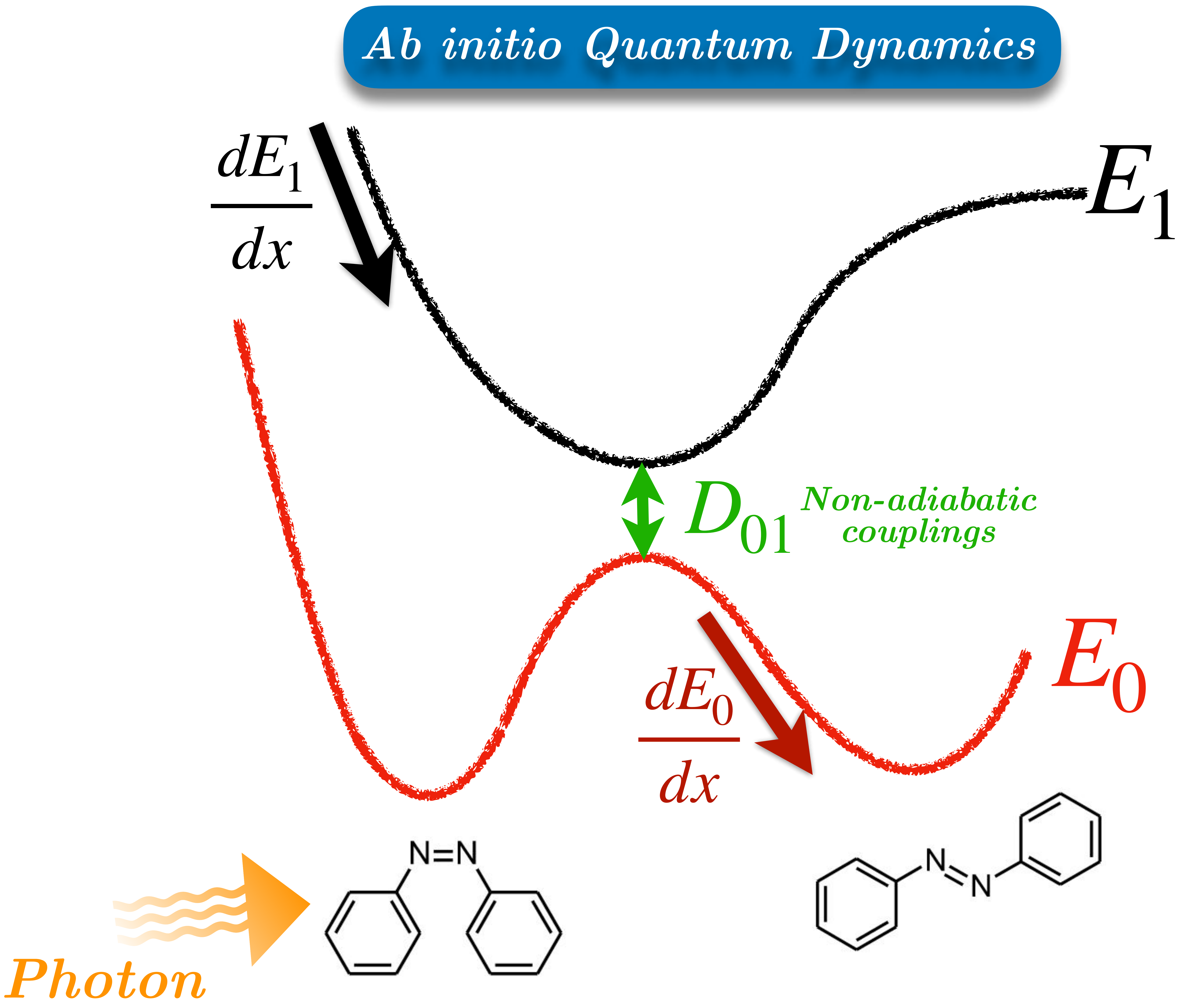
$$D_{IJ} = \langle \Psi_I | \frac{d}{dx} \Psi_J \rangle$$

Coupling between two states through nuclear vibrations



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$$\frac{dE_I}{dx} \xrightarrow{\text{PROBLEM !}} \frac{\partial E_I}{\partial \kappa_{pq}} \neq 0 \ \ \& \ \ \frac{\partial E_I}{\partial \theta_n} \neq 0$$

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Lagrange multiplier method

$$\mathcal{L}_I = E_I + \sum_{pq} \bar{\kappa}^I_{pq} \frac{\partial E^{SA}}{\partial \kappa_{pq}} + \sum_n \bar{\theta}^I_n \frac{\partial E^{SA}}{\partial \theta_n}$$

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

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Can be measured out of the circuit !

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Can be measured out of the circuit !

Final analytical form

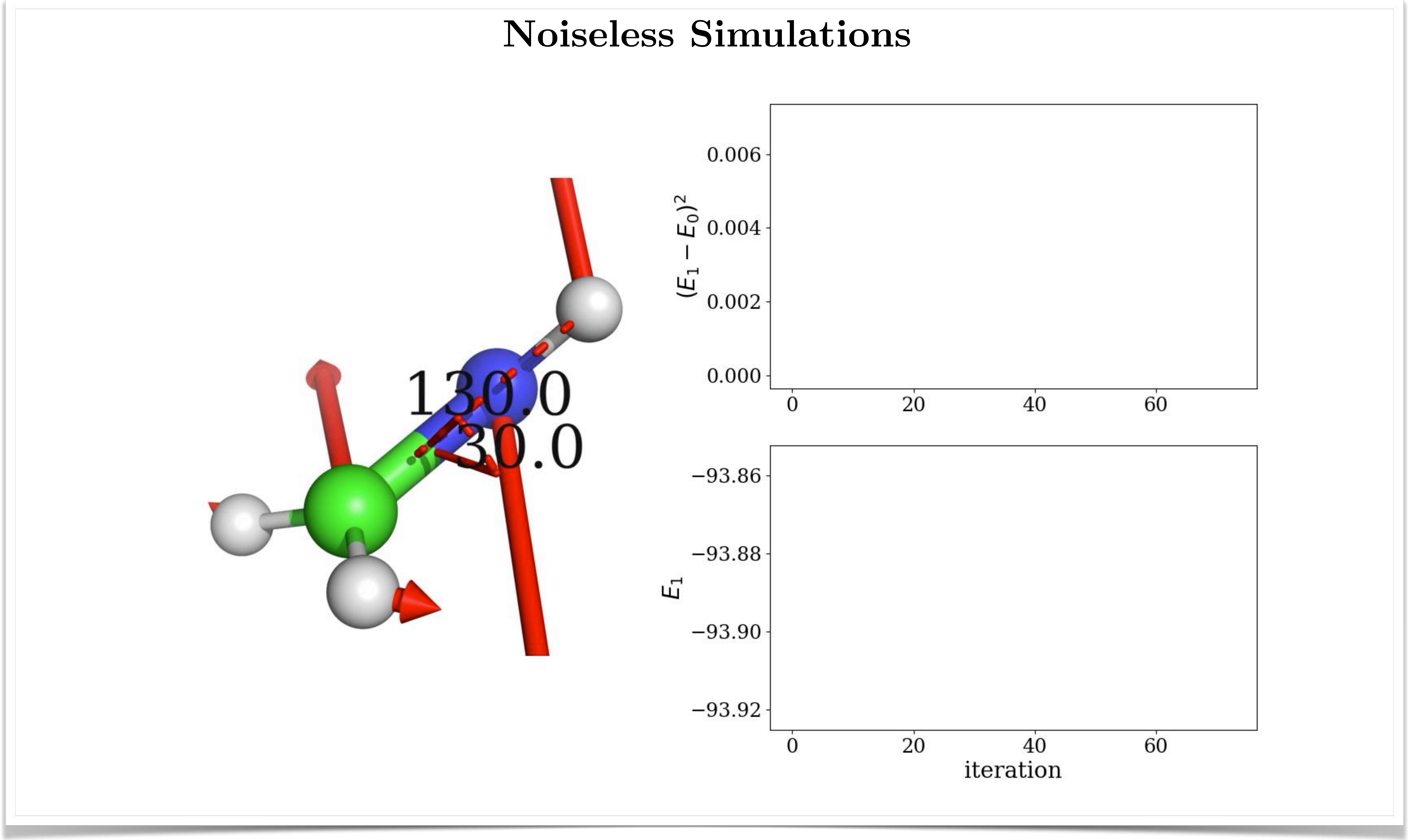
$$\frac{dE_I}{dx} = \sum_{pq} \frac{\partial h_{pq}}{\partial x} \gamma^{I,eff}_{pq} + \frac{1}{2} \sum_{pqrs} \frac{\partial g_{pqrs}}{\partial x} \Gamma^{I,eff}_{pqrs} + \sum_J \sum_n w_J \bar{\theta}^I_n G^{C,J}_n \left(\frac{\partial \hat{H}}{\partial x}\right)$$

III) Quantum algorithm for photochemistry

Ingredients:

- **Nuclear gradients**
- **Non-adiabatic couplings**

Research of Minimal-energy conical-intersection (MECI)



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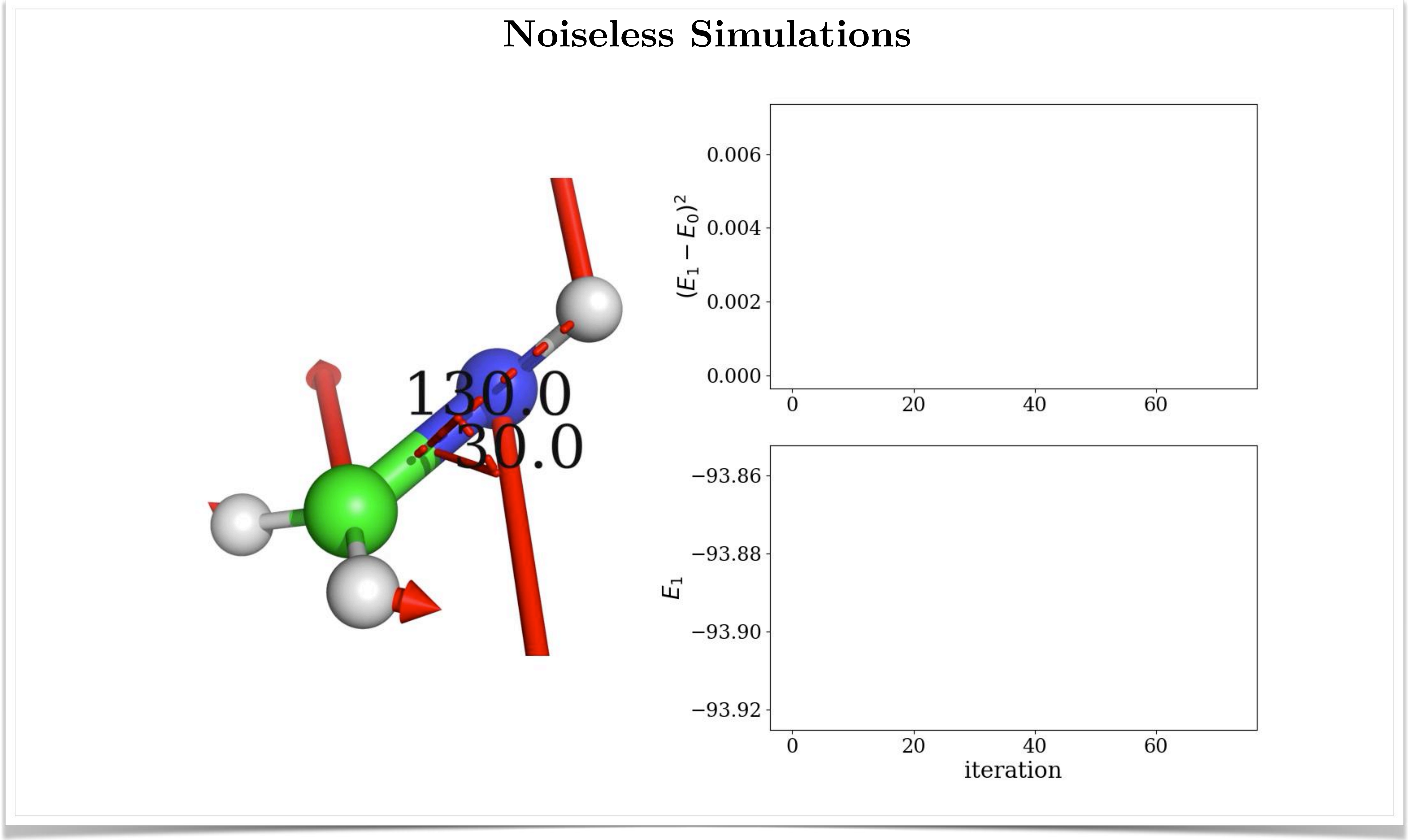

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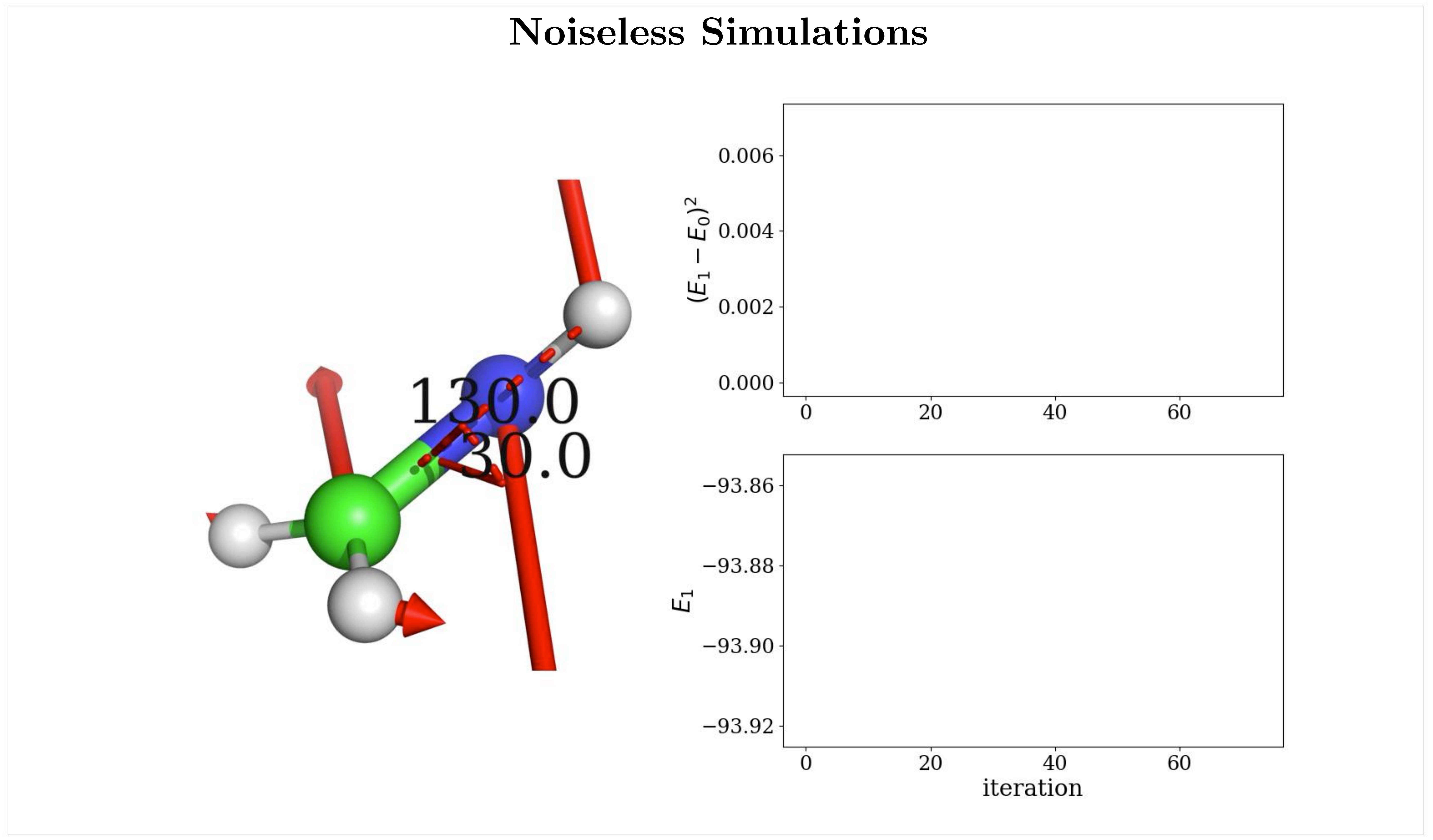

SA-OO-VQE = Quantum analog of SA-CASSCF

Take Home Messages

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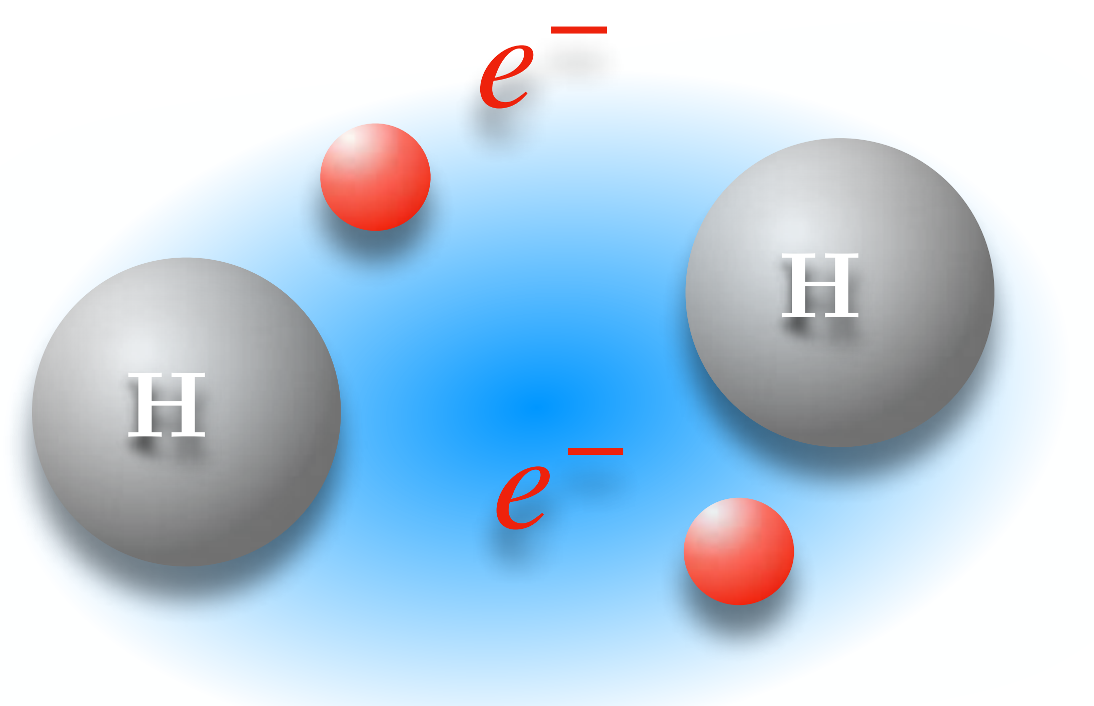

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

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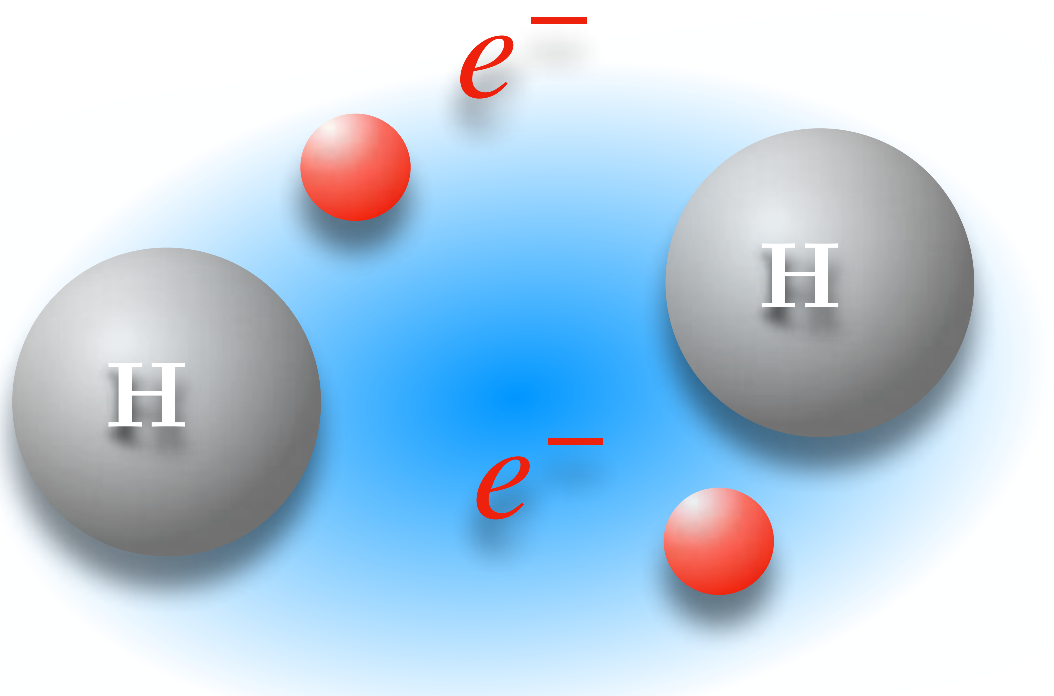

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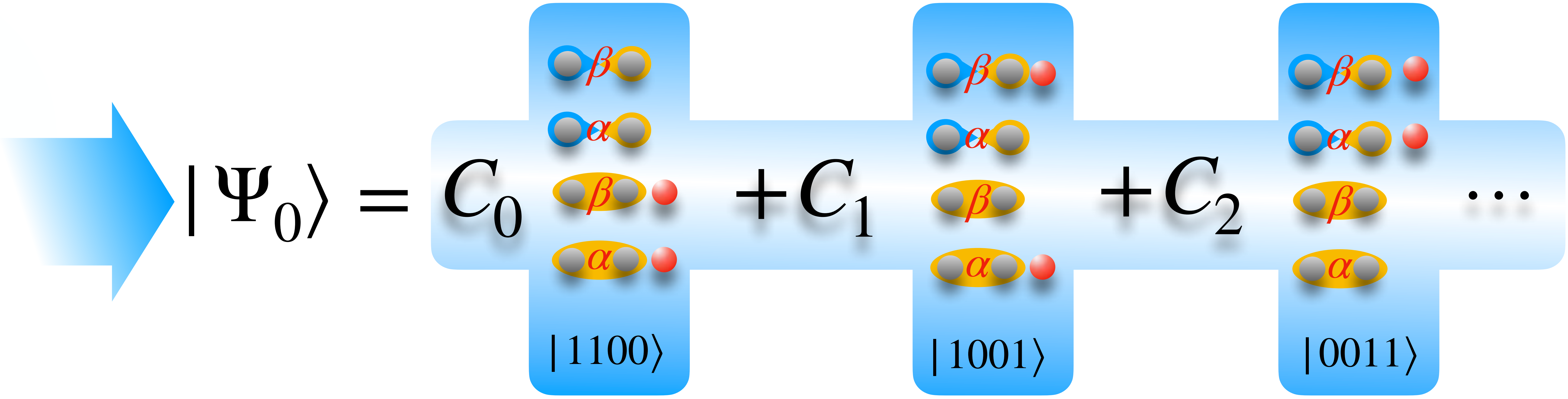

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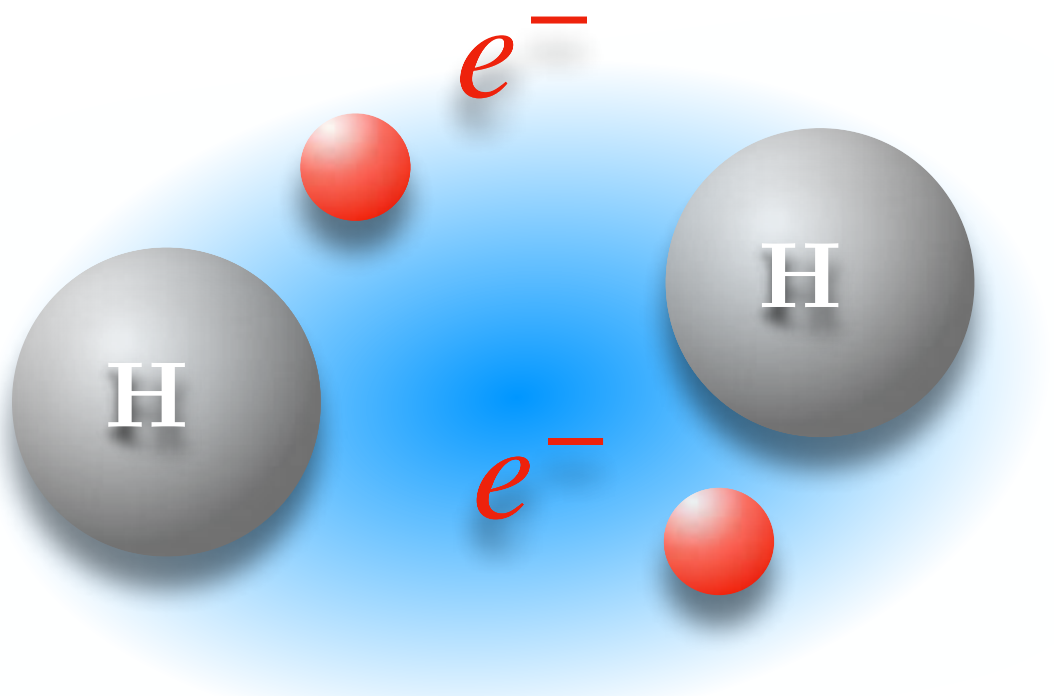

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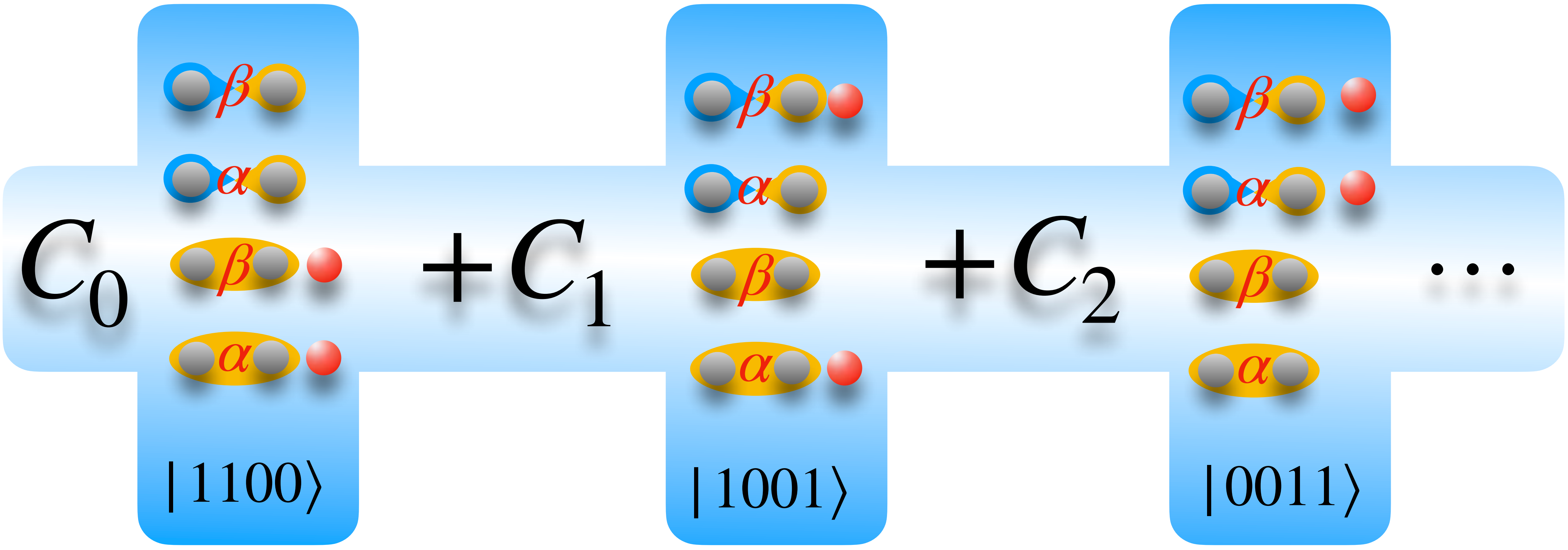
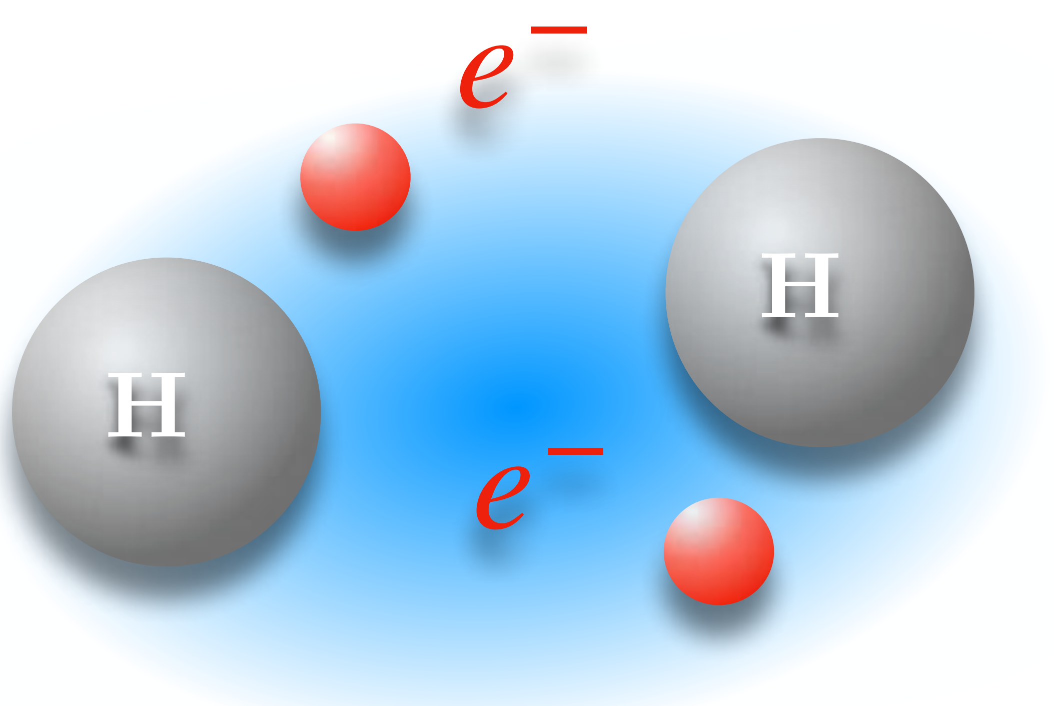


Quantum Algorithm

Take Home Messages



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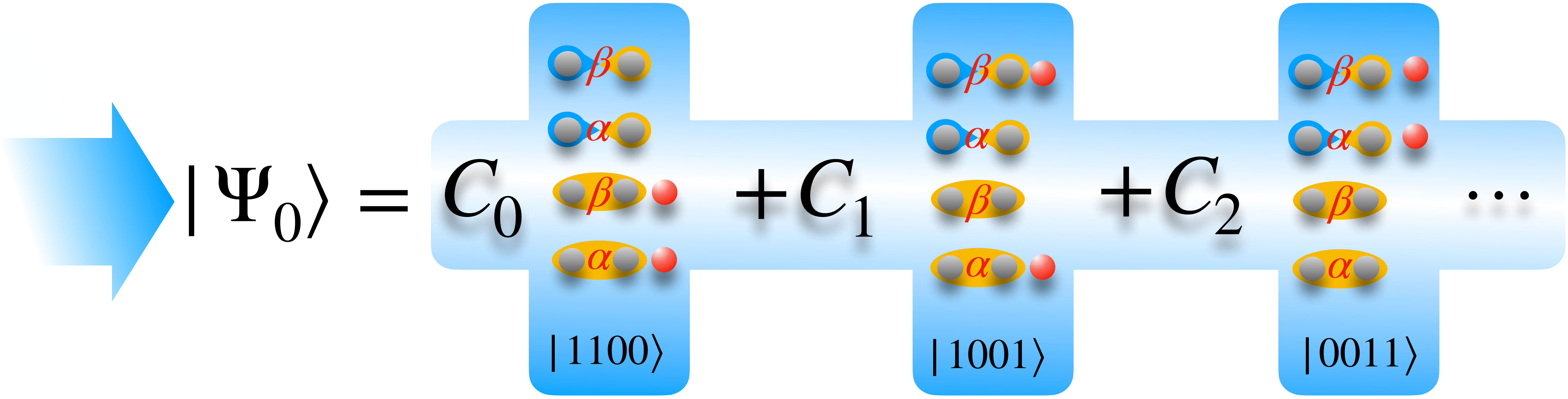

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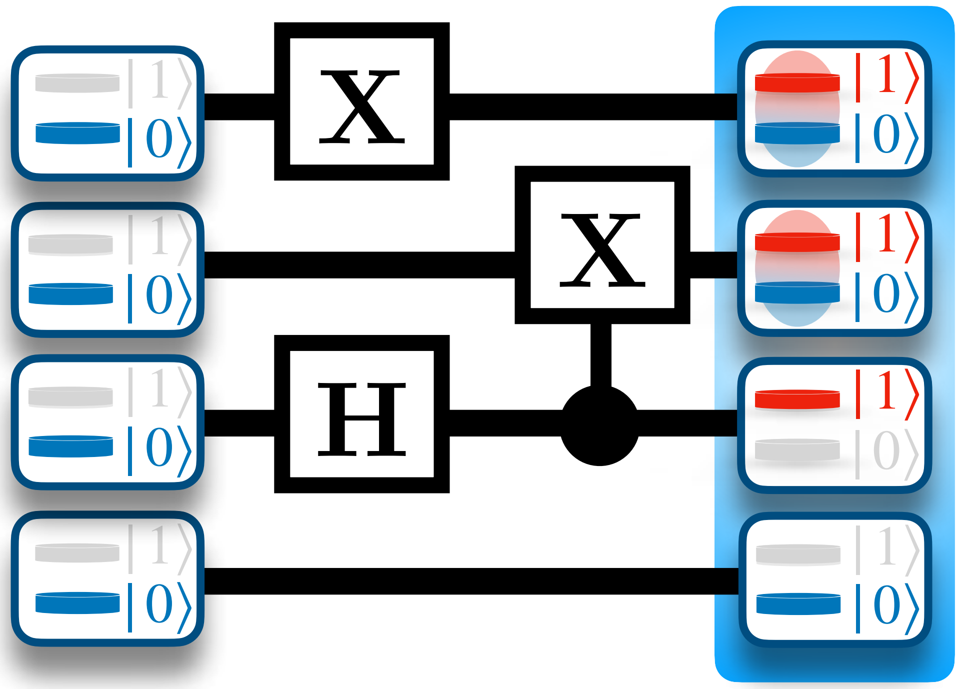

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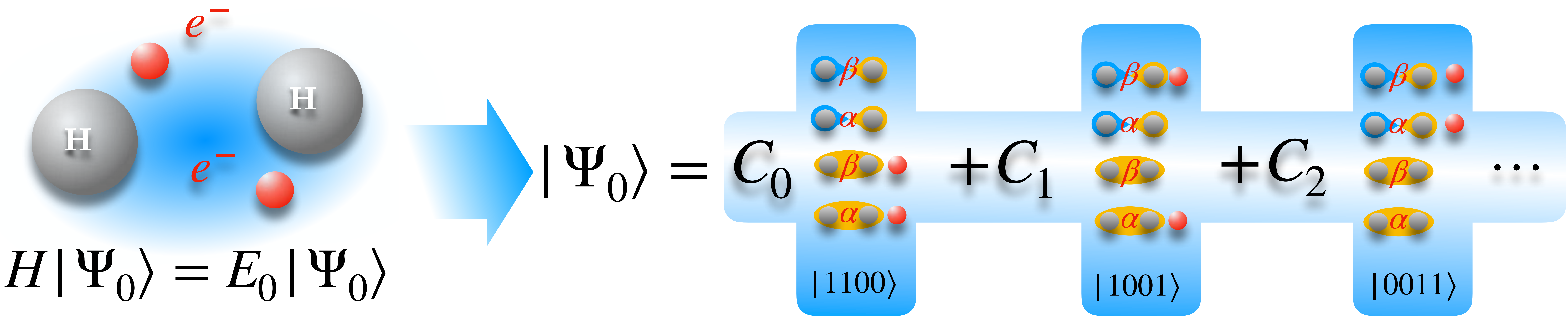

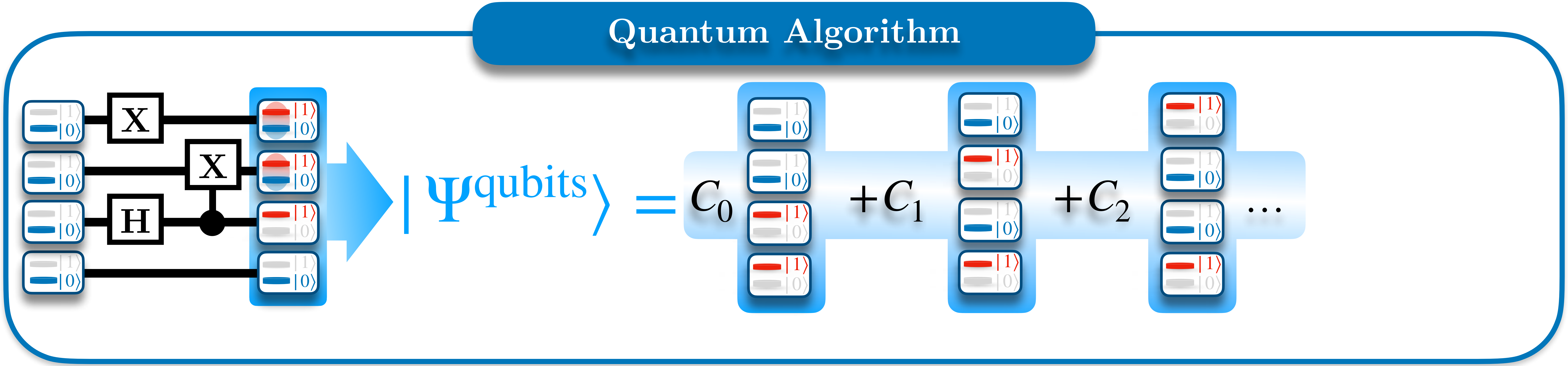

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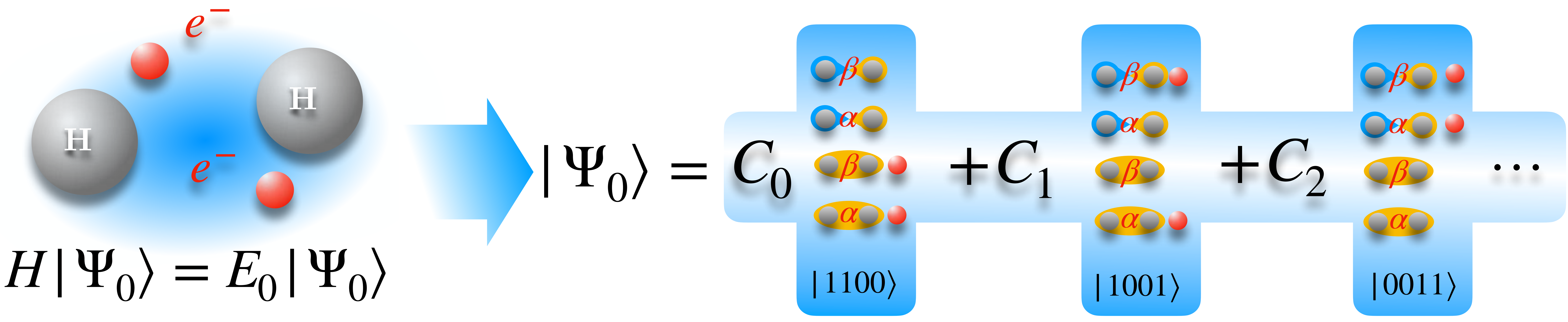

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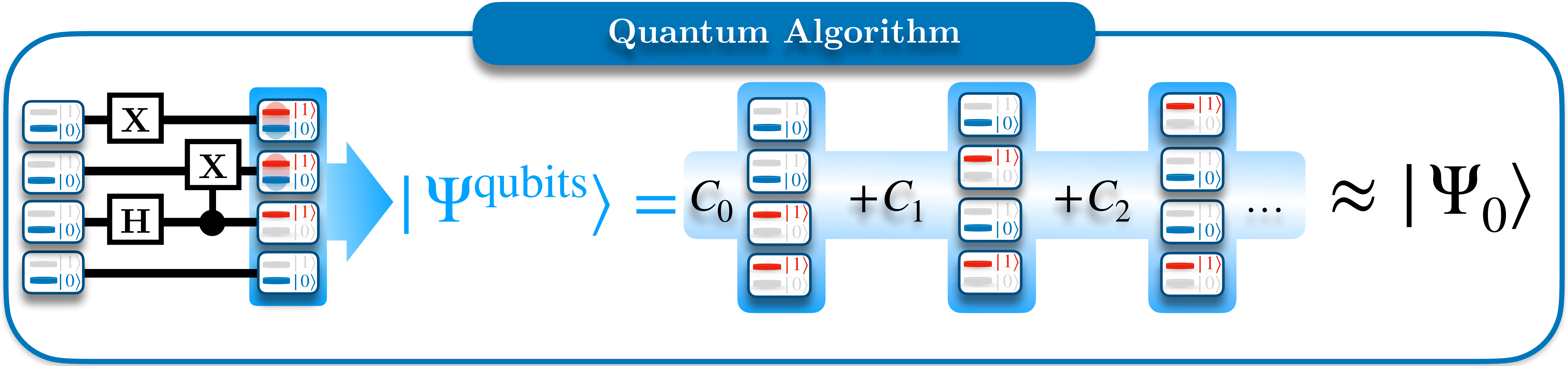

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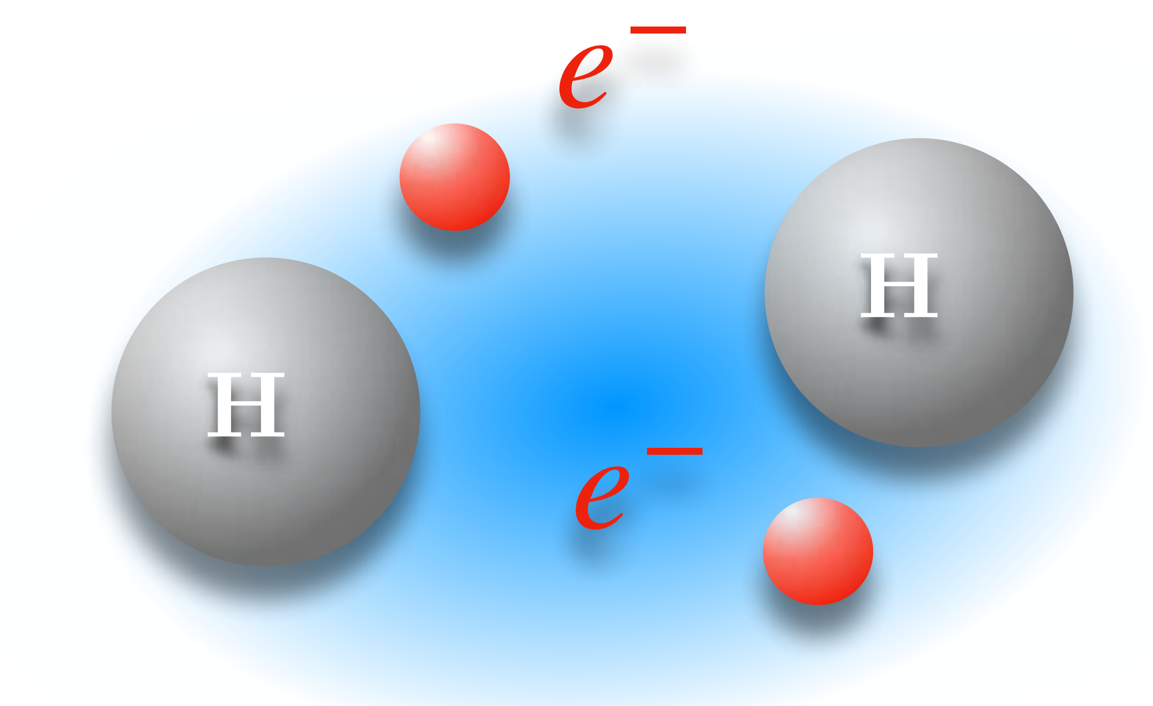

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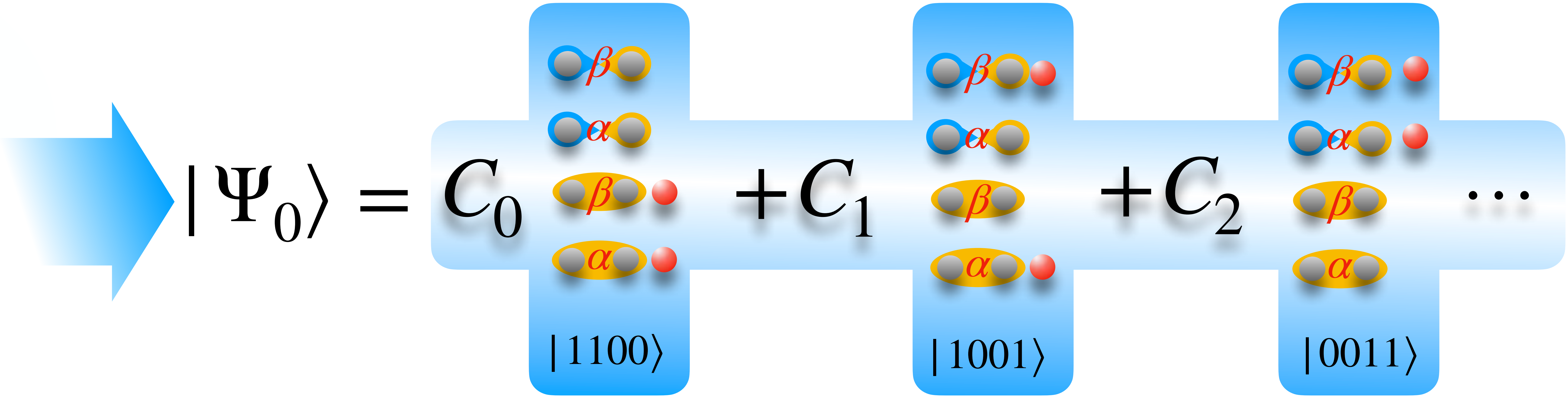
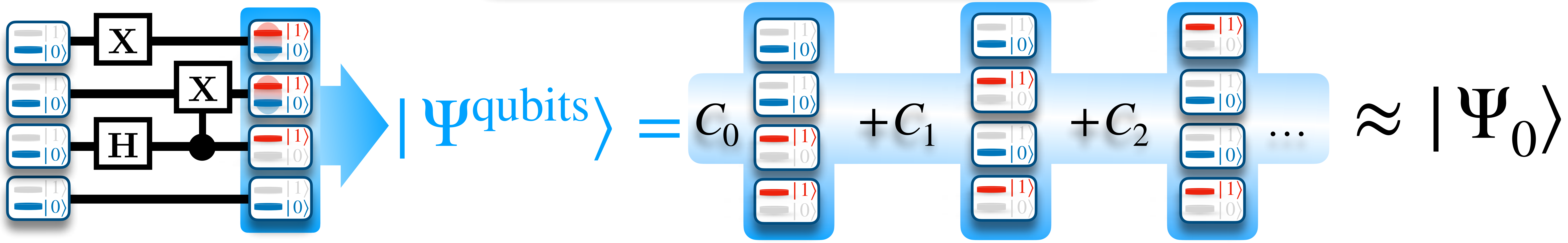


Quantum Algorithm



NISQ era (ressources limitations)

Take Home Messages

SA-OO-VQE: Quantum algorithm for photo-chemistry

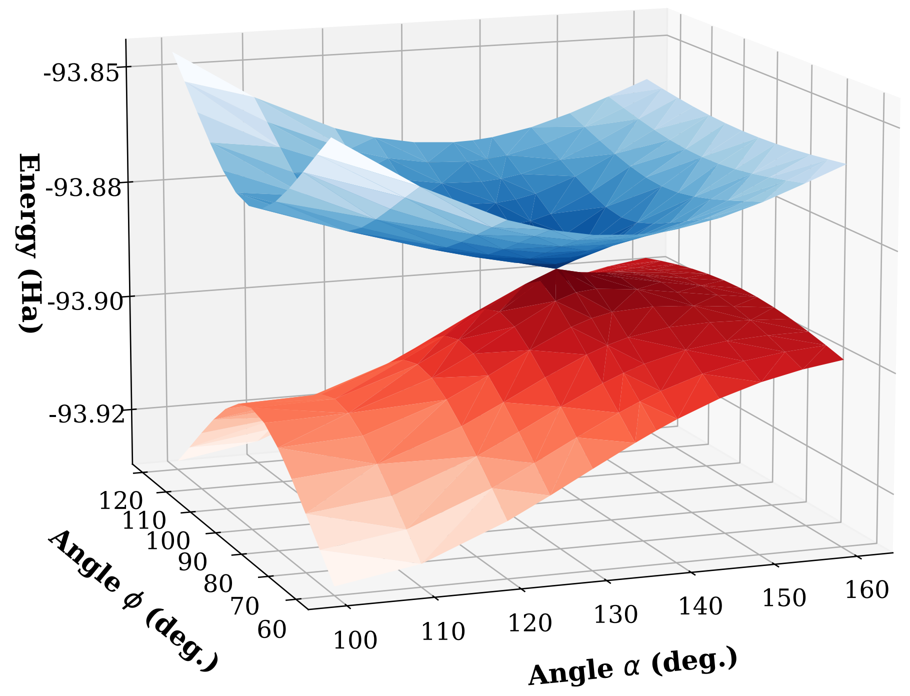
S. Yalouz et al. *Quantum Science and Technology* 6.2 (2021): 024004.

S. Yalouz et al. *Journal of chemical theory and computation* 18.2 (2022): 776-794.

Take Home Messages

SA-OO-VQE: Quantum algorithm for photo-chemistry

Description of degenerated PES



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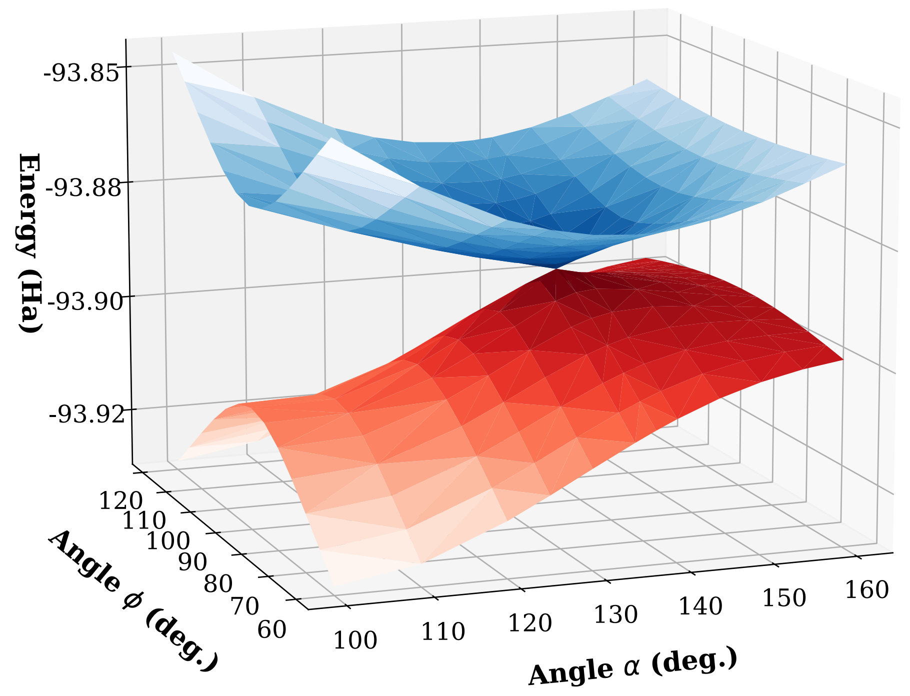

Nuclear derivatives

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

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Take Home Messages

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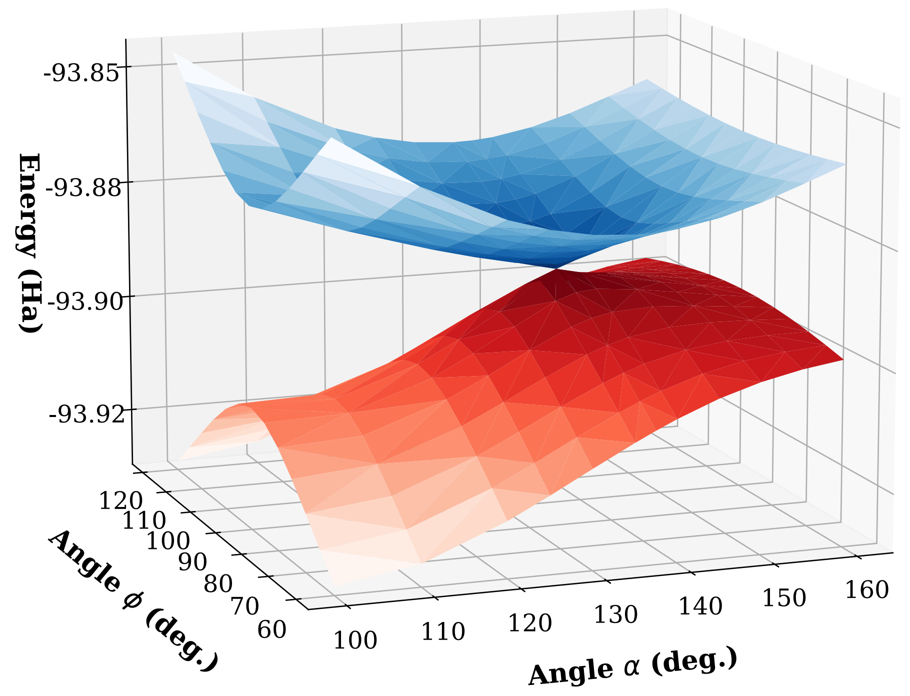

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Non-adiabatic couplings

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

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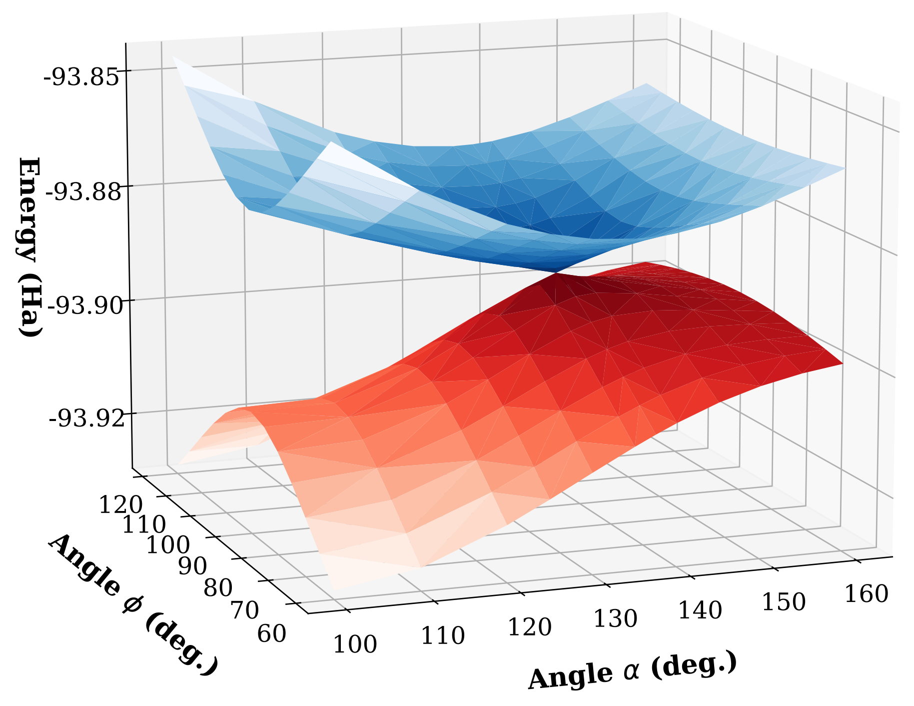

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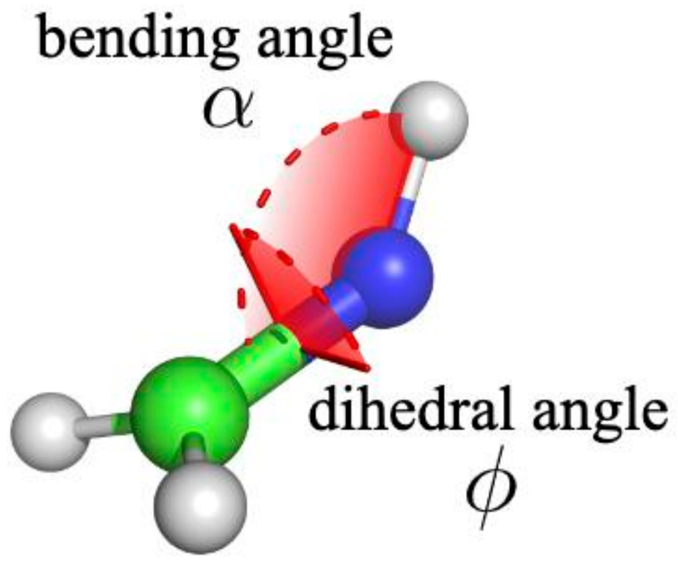

MECI optimization

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Take Home Messages

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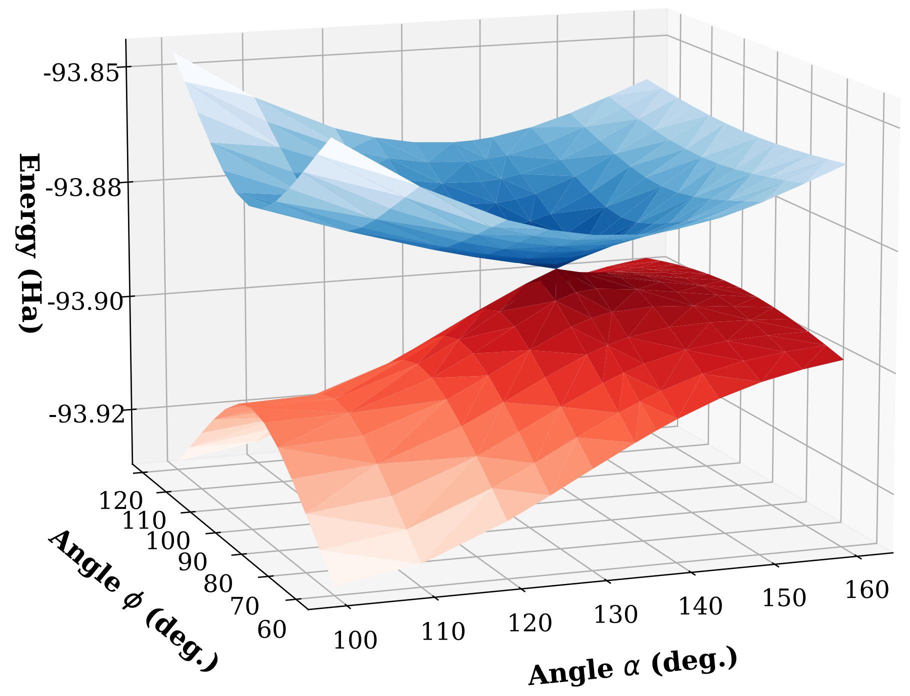

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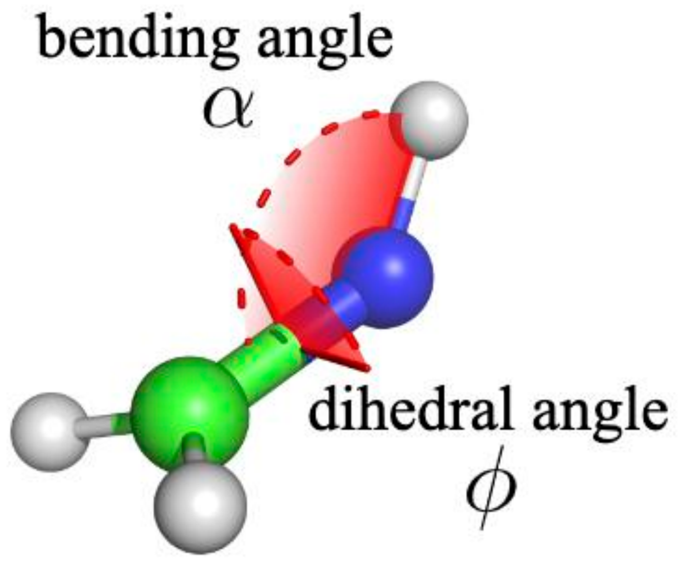

MECI optimization

⟨LCQ|S⟩

Quantum Software/Hardware

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Take Home Messages

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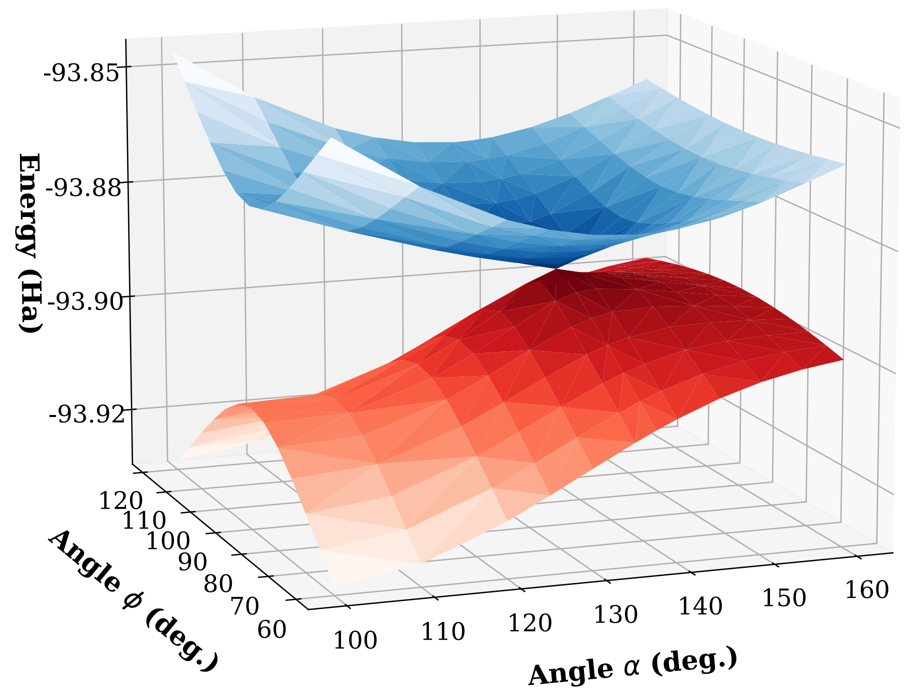

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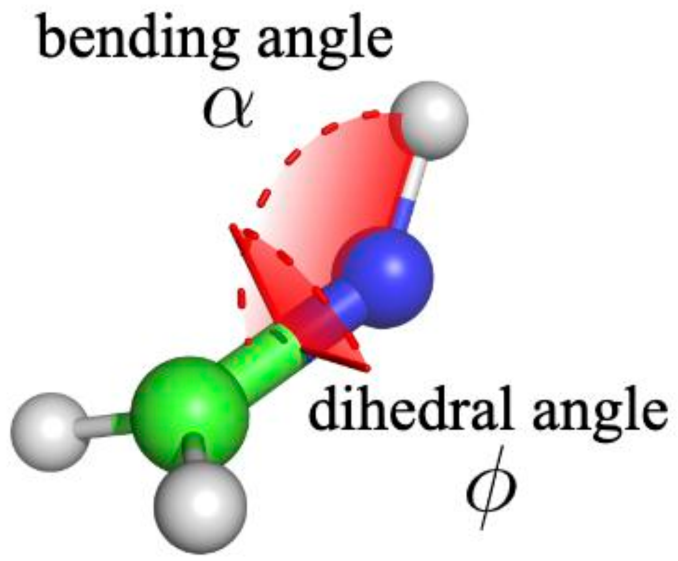

MECI optimization

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Quantum Software/Hardware

Thank you for your attention !

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