Describing conical intersections with near term quantum computers

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Content

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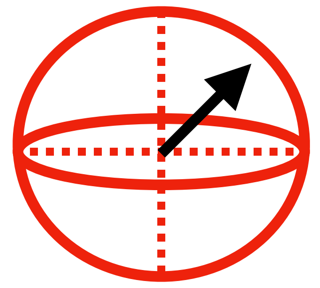
I) From Quantum Computing to Quantum Chemistry

Quantum computer : *the tool we use*

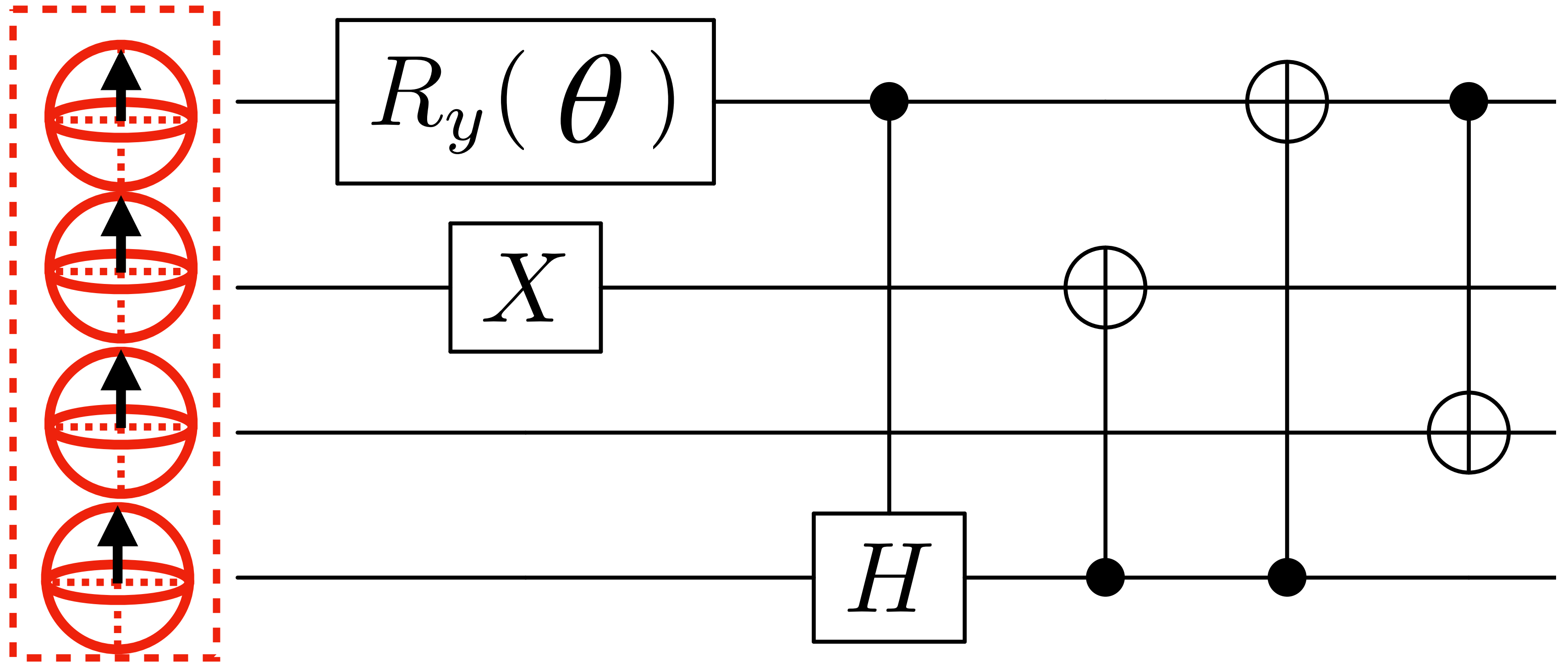
$|0_Q\rangle$



$|1_Q\rangle$

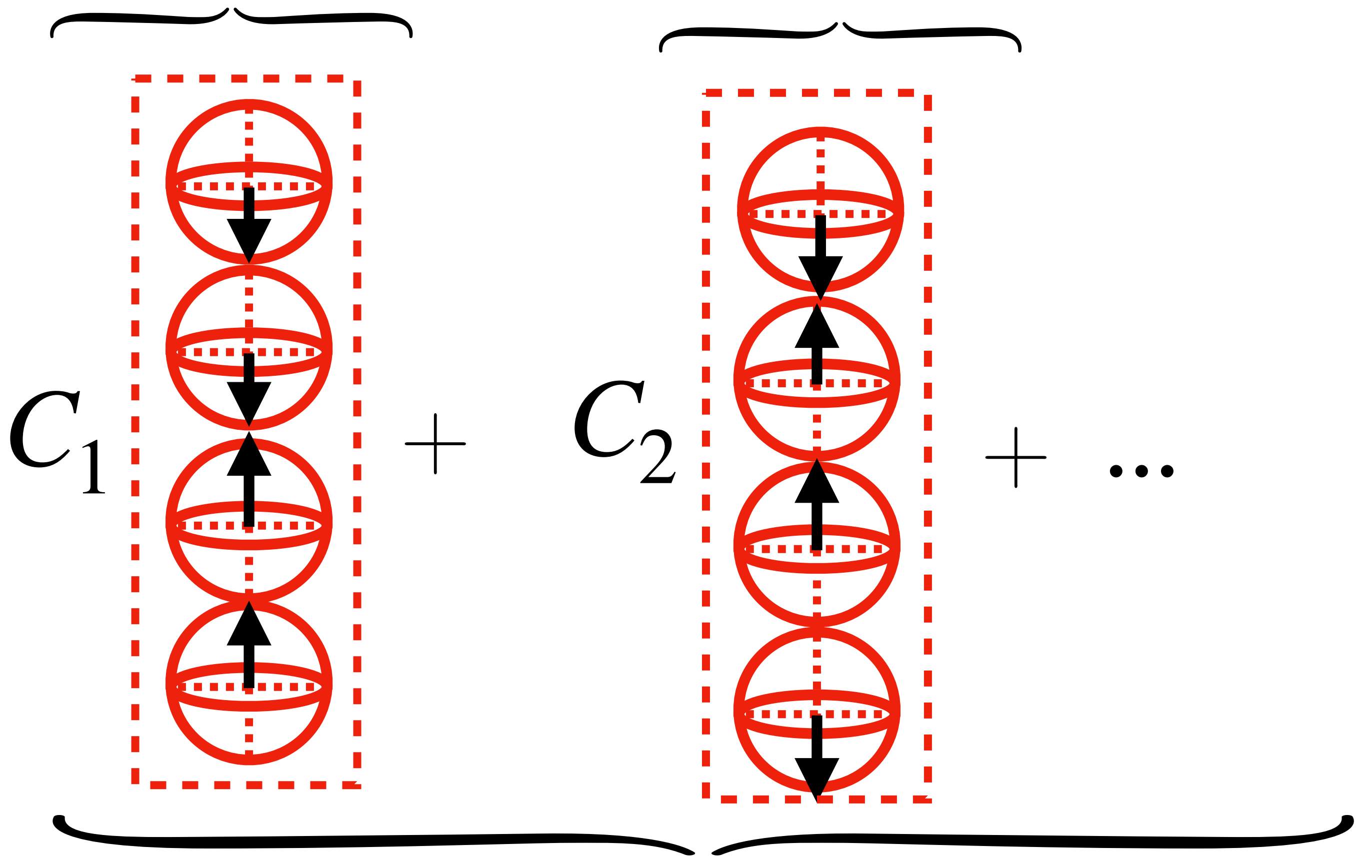
$$|Q\rangle = c_0|0_Q\rangle + c_1|1_Q\rangle$$

The Qubit : a two-level system



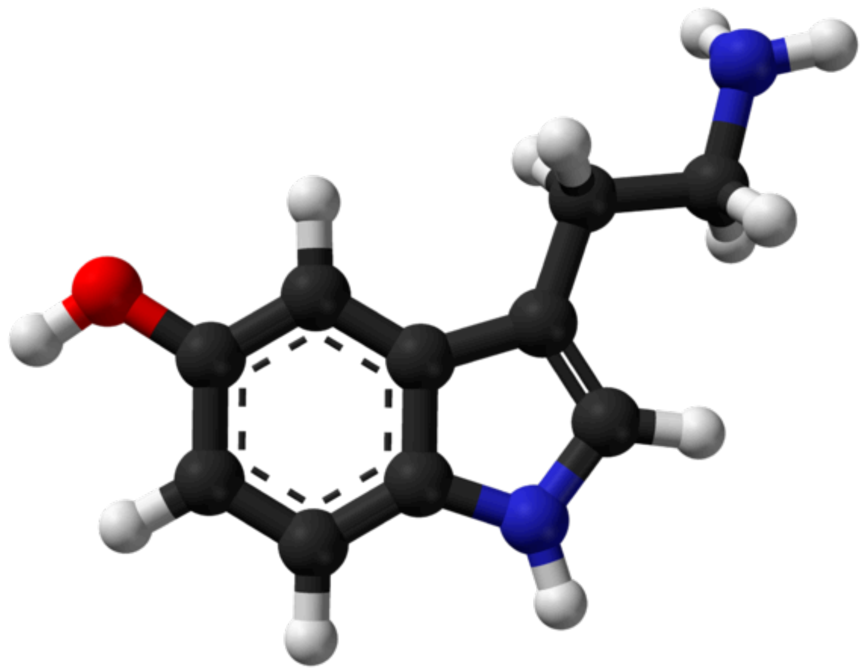
$|0000\rangle$

Quantum circuits



$|\Psi(\vec{\theta})\rangle$

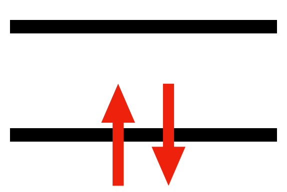
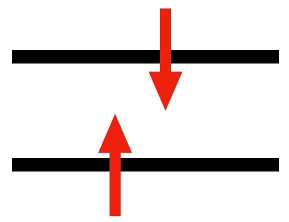
Electronic structure problem : *what we want to solve*



Electronic structure Hamiltonian

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

$$\longrightarrow \mathscr{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$|\Psi_0\rangle =$ C_1  $+ \; C_2$  $+ \dots$

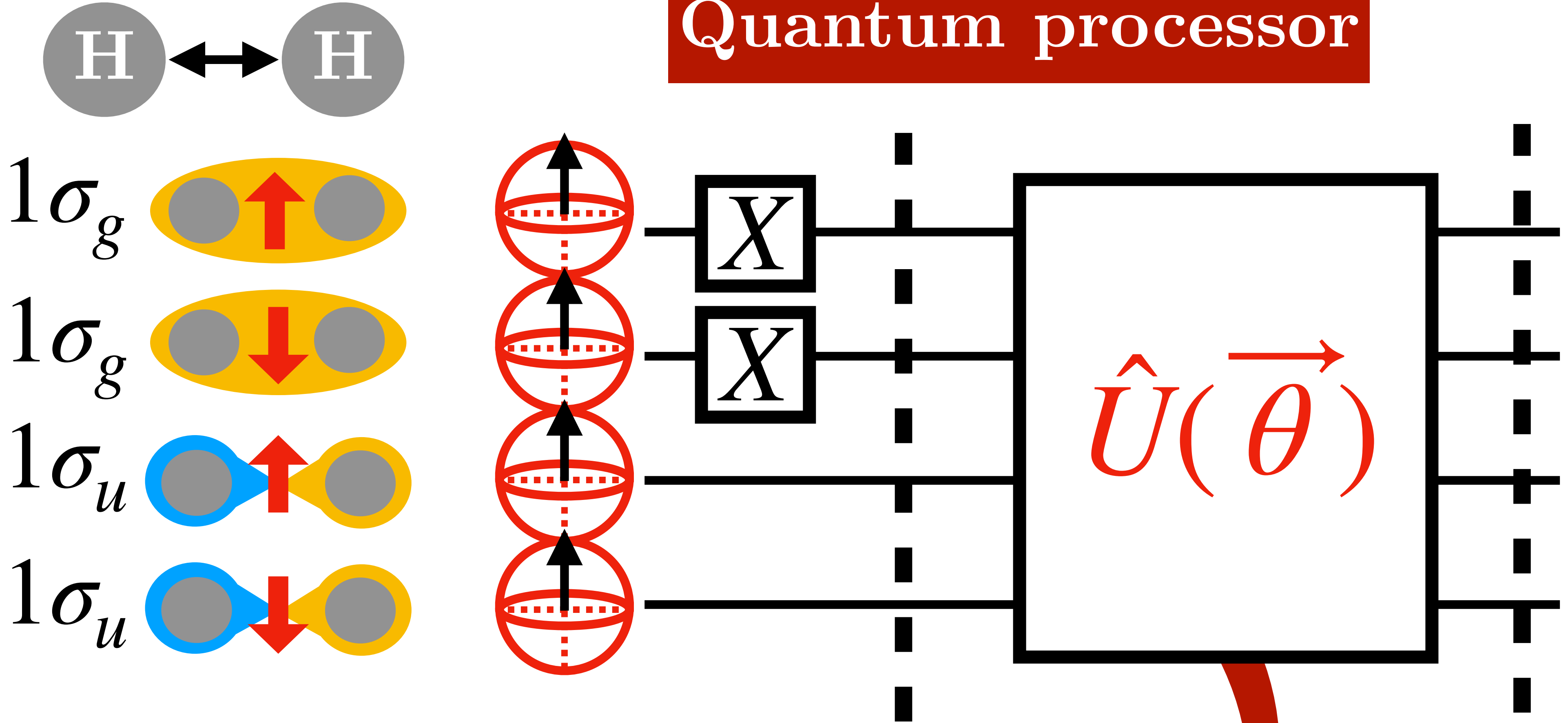
$|1100\rangle$ $\quad$ $|1001\rangle$

I) From Quantum Computing to Quantum Chemistry

VARIATIONAL QUANTUM EIGENSOLVER (VQE)

H_2 *molecule*

Quantum processor



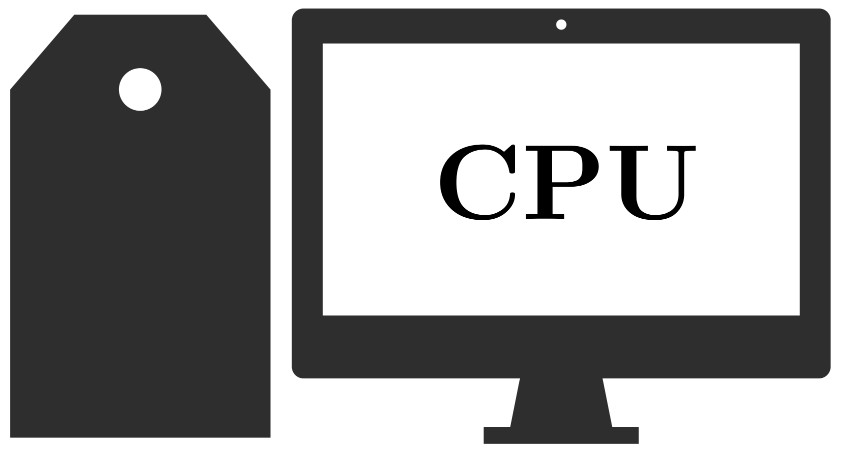
$|\Phi_{HF}\rangle = |1100\rangle$

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

Circuit parameters $\vec{\theta}$

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

Classical processor

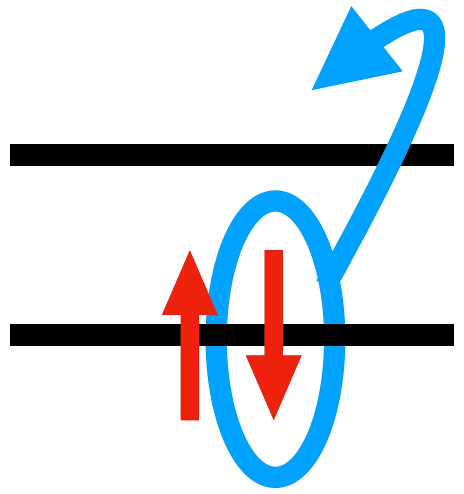


Classical Optimization of $\vec{\theta}$

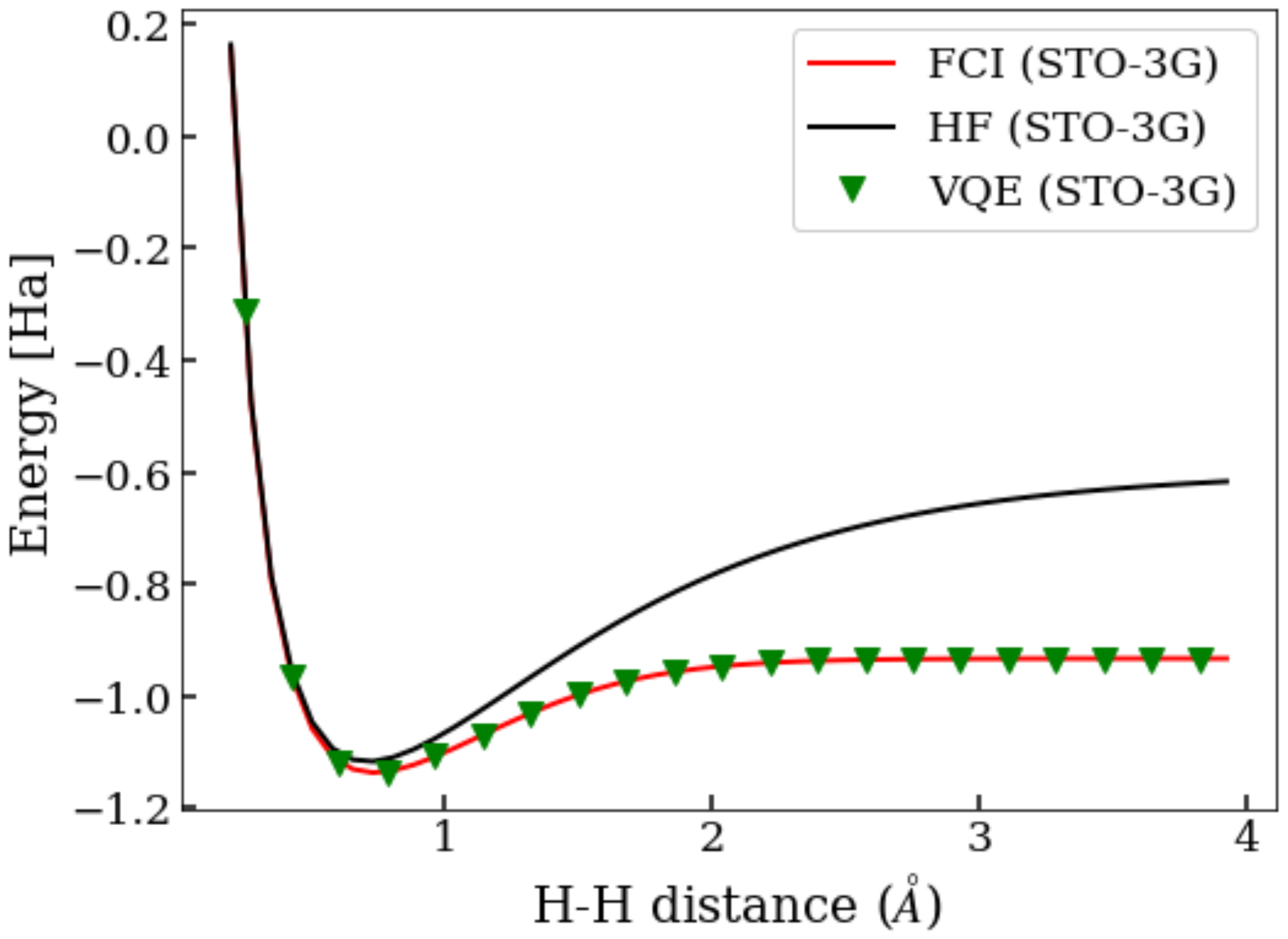
Unitary coupled cluster ansatz

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

$$T(\vec{\theta}) = \sum_{a}^{virt} \sum_{i}^{occ} \theta_i^a a_a^\dagger a_i + \sum_{a>b}^{virt} \sum_{i>j}^{occ} \theta_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j$$



Simulation of the VQE algorithm



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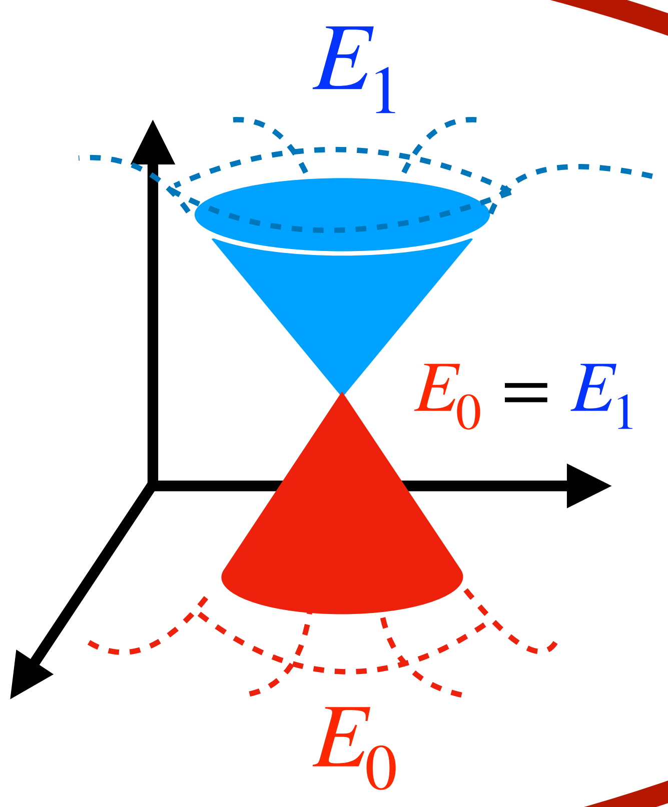
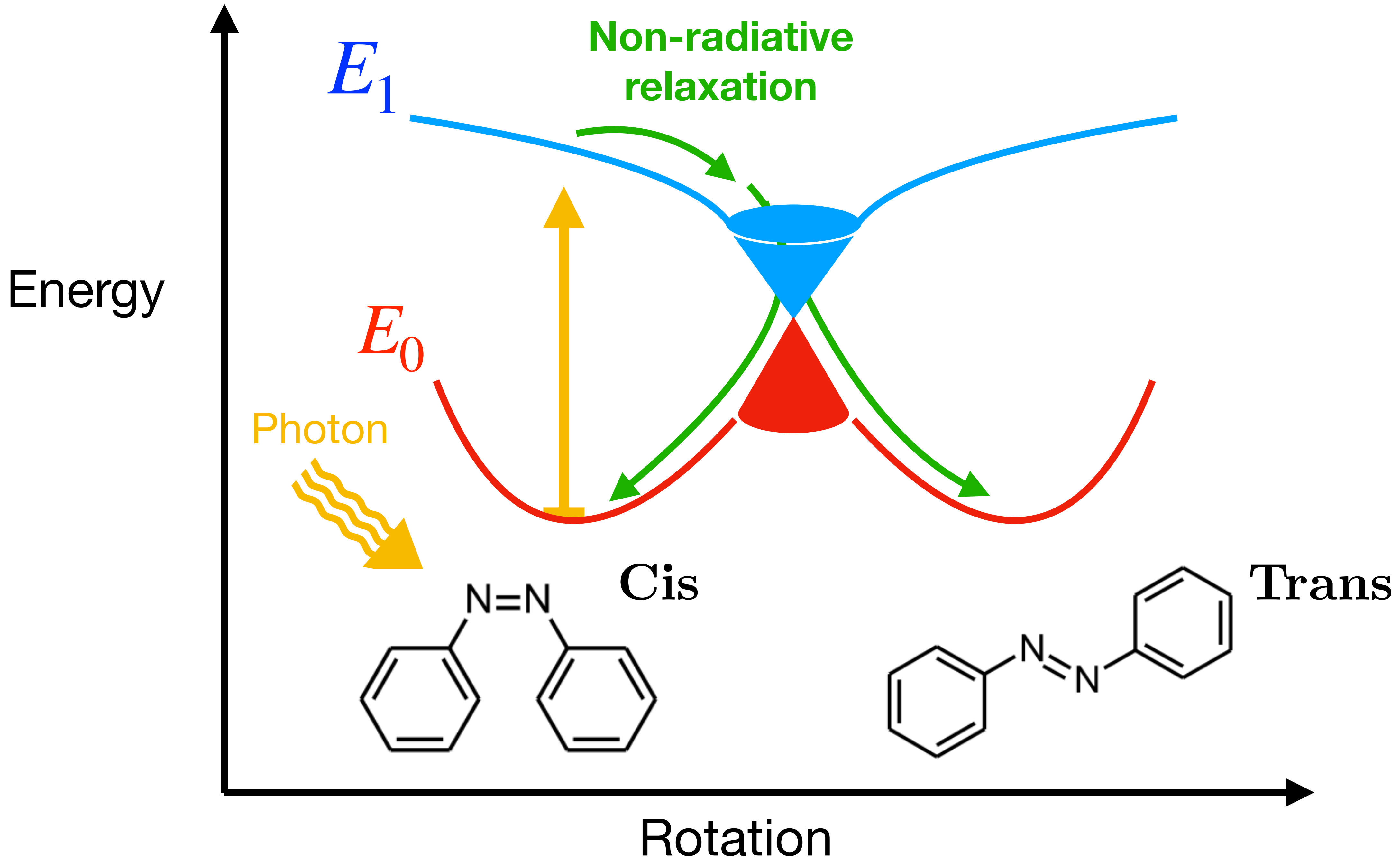
II) SA-OO-VQE: a quantum algorithm for photochemistry

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



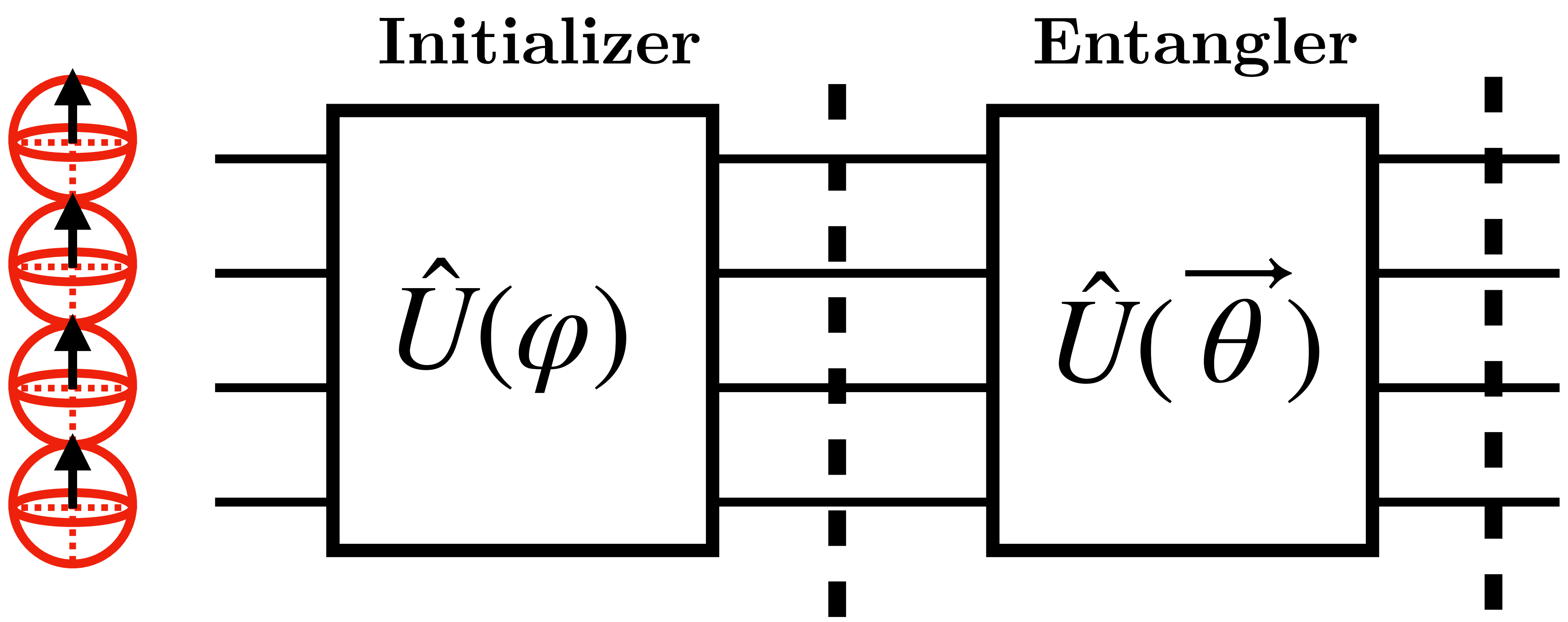


State-Averaged Orbital-Optimized VQE

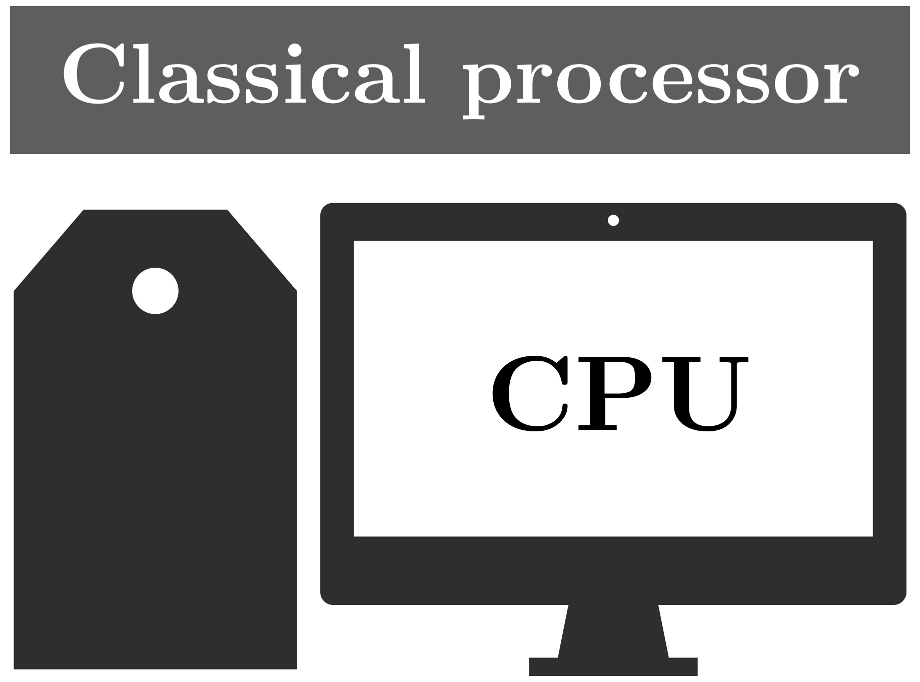
FEATURES OF THE QUANTUM ALGORITHM

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

II) SA-OO-VQE: a quantum algorithm for photochemistry



$$E^{SA}(\vec{\theta}) = E_0(\vec{\theta}) + E_1(\vec{\theta})$$



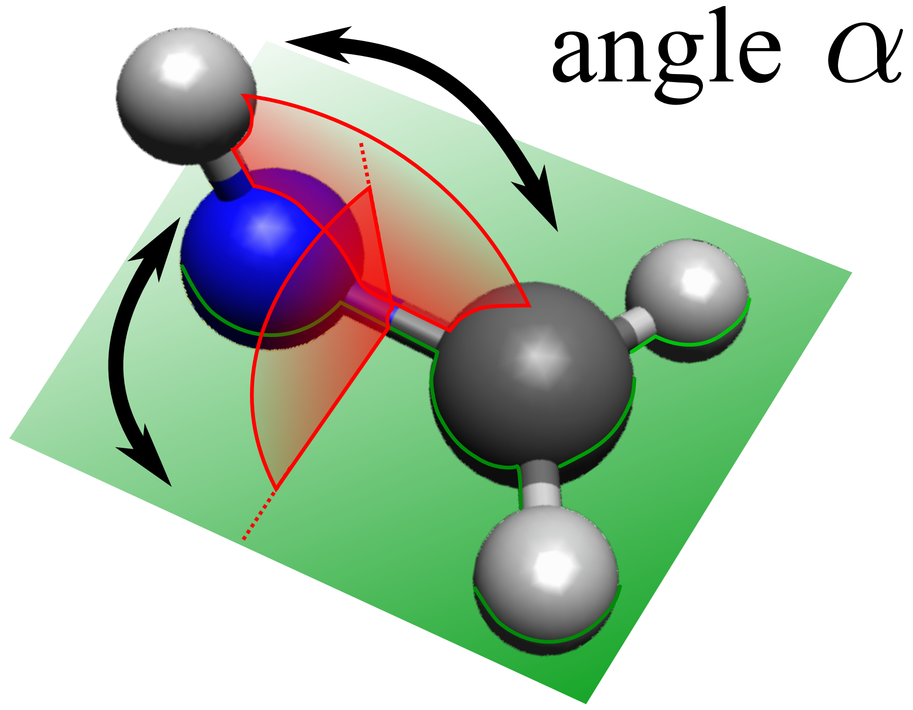
Optimization of $\vec{\theta}$
(+ SA orbital-Opt.)

$$\varphi = 0 \longrightarrow |\Phi_0\rangle \qquad |\Psi_0(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|\Phi_0\rangle$$

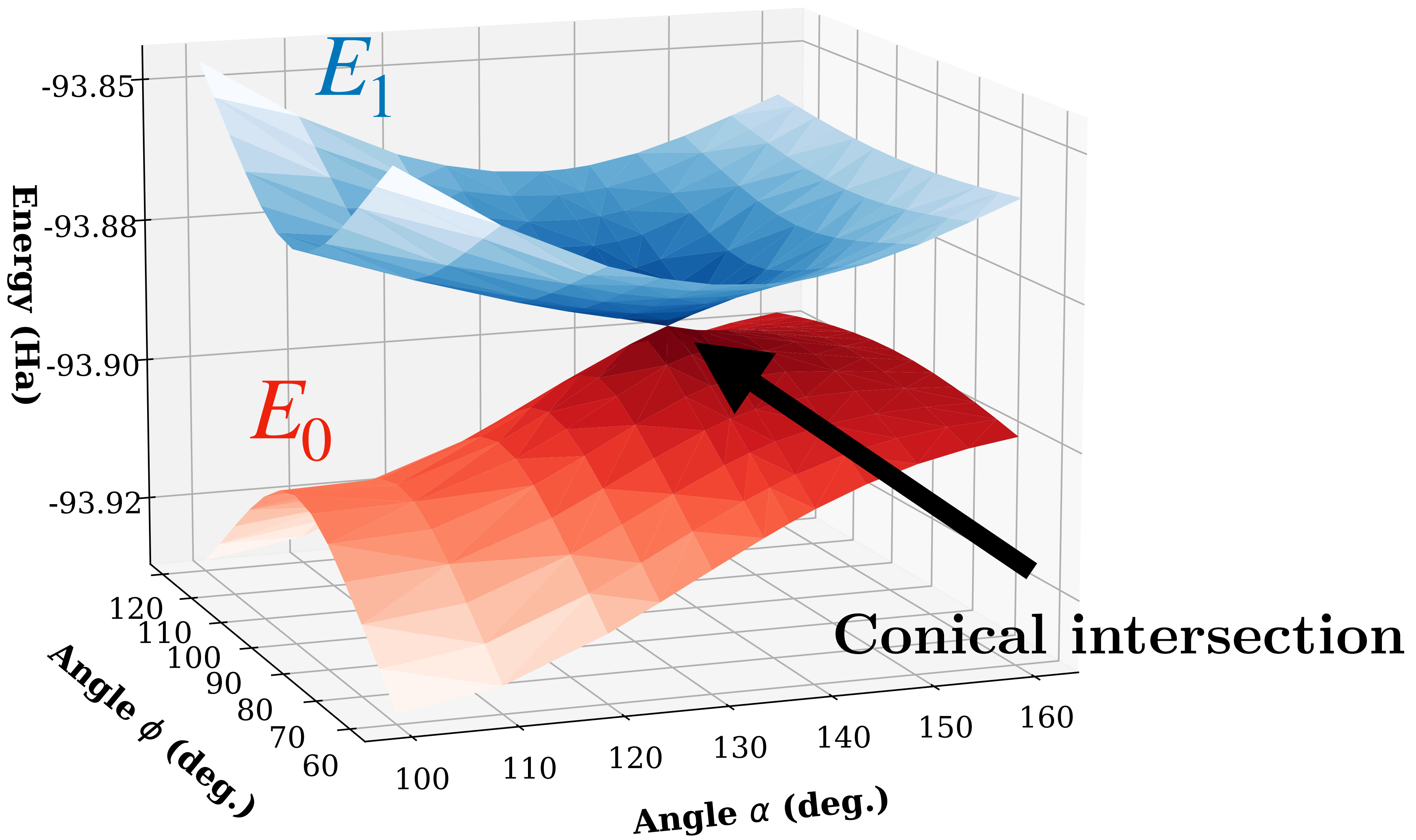
$$\varphi = \frac{\pi}{2} \longrightarrow |\Phi_1\rangle \qquad |\Psi_1(\vec{\theta})\rangle = \hat{U}(\vec{\theta})|\Phi_1\rangle$$

bending angle α

dihedral angle ϕ



PES from SA-OO-VQE



II) SA-OO-VQE: a quantum algorithm for photochemistry

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

$$E_I \qquad \frac{\partial E_I}{\partial \theta_n} \neq 0 \qquad \frac{\partial E_I}{\partial \kappa_{pq}} \neq 0$$

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

$$\frac{\partial \mathscr{L}_I}{\partial \kappa^I_{pq}} = \frac{\partial \mathscr{L}_I}{\partial \theta^I_n} = 0$$

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

Can be measured out of the circuit !

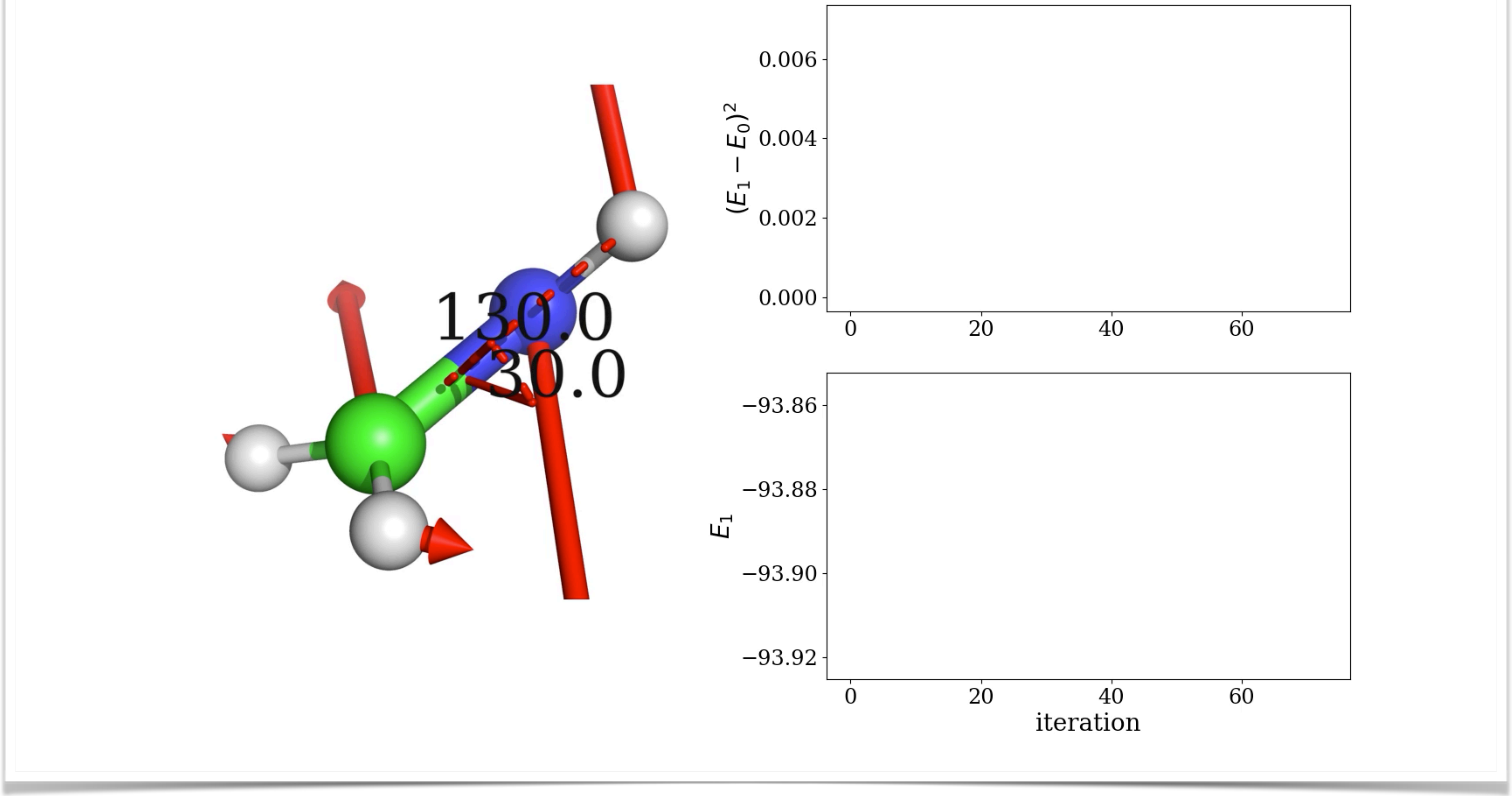
$$\frac{dE_I}{dx} = \sum_{pq} \frac{\partial h_{pq}}{\partial x} \gamma^{I,eff}_{pq} + \frac{1}{2} \sum_{pqrs} \frac{\partial g_{pqrs}}{\partial x} \Gamma^{I,eff}_{pqrs} + \sum_J \sum_n w_J \bar{\theta}^I_n G^{C,J}_n\left(\frac{\partial \hat{H}}{\partial x}\right)$$

II) SA-OO-VQE: a quantum algorithm for photochemistry

Ingredients:
- Nuclear gradients
- Non-adiabatic couplings

Research of Minimal-energy conical-intersection (MECI)

SA-OO-VQE = SA-CASSCF



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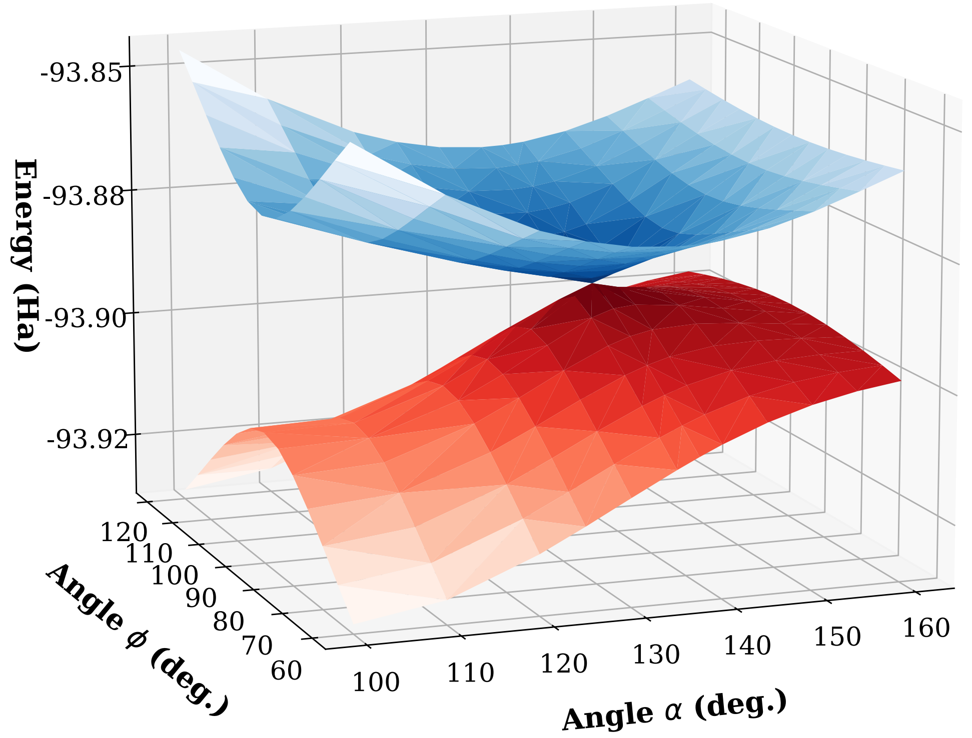
IV) Take home messages

SA-OO-VQE

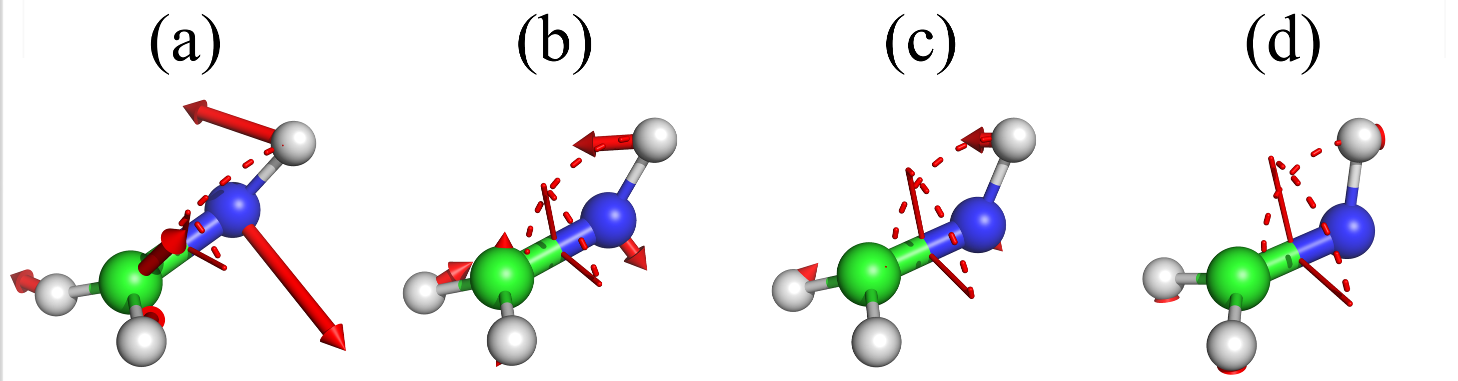
Potential energy surfaces



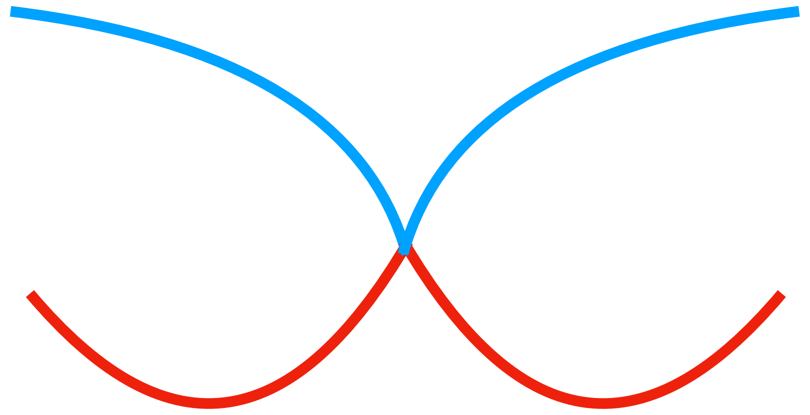
Analytical derivatives

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

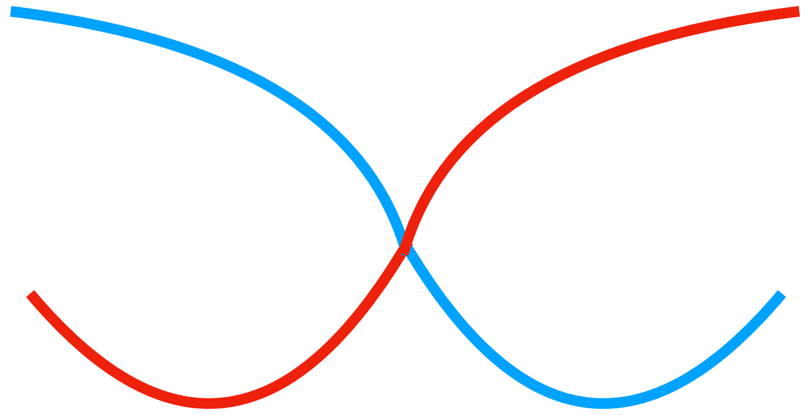
MECI optimisation



Adiabatic basis



Diabatic basis



Next steps:

1) Switching to diabatic states ?

2) Application to quantum dynamics ?

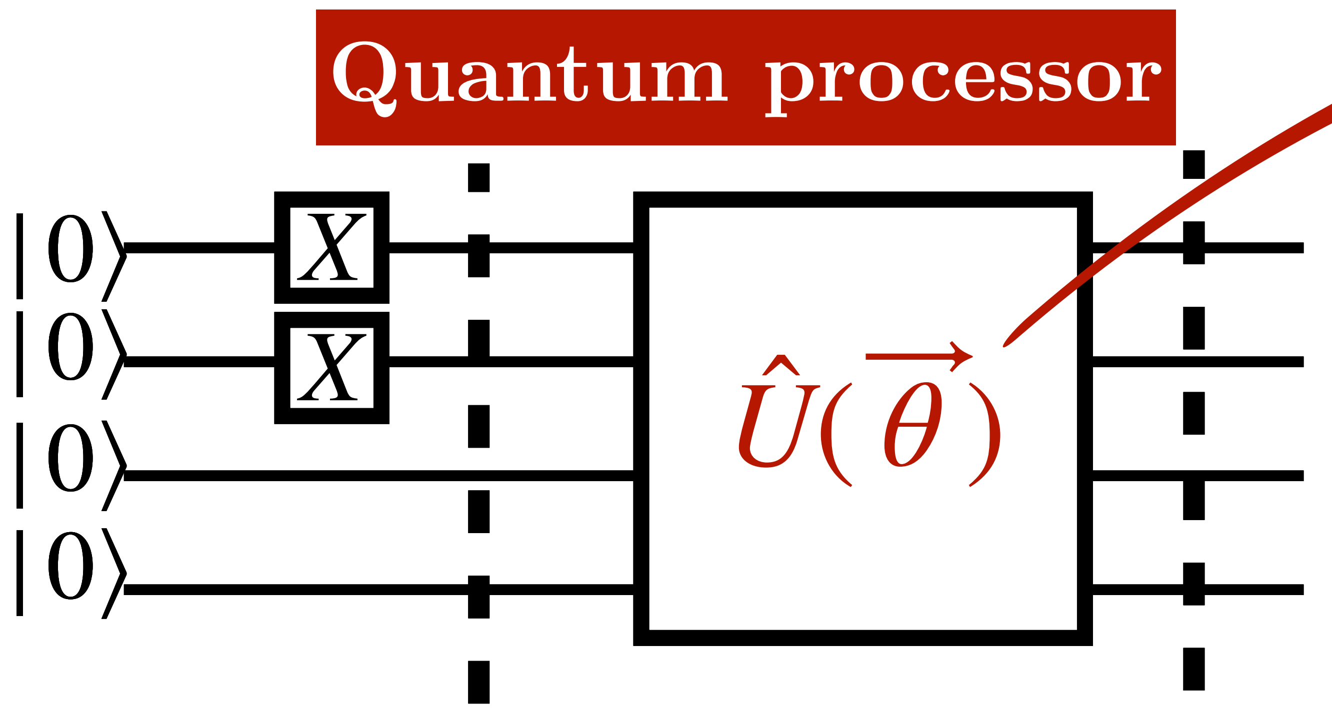
Thanks to my colleagues

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

Thank you for your attention !

S. Yalouz, B. Senjean, J. Gunther, F. Buda, T. E. O'Brien, L. Visscher. **Quantum Sci. Technol., 6(2), 024004. (2021)**

S. Yalouz, E. Koridon, B. Senjean, B. Lasorne, F. Buda, L. Visscher **(2021). arXiv:2109.04576. (accepté, journal JCTC)**



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Unitary coupled cluster ansatz

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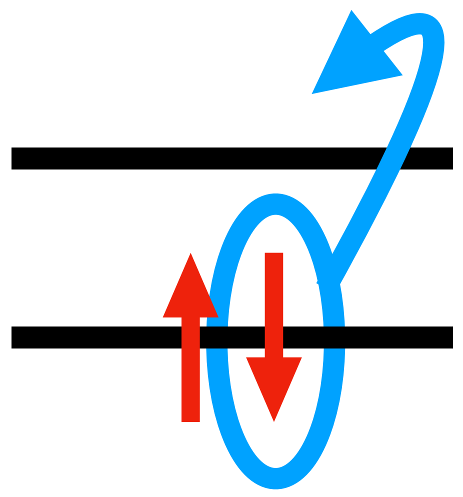

Jordan-Wigner transformation

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

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

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

$\hat{U}(\vec{\theta}) \approx$