# Quantum algorithm developments and applications : from WFT to DFT

**Saad Yalouz**

*Laboratoire de Chimie Quantique*
*Université de Strasbourg*

Université de Strasbourg
Excellence University

cnrs

Institut de Chimie de Strasbourg
UMR 7177

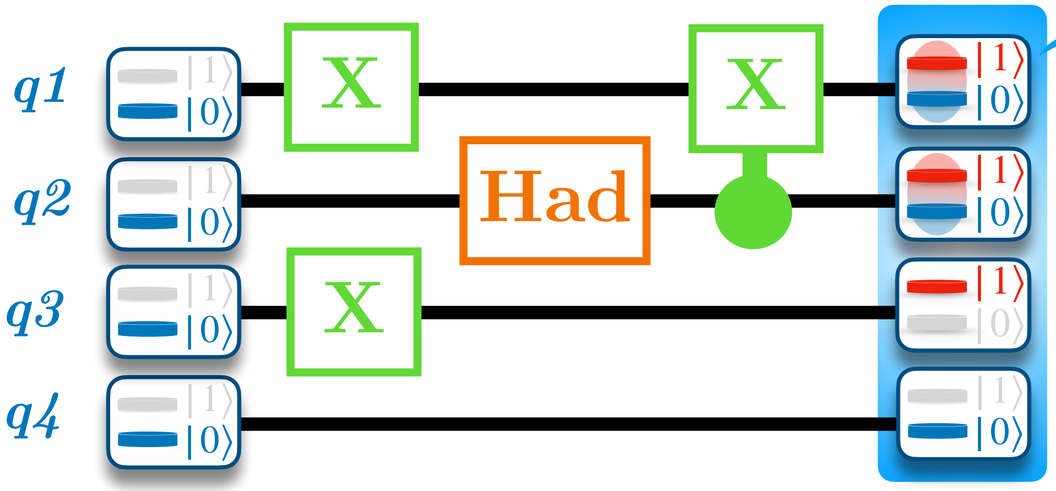
# Introduction

**A new unit of information : *the qubit***


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

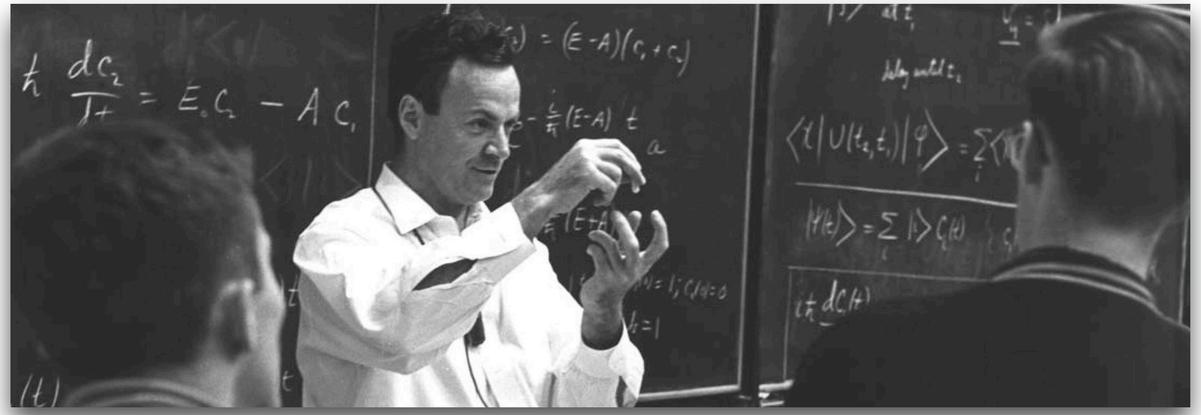
***A two-level system***

**Quantum circuit**

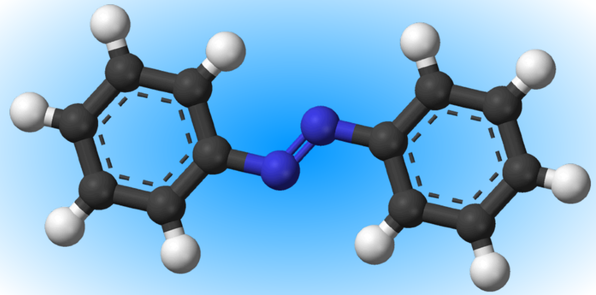



$$|\Psi^{Qubits}\rangle$$

**Correlated qubits**



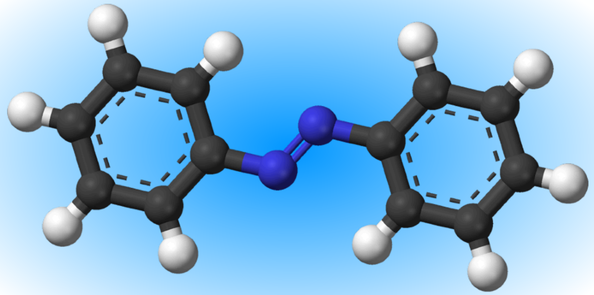
-Richard P. Feynman



**Electronic structure**

# Introduction

**Electronic structure**



**Quantum algorithms**

**Wave Function Theory (WFT)**

**Density Functional Theory (DFT)**

**SA-OO-VQE**

**Q-DFT**

Motivations ?

How does it work ?

Examples ?

# Introduction

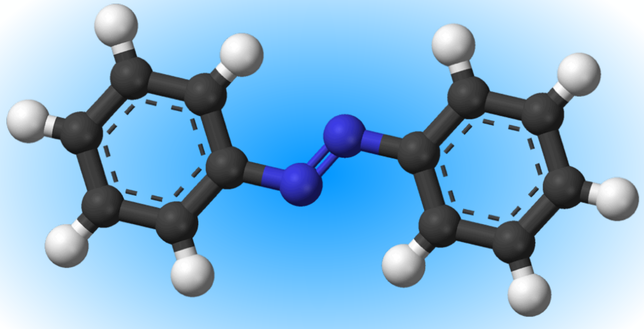
I) From qubits to WFT ← EXERCISE

II) Ground state calculation : VQE ← DEMO

III) Excited states calculation : SA-OO-VQE

IV) Q-DFT : a quantum algorithm for DFT

# I) From qubits to WFT

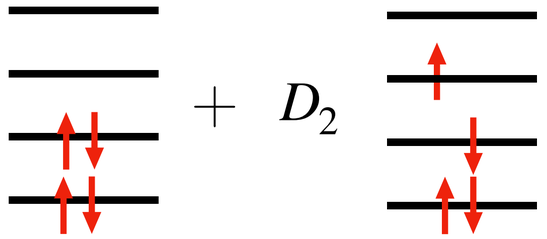


$$\mathscr{H} = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q$$

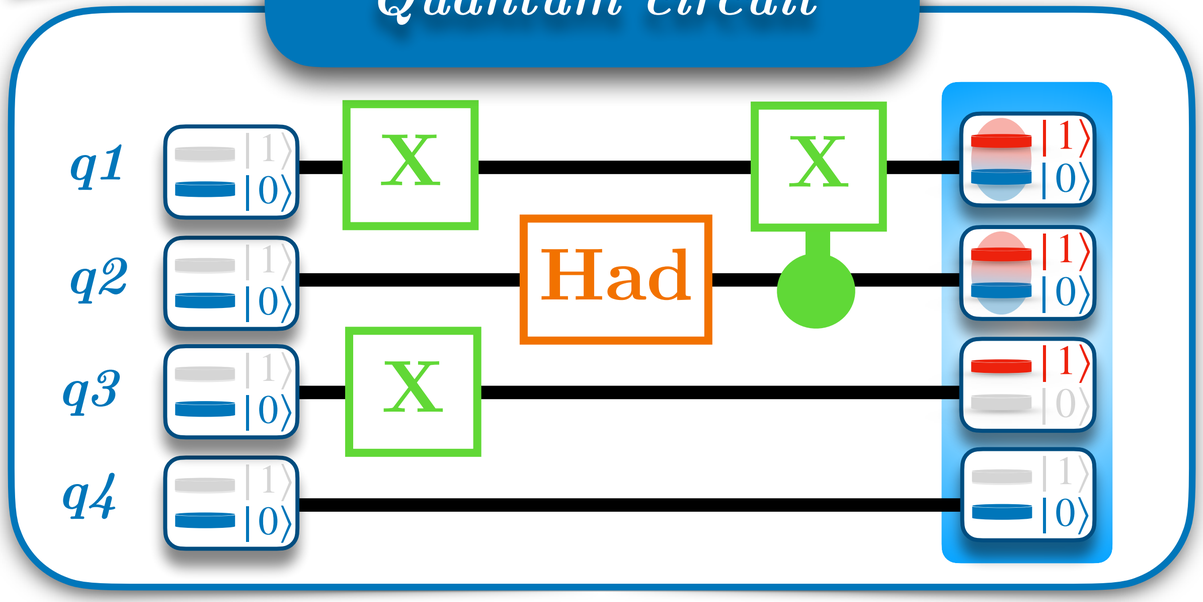
$$\mathscr{H} |\Psi_k\rangle = E_k |\Psi_k\rangle$$

*Configuration Interaction view*

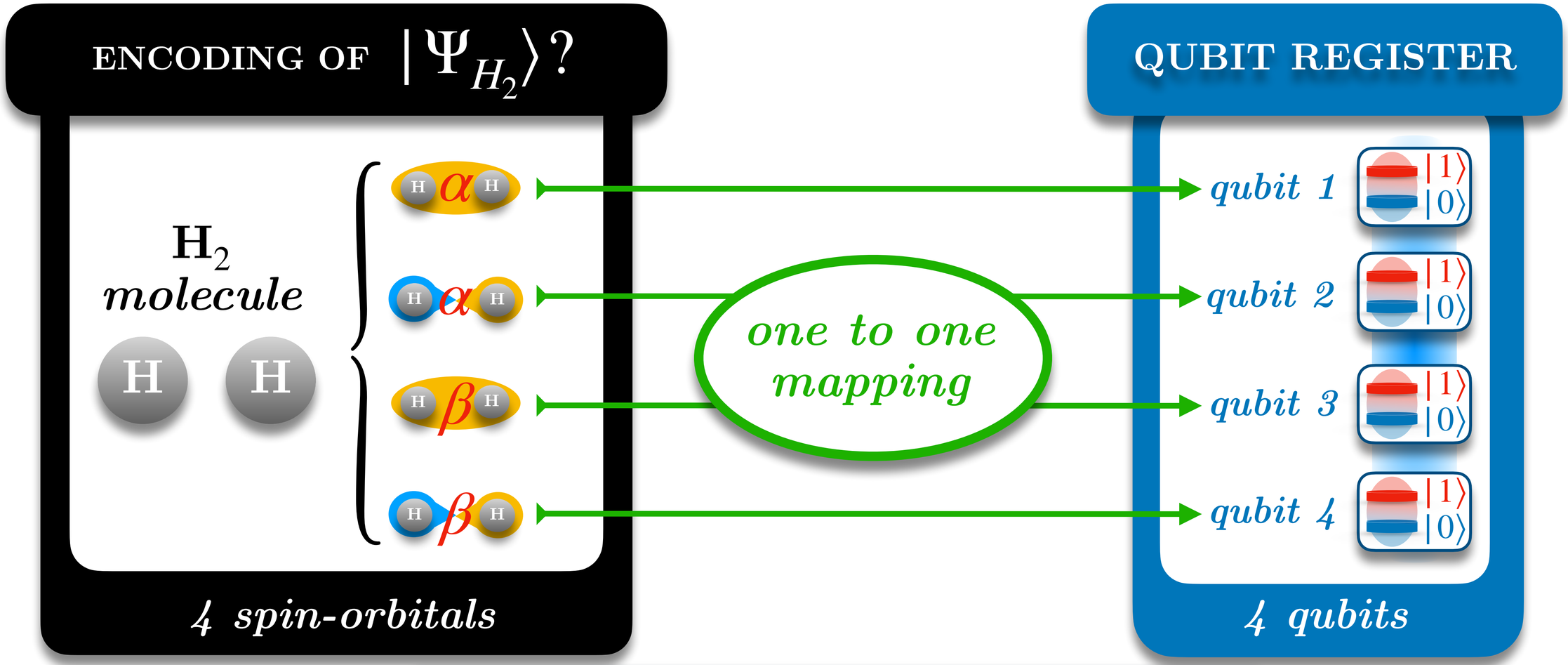
$$|\Psi_k\rangle = D_1 + D_2 + \dots$$



*Quantum circuit*



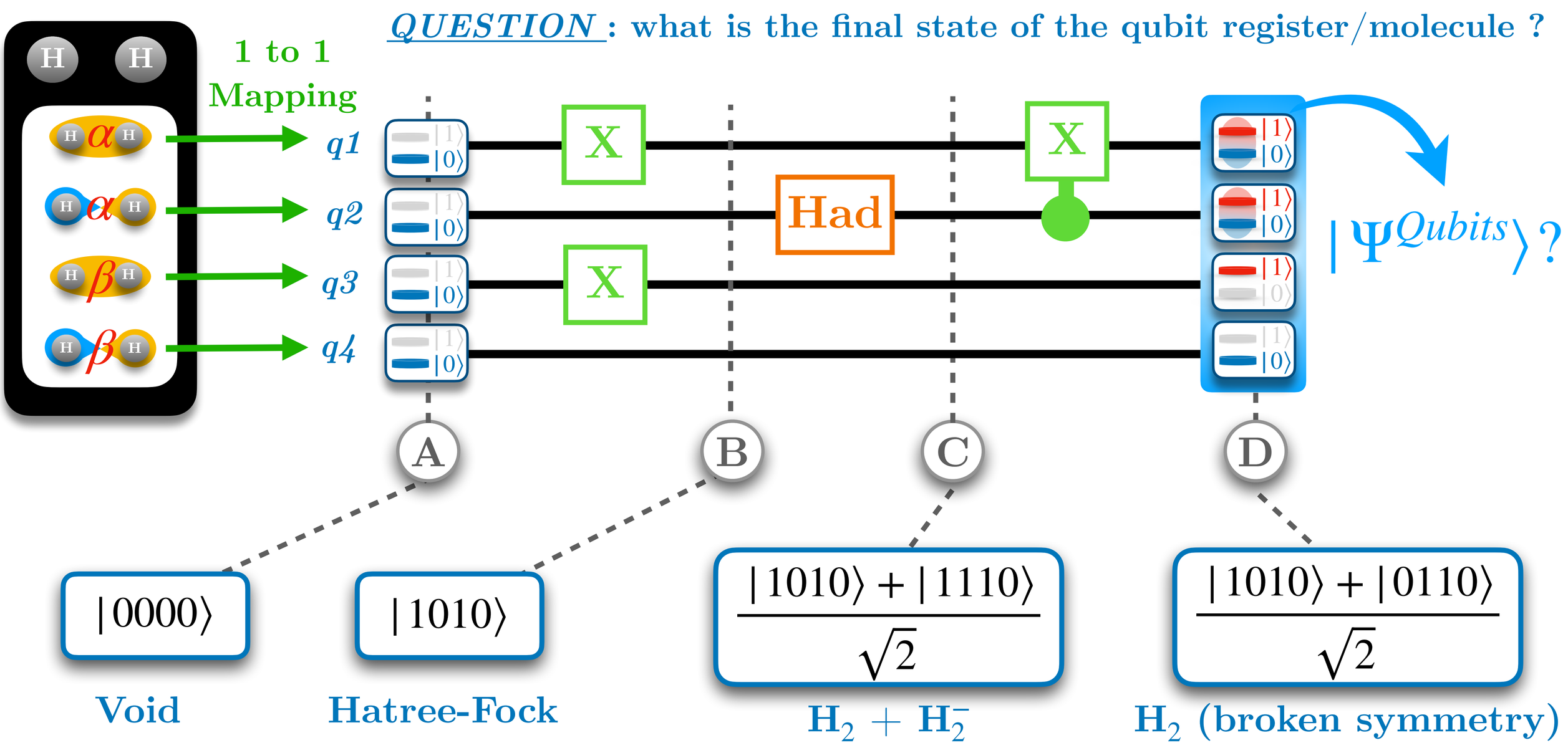
# I) From qubits to WFT




Qubit register = auxiliary quantum system

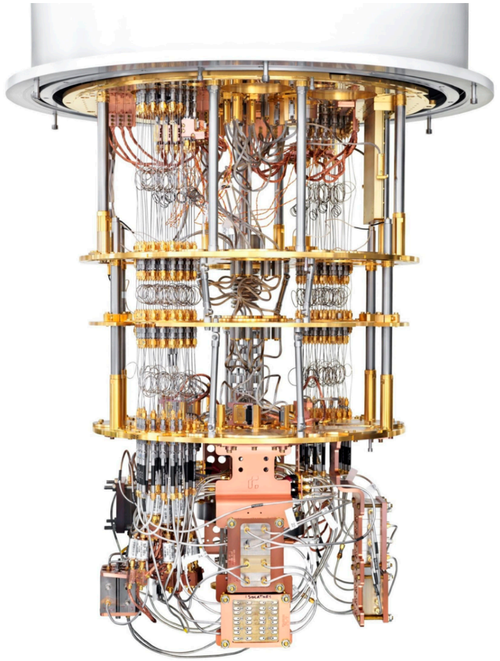
$$|\Psi_{H_2}\rangle = |\Psi^{qubits}\rangle$$

1) Exponentially reduced number of information units
2) Polynomial cost for CI calculations (*Fault tolerant*)


QUESTION : what is the final state of the qubit register/molecule ?
1 to 1
Mapping
H H
H α H
H α H
H β H
H β H
q1
q2
q3
q4
|1⟩
|0⟩
X
Had
X
X
A
B
C
D
|Ψ Qubits⟩ ?
|0000⟩
|1010⟩
(|1010⟩ + |1110⟩)/√2
(|1010⟩ + |0110⟩)/√2
Void
Hatree-Fock
H2 + H2−
H2 (broken symmetry)

# II) Ground state calculation : Variational Quantum Eigensolver

# II) Ground state calculation : VQE



**Emerging quantum computers are "NISQ" devices.**

**(NISQ : Noisy Intermediate-Scale Quantum)**

Quantum decoherence

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

Only **a few qubits** accessible

$N_{qubits} \sim 10$

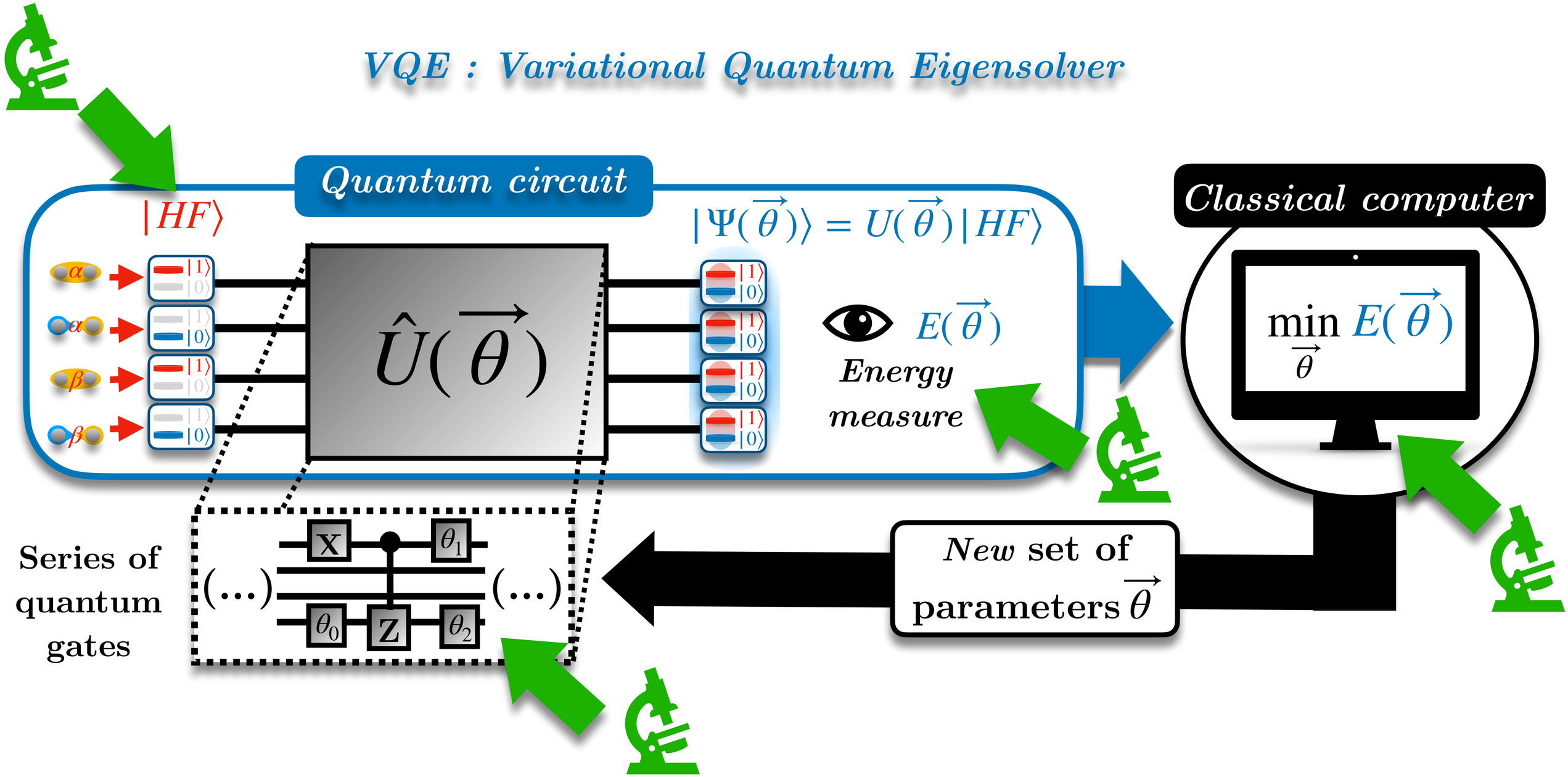
## *NISQ algorithms*

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

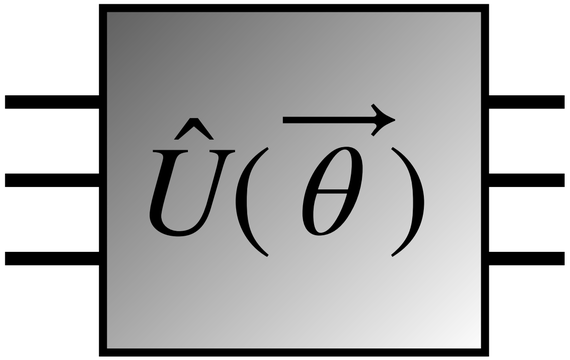
***Quantum speedup is still an open question !***

**Fault tolerant quantum computing (see Zachary's talk !)**

# II) Ground state calculation : VQE



# II) Ground state calculation : VQE




*Which ansatze ?*

*How do we build them ?*

*Hardware-efficient ansatz*

*Unitary Coupled Cluster ansatz*

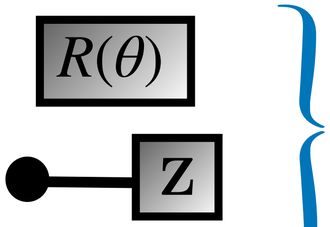
Demo

# II) Ground state calculation : VQE

## *Hardware-efficient ansatz*

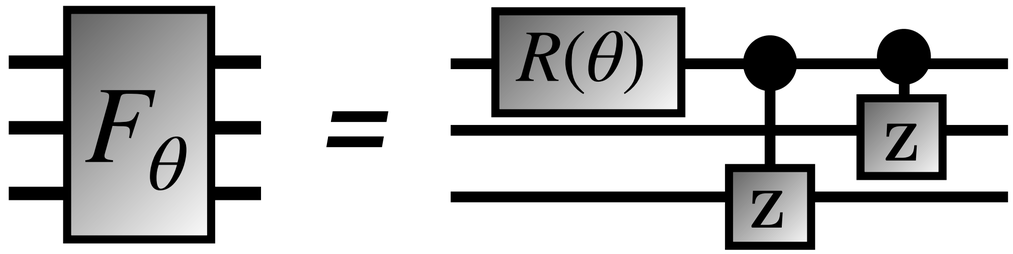
**Kandala, Abhinav, et al.** "Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets." *Nature* 549.7671 (2017): 242-246.

### 1) Start from a set of gates

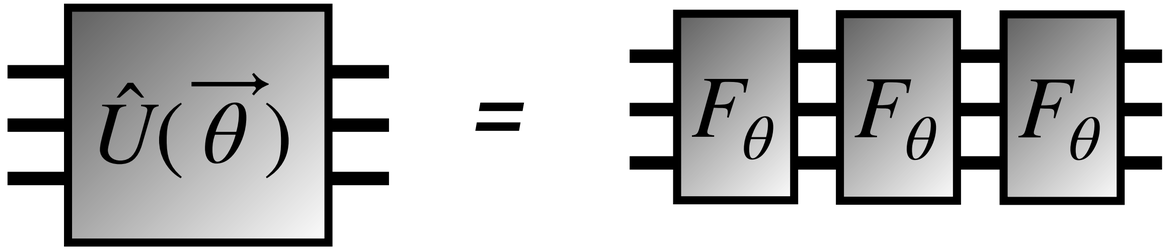



***Efficient gates***
**(not expansive)**

### 2) Create a fragment of circuit




### 3) Build a circuit including several fragments




***Repeated fragment***

✓ **Not expensive**

✓ ✗ **May break symmetries**

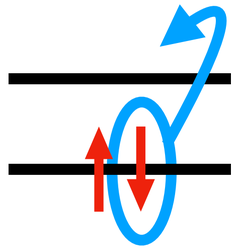
✗ **Optimisation seems hard**

## *Unitary Coupled Cluster ansatz*

**Romero, Jonathan, et al.** "Strategies for quantum computing molecular energies using the unitary coupled cluster ansatz." *Quantum Science and Technology* 4.1 (2018): 014008.

### 1) Start from an excitation operator

$$T(\vec{\theta}) = \sum_{l}^{exc.\ op.} \theta_l \tau_l$$



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

***Trotterization***

$$\hat{U}(\vec{\theta}) \approx \prod_{l} e^{\theta_l(\tau_l - \tau_l^\dagger)}$$

### 2) Use Jordan-Wigner to translate into qubit algebra

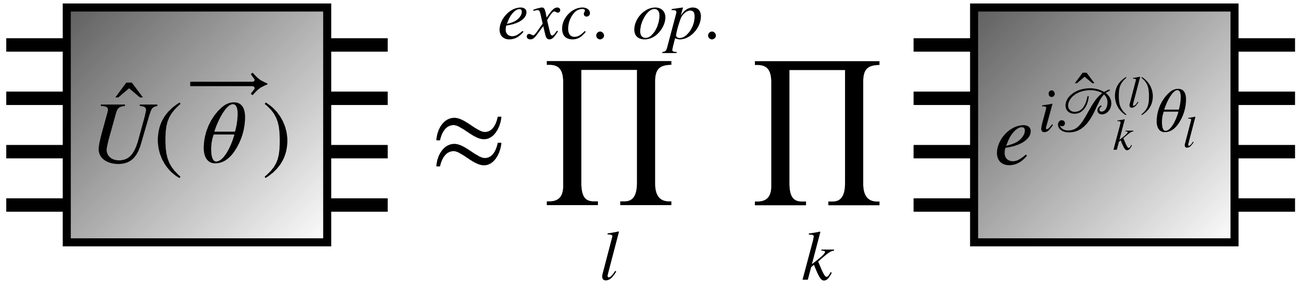
$$a_p \xrightarrow{JW} \frac{1}{2}(X_p + iY_p)\bigotimes_{q=0}^{p-1} Z_l \qquad a_p^\dagger \xrightarrow{JW} \frac{1}{2}(X_p - iY_p)\bigotimes_{q=0}^{p-1} Z_q$$

$$\hat{U}(\vec{\theta}) \approx \prod_{l}^{exc.\ op.} \prod_{k} e^{-i\theta_l \hat{\mathscr{P}}_k^{(l)}}$$

$\hat{\mathscr{P}}_k$ **are "Pauli strings"**

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

### 3) Build the associated circuit




✓ ✗ **Polynomial cost** ✓ **Conserved number of particle** ✓ **Simpler to optimize**

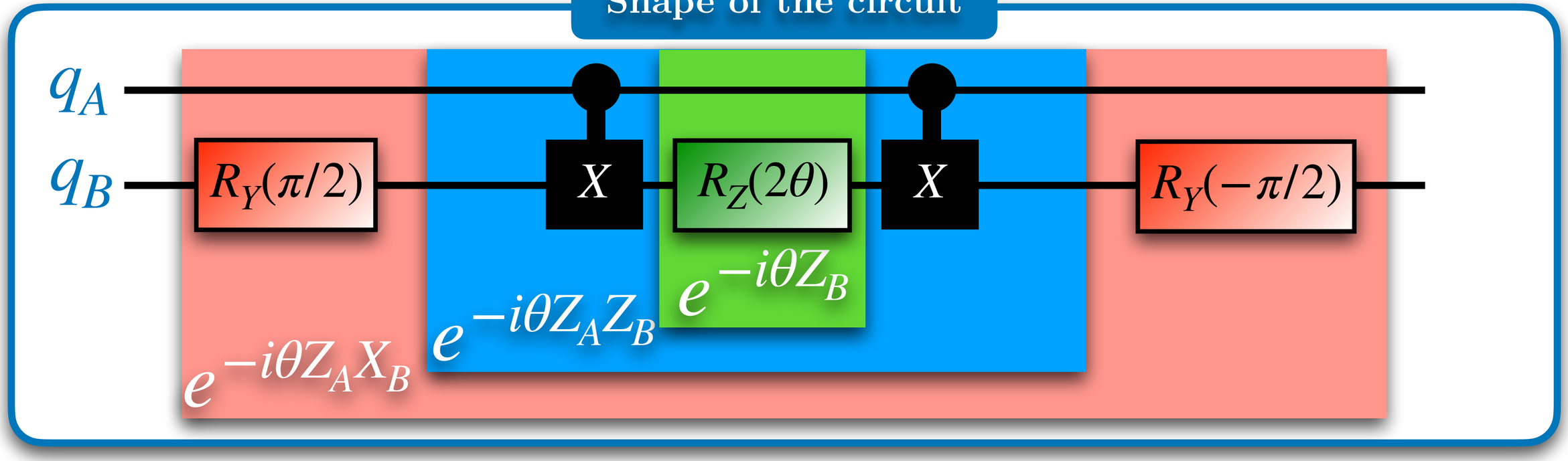
# II) Ground state calculation : VQE

$$\hat{U}(\vec{\theta}) \approx \prod_{l}^{exc.\ op.} \prod_{k} e^{i\hat{\mathscr{P}}_k^{(l)}\theta_l}$$

***QUESTION*** : *what is the circuit that encodes the following operator ?*

$$e^{-i\theta Z_A X_B} = \cos(\theta)\mathbf{1} - i\sin(\theta) Z_A X_B$$

**Shape of the circuit**



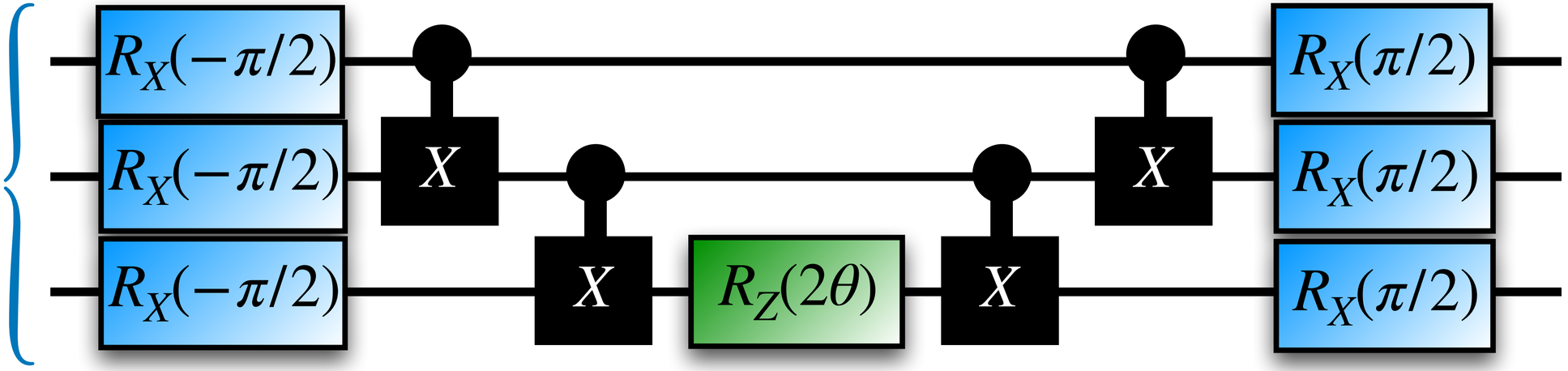

$$R_{Z_q}(2\theta) = e^{-i\theta Z_q} = \cos(\theta)\mathbf{1}_q - i\sin(\theta) Z_q$$

$$C^X_{qq'}\ Z_q\ C^X_{qq'} = Z_q Z_{q'}$$

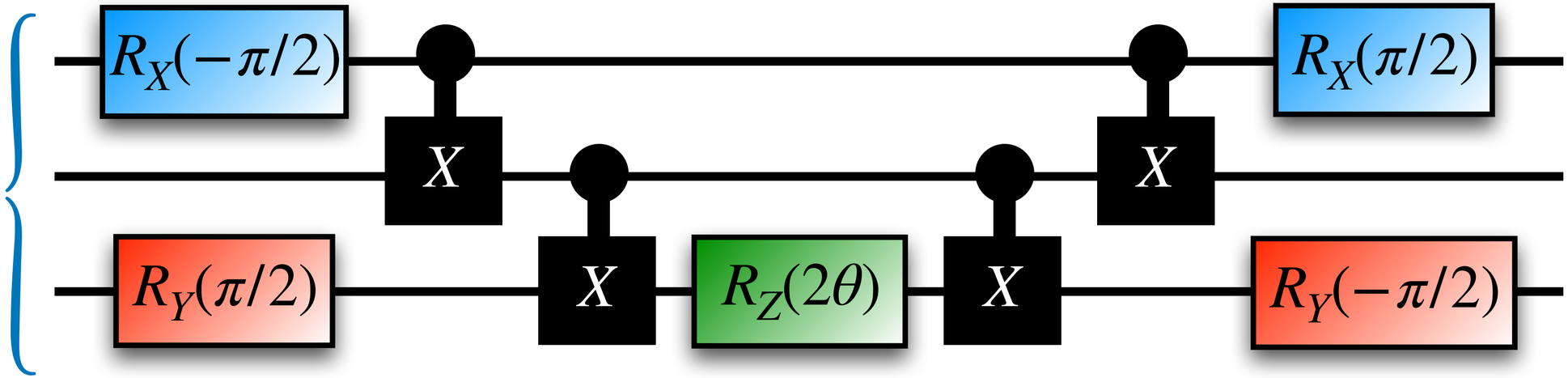
$$R_{Y_q}(\pi/2)\ Z_q\ R_{Y_q}(-\pi/2) = X_q$$

# II) Ground state calculation : VQE

$e^{-i\theta Y_0 Y_1 Y_2}$




$e^{-i\theta Y_0 Z_1 X_2}$



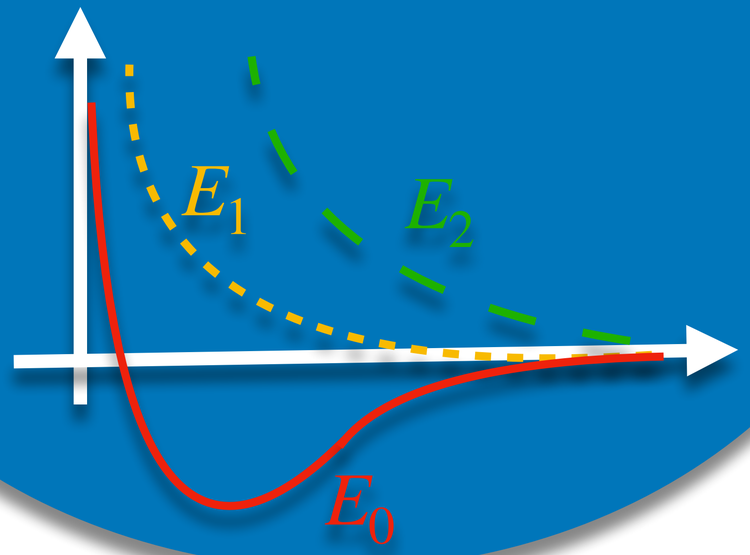
# III) Excited states calculation : SA-OO-VQE

# III) Excited states calculation: SA-OO-VQE

**QSE: Quantum-subspace extension**

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

## VQE extensions for the computation of excited states




**SS-VQE: subspace search VQE**

K. M. Nakanishi *et al.*, **Phys. Rev. Res. 1.3 (2019): 033062**

**VQD: variational quantum deflation**

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

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

R. M. Parrish *et al.*, **Phys. Rev. Lett. 122, 230401 (2019).**

**SA-OO-VQE: State-averaged orbital-optimised VQE**

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

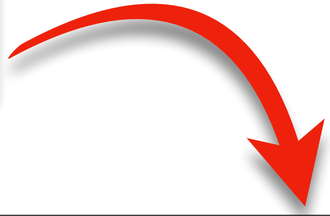
**S. Yalouz et al. *Journal of chemical theory and computation* 18.2 (2022): 776-794.**

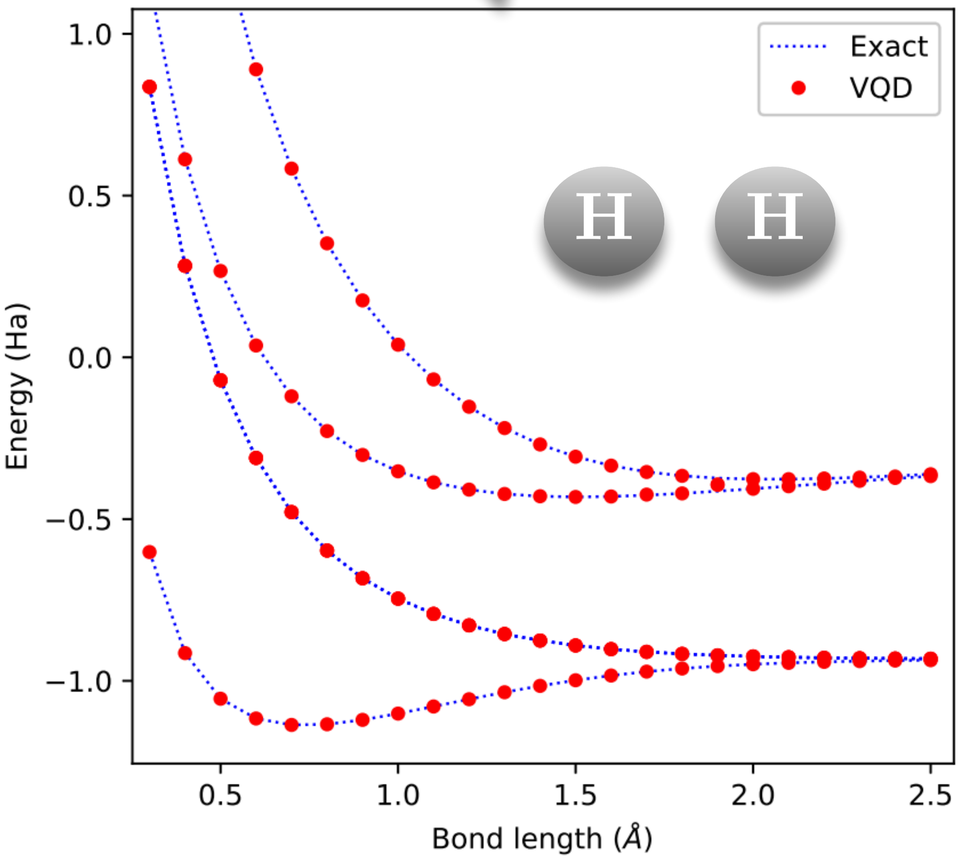
# III) Excited states calculation: SA-OO-VQE


Hamiltonian $\hat{H}$

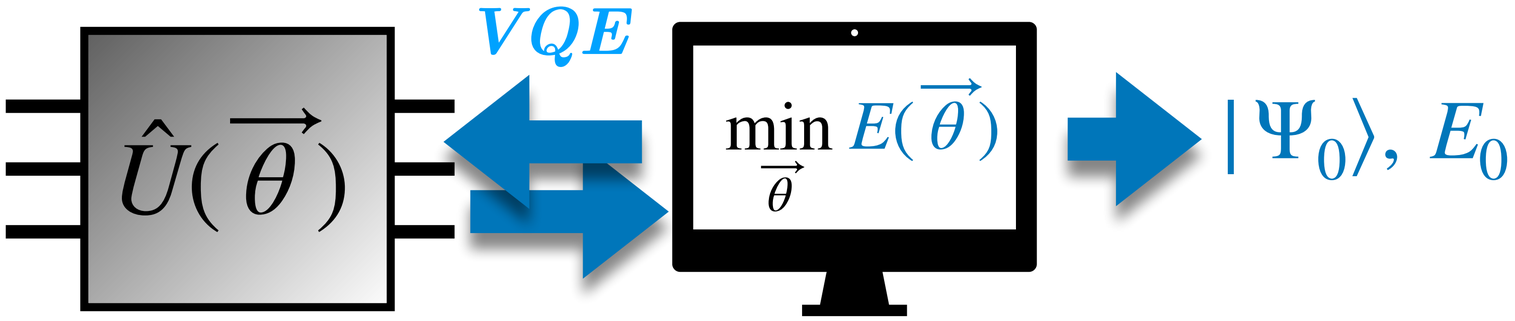
**VQD: variational quantum deflation**

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



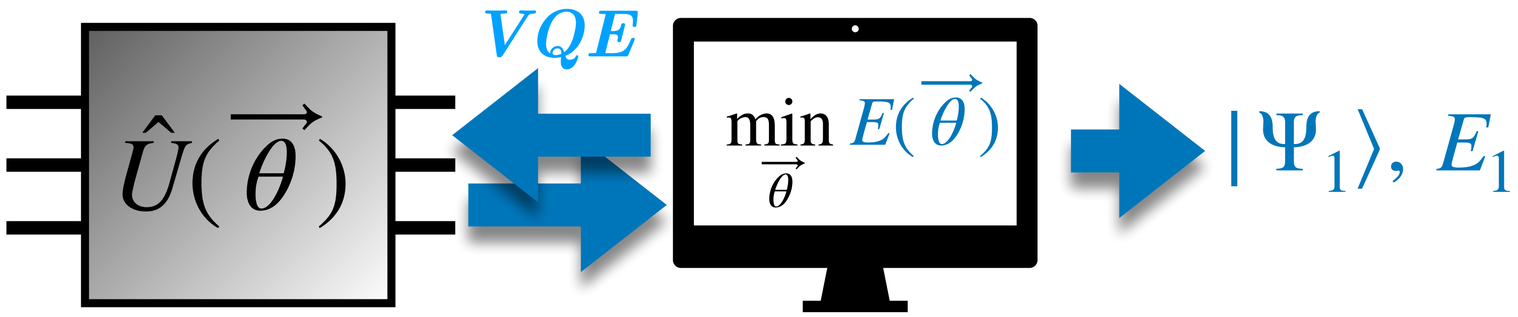



*1st step*




*2nd step*

New Hamiltonian $\hat{H} \leftarrow \hat{H} + \Lambda |\Psi_0\rangle\langle\Psi_0|$

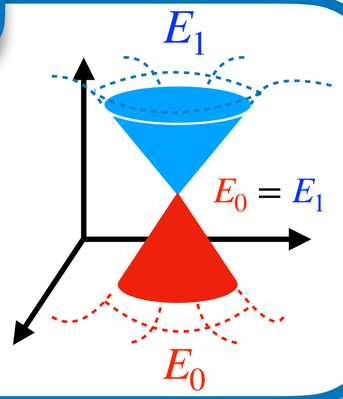


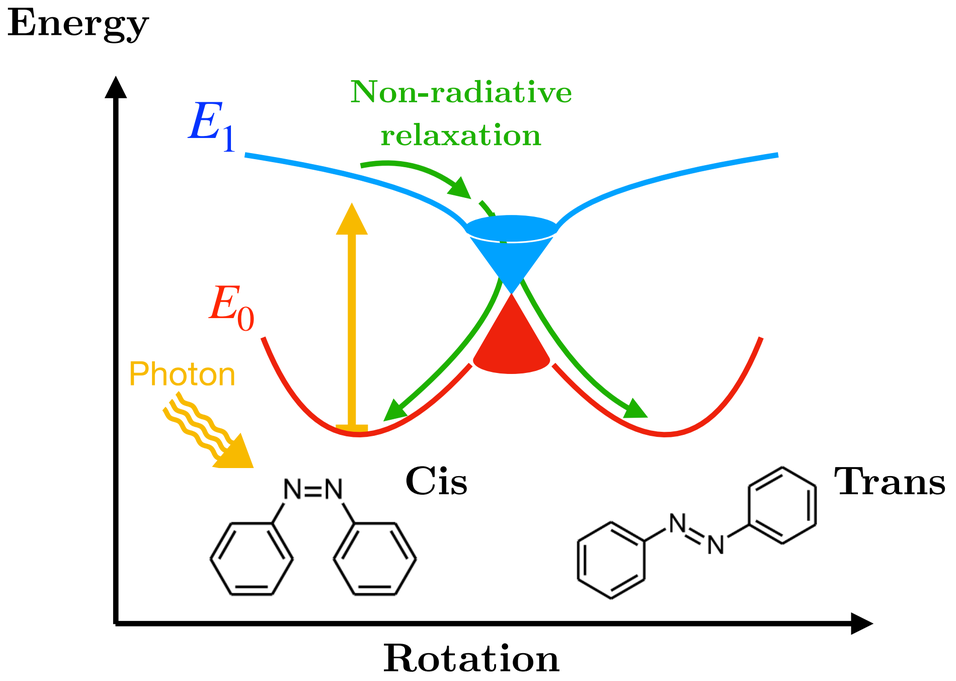
# III) Excited states calculation: SA-OO-VQE

## What are the motivations ?

### Conical intersection

Singular point of degeneracy
connecting two
Potential Energy Surfaces




Need of a dedicated method

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

***Features:***

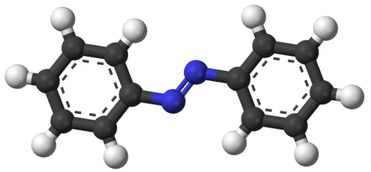
- Adapted to near term quantum computers (VQE-like)
- Provides useful data for photochemistry studies (*e.g.* PES, gradients and NAC)

# III) Excited states calculation: SA-OO-VQE

S. Yalouz et al. *Journal of chemical theory and computation* 18.2 (2022): 776-794.
S. Yalouz et al. *Quantum Science and Technology* 6.2 (2021): 024004.

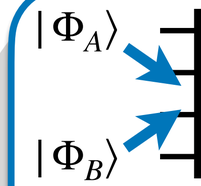
## How does it work ?

*Molecular system*



$\hat{H}^{AS}$

### State-Averaged VQE




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

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

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

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

$\vec{\theta}$ **Optimisation cycle**

**CPU** *optimizer*

**State-averaged energy cost function**

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

### State-Averaged Orbital-Optimizer

**Orbital rotated Hamiltonian**

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

$\hat{U}_{OO}(\vec{\kappa}) = \exp(-\vec{\kappa})$ $\longrightarrow$ **Change of the 1- and 2-body integrals**

$\vec{\kappa}$ **Optimisation cycle**

**State-averaged orbital dependant cost function**

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

**Optimized correlated states**

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

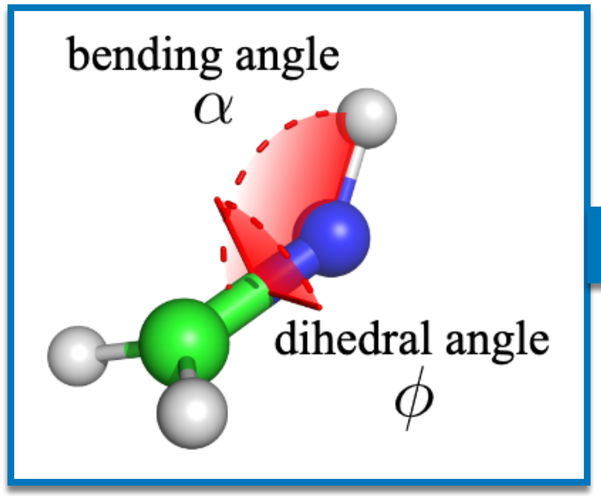
*(1- & 2-RDMs)*

# III) Excited states calculation: SA-OO-VQE

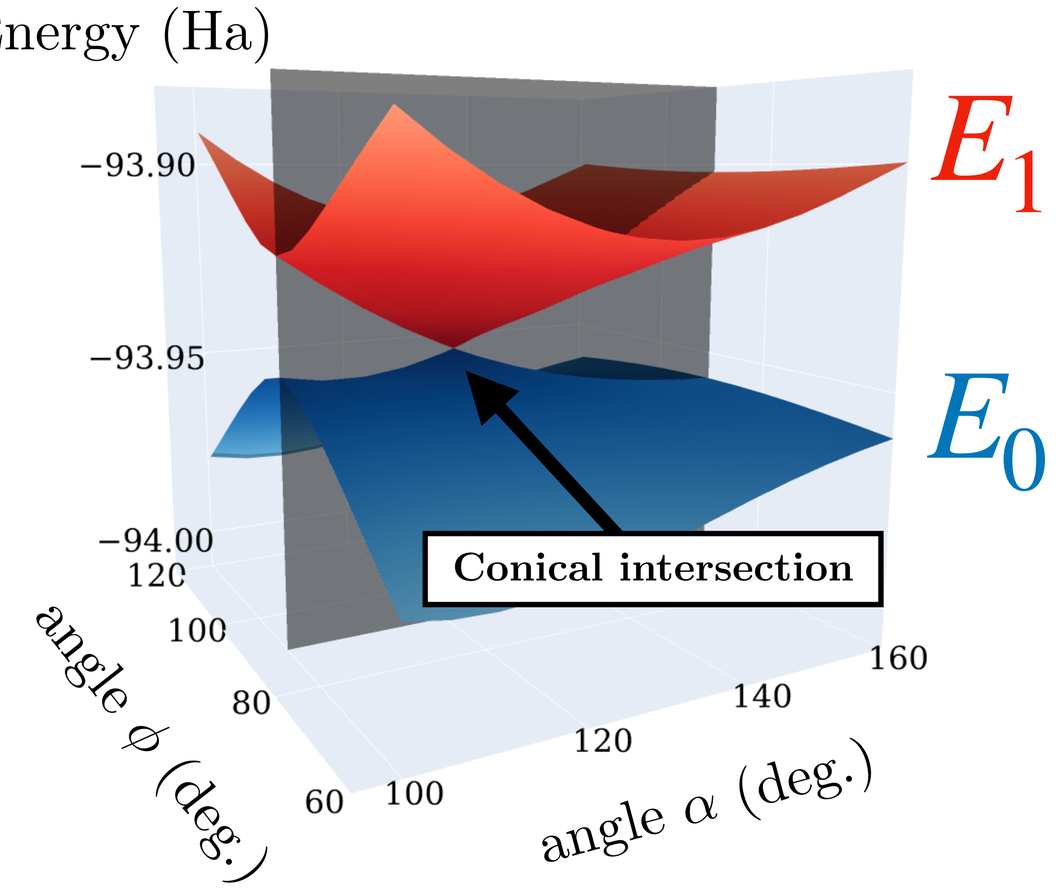
S. Yalouz et al. *Journal of chemical theory and computation* 18.2 (2022): 776-794.

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

## Example




**SA-OO-VQE**
**Noiseless**
**Simulations**




***Ground and first excited state PESs***

***Setup :***

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

# III) Excited states calculation: SA-OO-VQE

## How does it work ?

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

**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

**Lagrange multiplier method**

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

$$\frac{\partial \mathscr{L}_I}{\partial \kappa_{pq}} = \frac{\partial \mathscr{L}_I}{\partial \theta_n} = 0$$

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

Can be measured out of the circuit !

Final analytical form

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

# III) Excited states calculation: SA-OO-VQE

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

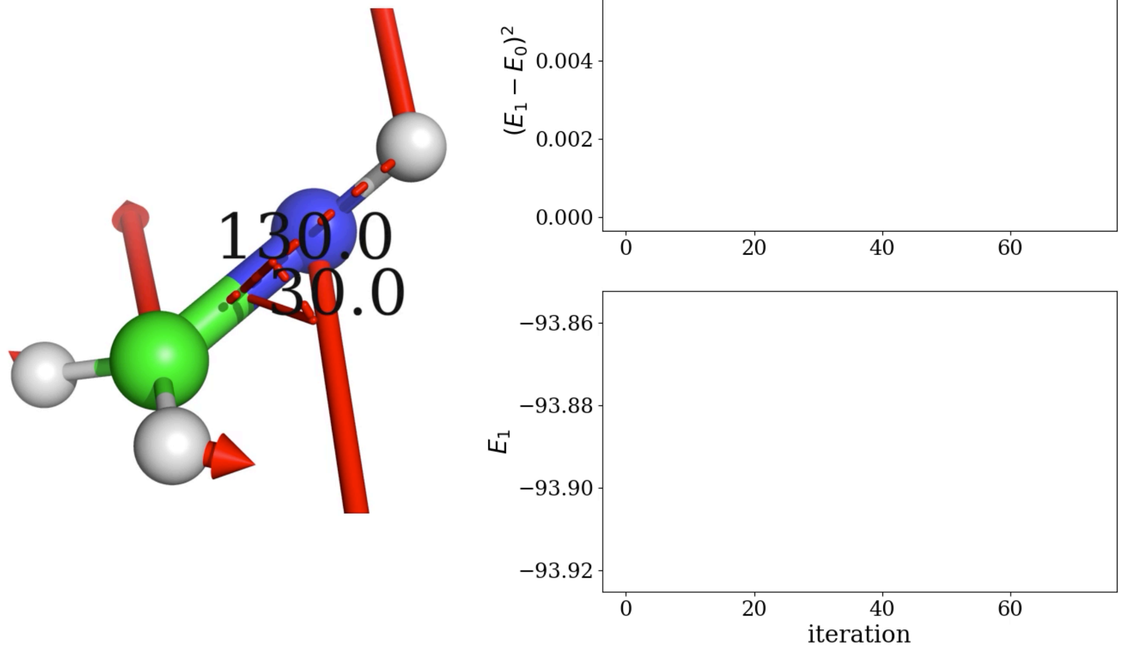
S. Yalouz et al. *Quantum Science and Technology* 6.2 (2021): 024004.

## Example

*Ingredients:*
- Nuclear gradients
- Non-adiabatic couplings

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

**Noiseless Simulations**



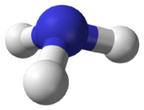

***SA-OO-VQE = Quantum analog of SA-CASSCF***

# IV) Q-DFT: a quantum algorithm for DFT

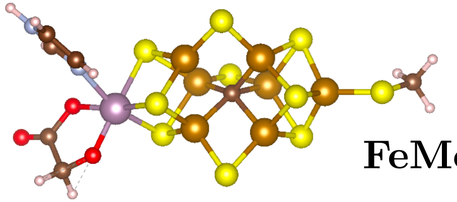
# IV) Q-DFT: a quantum algorithm for DFT

## What are the motivations ?

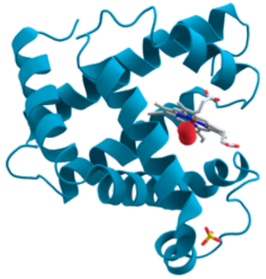
### Example of systems



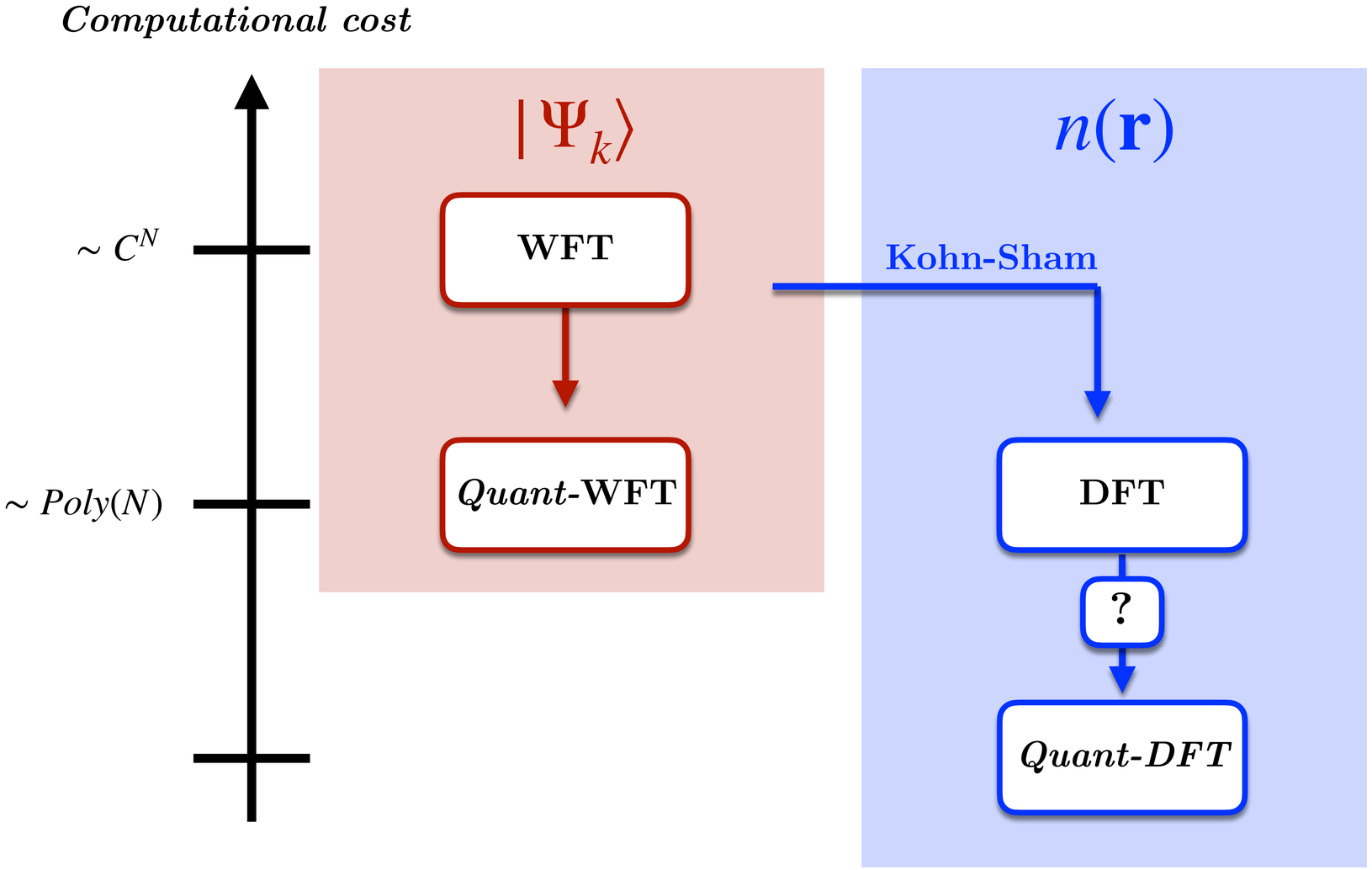
$NH_3$



FeMoco



Myoglobin

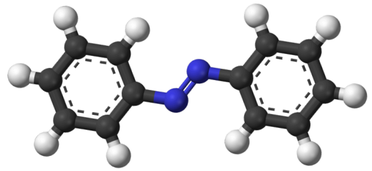


# IV) Q-DFT: a quantum algorithm for DFT

B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443
(accepted in SciPost Physics)

## How does it work ?

*Interacting system*



$$\hat{\mathscr{H}}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

**DFT = Non-interacting system**

**Kohn-Sham Self-consistent equations**

$$n(\mathbf{r}) = \sum_{k=1}^{N_{elec}} |\phi_k(\mathbf{r})|^2$$

$$\hat{h}^{KS}(n(\mathbf{r}))\phi_k = \epsilon_k \phi_k$$

$$\hat{h}^{KS}(n(\mathbf{r})) = \hat{T} + \hat{v}^{KS}(n(\mathbf{r}))$$

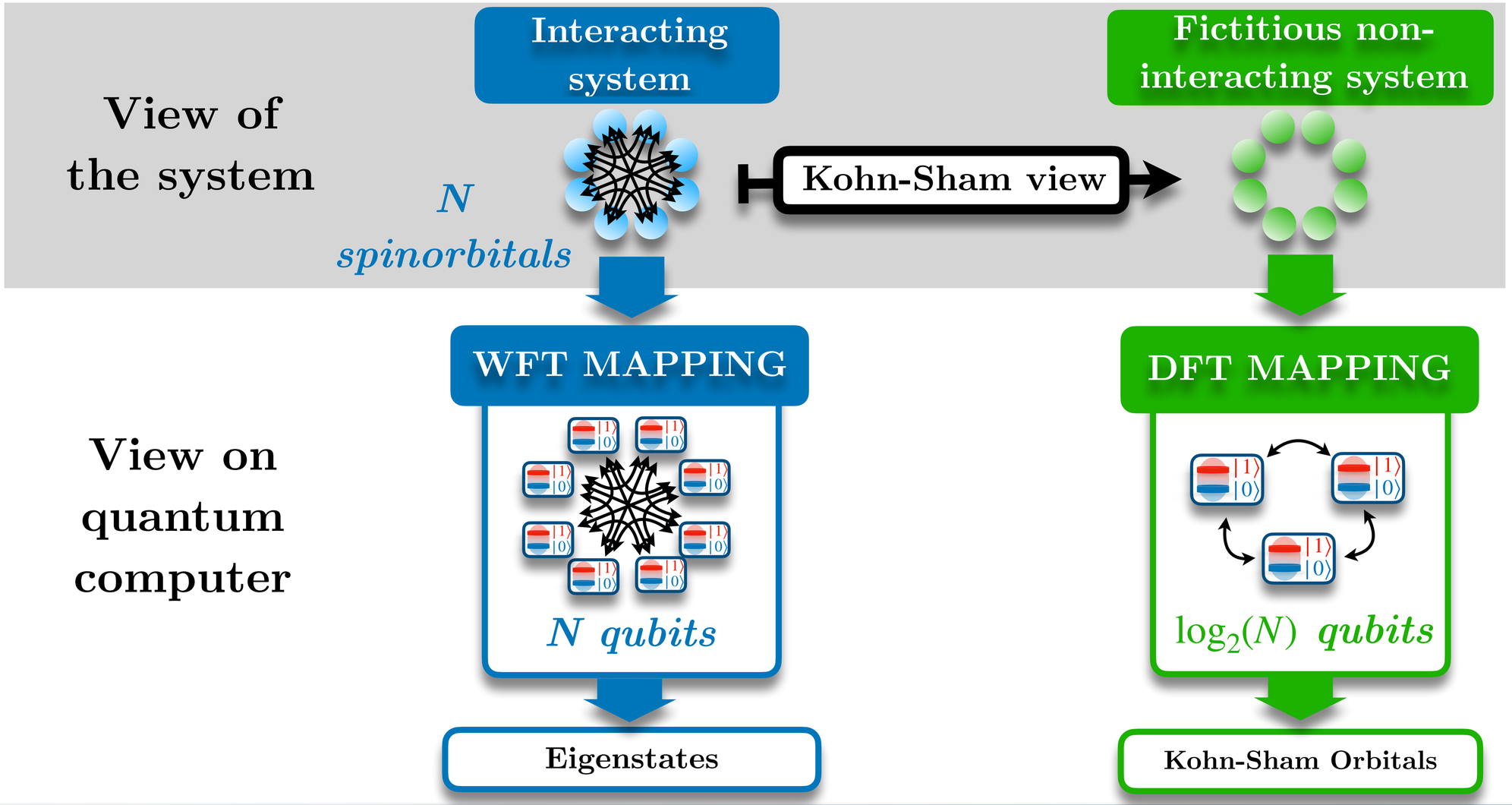
**GS energy**

$$E_0 = \sum_k \epsilon_k + E_{Hxc}[n(\mathbf{r})] - \int \mathbf{v}^{Hxc}[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r}$$

# IV) Q-DFT: a quantum algorithm for DFT

B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443
(accepted in SciPost Physics)

## How does it work ?



# IV) Q-DFT: a quantum algorithm for DFT

B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443
(accepted in SciPost Physics)

## How does it work ?

**Computational basis mapping**

$$\{|\chi_I\rangle\} \longrightarrow \{|CB_I\rangle\}$$

**Kohn-Sham matrix**

$$\mathbf{h^{KS}}_{i,j} = \langle \chi_i | \hat{h}^{KS} | \chi_j \rangle$$

**Non-interacting**
**$N$ spin-orbitals**

$$\chi_0 \longrightarrow |000\rangle$$
$$\chi_1 \longrightarrow |001\rangle$$
$$\chi_2 \longrightarrow |010\rangle$$
$$\chi_3 \longrightarrow |011\rangle$$
$$\chi_4 \longrightarrow |100\rangle$$
$$\chi_5 \longrightarrow |101\rangle$$
$$\chi_6 \longrightarrow |110\rangle$$
$$\chi_7 \longrightarrow |111\rangle$$

$$\hat{H}^{aux,int} = \sum_{IJ} \mathbf{H}^{aux,int}_{I,J} |CB_I\rangle\langle CB_J|$$

**Interacting**
**$\log_2(N)$ qubits**

$$N_{qubit} = \log_2(N) \rightarrow \text{ 8 MO = 3 qubits}$$

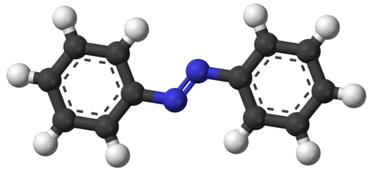
# IV) Q-DFT: a quantum algorithm for DFT

B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443
(accepted in SciPost Physics)

## How does it work ?

$$n(\mathbf{r}) = \sum_{k=1}^{N_{elec}} |\phi_k(\mathbf{r})|^2$$

*Molecular system*



$$\hat{h}^{KS}(n(\mathbf{r})) = \hat{T} + \hat{v}^{KS}(n(\mathbf{r}))$$

**Counter intuitive Mapping**

$$\{|\chi_I\rangle\} \longrightarrow \{|CB_I\rangle\}$$

$$\chi_0 \longrightarrow |000\rangle$$
$$\chi_1 \longrightarrow |001\rangle$$
$$\chi_2 \longrightarrow |010\rangle$$
$$\chi_3 \longrightarrow |011\rangle$$
$$\chi_4 \longrightarrow |100\rangle$$
$$\chi_5 \longrightarrow |101\rangle$$
$$\chi_6 \longrightarrow |110\rangle$$
$$\chi_7 \longrightarrow |111\rangle$$

$$\mathbf{h}^{\mathbf{KS}}{}_{i,j} = \langle\chi_i|\hat{h}^{KS}|\chi_j\rangle$$

$$\hat{H}^{aux,int} = \sum_{IJ} \mathbf{H}^{aux,int}_{I,J} |CB_I\rangle\langle CB_J|$$

$N_{qubit} = \log_2(N_{orb}) \rightarrow$ 8 MO = 3 qubits

**State-Averaged VQE**

$$|CB_I\rangle \rightarrow \hat{U}(\vec{\theta}) \rightarrow |\phi_I(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|CB_I\rangle$$

***MEASURES*** $\left\{ \langle\phi_I(\vec{\theta})|\hat{H}^{AUX.INT}|\phi_I(\vec{\theta})\rangle \right\}_{I=1}^{N_e}$

$\vec{\theta}$ **Optimisation cycle**

**CPU** *optimizer*

**State-averaged energy cost function**

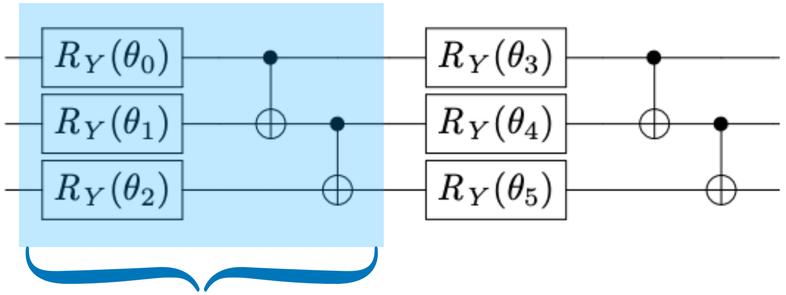
$$E^{SA-VQE}(\vec{\theta}) = \sum_{I}^{N_e} \langle\phi_I(\vec{\theta})|\hat{H}^{AUX.INT}|\phi_I(\vec{\theta})\rangle$$

# IV) Q-DFT: a quantum algorithm for DFT

B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443
(accepted in SciPost Physics)

## Example

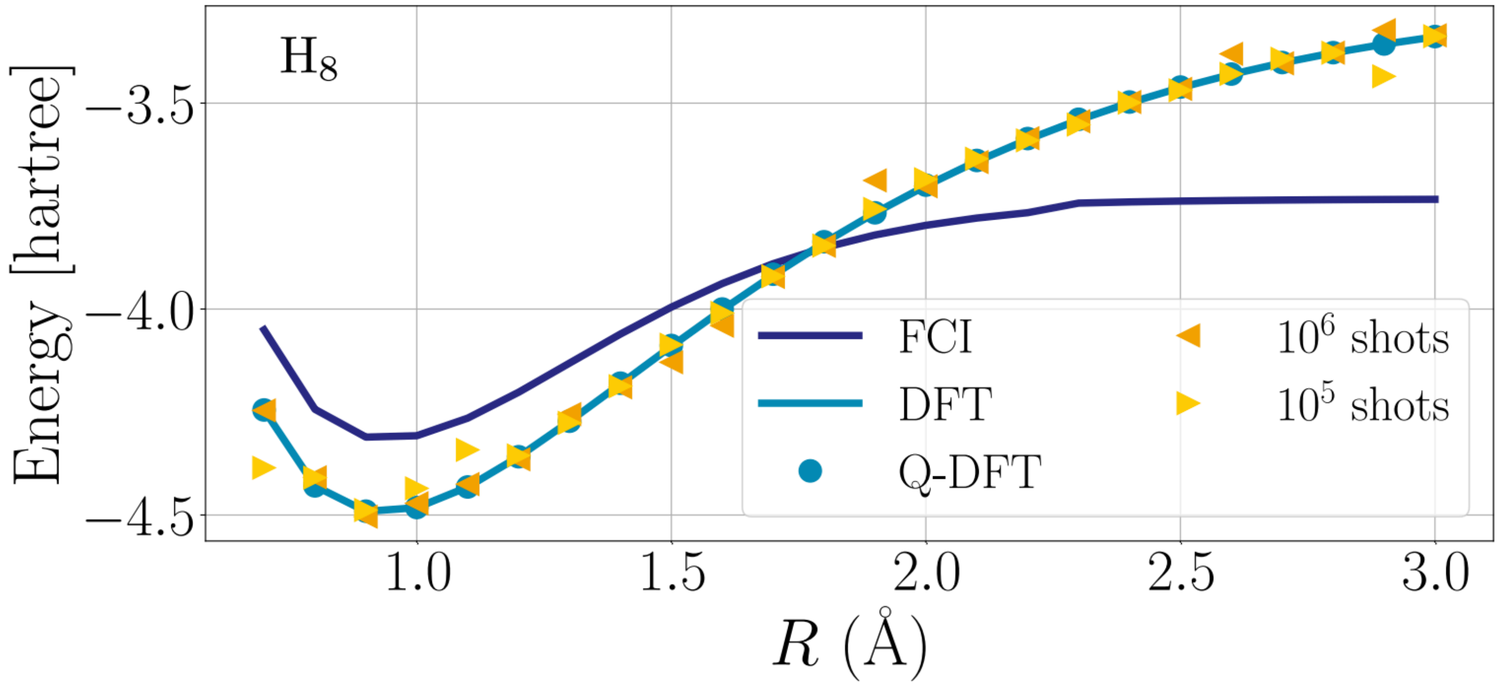
**Hardware efficient**
**$CNOT - R_Y$ ansatz**




***Setup :***

- STO-3g basis
- LDA functional
- Optimiser = SPSA
- 4 layers of ansatz (15 parameters)

**hydrogen chain (8 atoms)**



# Take home messages

# *Take home messages*

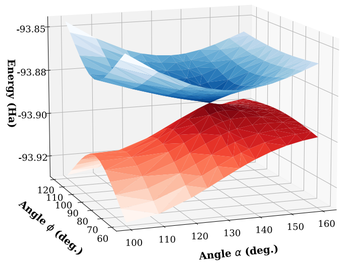
**NISQ algorithms :** VQE is a the heart of current research

**Ansatze :** Hardware efficient + UCC

**Ensemble VQE for two quantum algorithms (WFT and DFT based)**

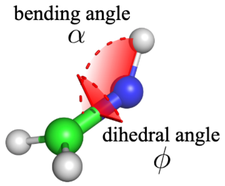
## SA-OO-VQE

**Description of degenerated PES**




**Nuclear derivatives**

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




**Non-adiabatic couplings**

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

**MECI optimization**

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

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

## Q-DFT

**New paradigm**

**Q-WFT**

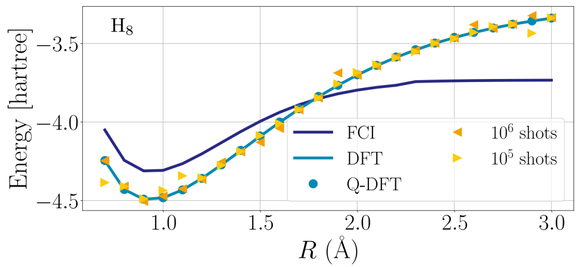
$N_{qubit} \propto N_{orb}$

***V.S.***

**Q-DFT**

$N_{qubit} \propto \log_2(N_{orb})$

**Description of ground state PES**




B. Senjean, S. Yalouz and M. Saubanère. arXiv:2204.01443 (accepted in SciPost Physics)