### **Quantum Computer for Quantum Chemistry**

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### From the Molecular Hamiltonian to Qubits Hamiltonians



• Molecular Hamiltonian with *M* nuclei, *N* electrons

$$H_e = -\sum_{i} \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{\|\mathbf{r}_i - \mathbf{R}_I\|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|}$$

r<sub>i</sub>: electron coordinates R<sub>i</sub>: nuclear coordinates

• Hamiltonian in second quantization form

$$\begin{split} H_e &= \sum_{p,q} h_{pq} a_p^{\dagger} a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^{\dagger} a_q^{\dagger} a_r a_s \\ h_{pq} &= \int d\mathbf{x} \phi_p^*(\mathbf{x}) \left( -\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \phi_q(\mathbf{x}) \\ h_{pqrs} &= \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\phi_p^*(\mathbf{x}_1) \phi_q^*(\mathbf{x}_2) \phi_s(\mathbf{x}_1) \phi_r(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \end{split}$$

#### From the Molecular Hamiltonian to Qubits Hamiltonians

• Mapping the Fermion Fock space into qubits by (for instance) store the occupation number of an orbital in the |0> or |1> state of a qubit:



Hamiltonian in the qubit space as sum of N<sup>4</sup> products of Pauli matrices

$$H_e = \sum_{p,q} h_{pq} a_p^{\dagger} a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^{\dagger} a_q^{\dagger} a_r a_s \qquad \longrightarrow \qquad H = c_1 IIII + c_2 ZZII + c_3 XZXZ + \dots$$

#### Wave Function Ansatz from heuristic approach

• The heuristic ansatz wavefunction is:

$$|\psi(\vec{\theta})\rangle = \underbrace{R_y(\vec{\theta_D})U_{ent}\dots R_y(\vec{\theta_1})U_{ent}}_{\text{D times}} R_y(\vec{\theta_0}) |00\dots0\rangle$$

where  $R_y(\vec{\theta_i})$  is a rotation around axis y (generated by the Pauli matrix Y) on all qubits, and  $U_{ent}$  is an entangling block (CNOTs between neighbors)



<sup>©</sup> Very compact

😕 Lost of the physical and chemical meaning

### Variational Quantum Eigensolver



# limits of NISQ devices

- Few qubits available  $\approx O(10^2)/O(10^3)$
- Noisy gates and decoherence
- Barren plateau [1]: the noise causes the training landscape to have a vanishing gradient

**Remark:** noise-free barren plateaus are due to random parameter initialization and hence can be addressed by pre-training, correlating parameters, and other strategies

• Connectivity limitated by hardware constrains [2]

GOAL: Ansatz as short as possible and a kind of invariance of the results by respect to the entangler map

[1]: M. Cerezo, A. Sone, T. Volkoff, L. Cincio, and P. J. Coles, "Cost function dependent barren plateaus in shallow parametrized quantum circuits", *Nature Communications*, vol. 12, 2021.
[2]: <u>https://quantum-computing.ibm.com/services?services=systems&system=ibmq\_montreal</u>





# WAVEFUNCTION-ADAPTED HAMILTONIAN THROUGH ORBITAL ROTATIONS (WAHTOR)[5]

IDEA: The eigenvalues of an Hermitian operator are invariant under a unitary transformation

• A unitary matrix *U* can be written as  $U(\vec{R}) = e^{i\vec{R}\cdot\vec{T}}$ 

 $\vec{T}$  is a vector of a basis of Hermitian matrices

- $\vec{R}$  is a vector of real coefficients that parametrize the matrix  $U(\vec{R})$
- Quantum system with n single-particle orthonormal (molecular spin-orbitals) basis set identified with: latin letters = canonical basis set greek letters = transformed basis set
- A basis change is a unitary transformation and different molecular basis set are related by  $a_i^{\dagger} = \sum_{\alpha} U(\vec{R})_{\alpha i} a_{\alpha}^{\dagger}$   $a_i = \sum_{\alpha} U(\vec{R})_{i\alpha}^{\dagger} a_{\alpha}$  where  $i, \alpha = 1, ..., n$
- Define the transformed the one and the two body integrals  $(h^1, h^2)$  of the Hamiltonian

$$h^{1}_{\alpha\beta}(\vec{R}) \stackrel{\text{\tiny def}}{=} U(\vec{R})_{\alpha i} h^{1}_{ij} U(\vec{R})^{\dagger}_{j\beta} \quad h^{2}_{\gamma\delta\epsilon\zeta}(\vec{R}) \stackrel{\text{\tiny def}}{=} U(\vec{R})_{\gamma c} U(\vec{R})_{\delta d} h^{2}_{cdef} U(\vec{R})^{\dagger}_{e\epsilon} U(\vec{R})^{\dagger}_{f\zeta}$$

### WAHTOR

• Now the Hamiltonian depends on  $\vec{R}$ 

- Energy is a function of both set of parameters  $E(\vec{R}, \vec{\theta}) = \langle \Psi(\vec{\theta}) | H(\vec{R}) | \Psi(\vec{\theta}) \rangle$
- For fixed  $\vec{R}$ , the VQE algorithm can be used to minimize  $E(\vec{R}, \vec{\theta})$  respect to  $\vec{\theta}$
- For fixed  $\vec{\theta}$ , the  $\vec{R}$  parameters can be optimized using a trust region optimizer (we can calculate the analytic derivatives of  $h^1(\vec{R})$  and  $h^2(\vec{R})$ )

$$\frac{dh^{1}(\vec{R})}{dR_{l}}|_{\vec{R}=0} = i[T_{l}, h_{HF}^{1}] \qquad \qquad \frac{dh^{2}(\vec{R})}{dR_{l}}|_{\vec{R}=0} = i[T_{l} \otimes I + I \otimes T_{l}, h_{HF}^{2}] \\ \frac{d^{2}h^{1}(\vec{R})}{dR_{l}R_{k}}|_{\vec{R}=0} = \frac{i}{2} \left[ T_{l}, \frac{dh^{1}(\vec{R})}{dR_{k}}|_{\vec{R}=0} \right] \qquad \qquad \frac{dh^{2}(\vec{R})}{dR_{l}R_{k}}|_{\vec{R}=0} = \frac{i}{2} \left( \left[ T_{l}, \frac{dh^{2}(\vec{R})}{dR_{k}}|_{\vec{R}=0} \right] + \left[ T_{k}, \frac{dh^{2}(\vec{R})}{dR_{l}}|_{\vec{R}=0} \right] \right)$$



#### ENERGY AS A FUNCTION OF ANSATZ TOPOLOGY

System:

- 6-31G basis set (8 qubits, 16 derivatives)
- Jordan-Wigner mapping
- Depth 2
- Statevector simulator



- Green star: lowest energy obtained from 50 times VQE run
- Blue circle: WAHTOR energy obtained starting from the green star



WAHTOR states with same energy represent the same physical state



#### FIXED ANSATZ TOPOLOGY

#### System:

- 6-31G basis set (8 qubits, 16 derivatives)
- Jordan-Wigner mapping
- Depth 2
- Statevector simulator
- Entangler map:





- Green stars: VQE energies
- Blue circles: WAHTOR energies starting from the corresponding VQE



#### DISSOCIATION CURVE: $H_2 \rightarrow 2H$

#### System:

- 6-31G basis set (8 qubits, 16 derivatives)
- Jordan-Wigner mapping
- Depth 2
- Statevector simulator
- Entangler map:



For each atomic distance:

- Black circle: lowest energy obtained from 50 times VQE run
- Blue triangle: WAHTOR energy obtained starting from the black circle









# **CAN WE LEARN SOME CHEMISTRY?**

 $\delta \in [0,1]$ , measure how much the WAHTOR orbitals are close to the natural orbitals, taking as reference the Hatree-Fock orbitals

$\delta =$	$\sum_{i} ( \langle W_i   NO_i \rangle  -  \langle HF_i   NO_i \rangle )$
	$\boxed{N - \sum_{i}  \langle HF_i   NO_i \rangle }$

- $|W\rangle$  WAHTOR orbitals
- |*NO* | **Natural orbitals**
- rix  $|HF\rangle$  Hartree-Fock orbitals

N = number of optimized orbitals

$ W\rangle =  NO\rangle$
<i>W</i> / =   <i>N</i> 0 /

Why  $|NO\rangle$  are important?

It has been **conjectured** that, in this basis, the quantum state is expressed with the least number of determinants (Lödwin 1955)<sup>[6]</sup>

Natural Orbit	tals (NO) are the orbit	als that diagonalise the reduced one-body density matrix
molecule	atomic positions (Å)	basis set qubits % VOE % WAHTOR d

	atomic positions (A)	04515 500	quonos	70 VQL	// //////////	0
$H_2$	H 0.0 0.0 0.0 H 0.0 0.0 0.74	6-31g	8	47.08	98.05	0.998
LiH	Li 0.0 0.0 0.0 H 0.0 0.0 1.595	sto-3g	10	72.14	94.75	0.999
HF	$\begin{array}{c} {\rm F} \ 0.0 \ 0.0 \ 0.0 \\ {\rm H} \ 0.0 \ 0.0 \ 0.917 \end{array}$	sto-3g	10	71.51	93.03	0.999
$BeH_2$	H 0.0 0.0 0.0 Be 0.0 0.0 1.334 H 0.0 0.0 2.668	sto-3g	12	45.40	45.42	$ HF\rangle \equiv  NO\rangle$
$H_2O$	O 0.0 0.0 0.0 H 0.757 0.586 0.0 H -0.757 0.586 0.0	sto-3g	12	51.65	73.54	0.972
$H_2S$	S 0.0 0.0 0.0 H 0.0 0.9616 -0.9269 H 0.0 -0.9616 -0.9269	sto-3g	12	74.76	87.42	0.998
NH <sub>3</sub>	N 0.0 0.0 0.1211 H 0.0 0.9306 -0.2826 H 0.8059 -0.4653 -0.2826 H -0.8059 -0.4653 -0.2826	sto-3g	14	36.42	41.85	0.988

[6] P. Lödwin, "Quantum Theory of Many-Particle Systems. I. Physical Interpretations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction", Physical review, vol. 97, 1955

### **Quantum Mutual information**

#### **ORBITAL CORRELATIONS**

- |Ψ>
- $\rho = |\Psi\rangle\langle\Psi|$
- $\rho_i = tr_{k\neq i}(\rho)$
- $S(1)_i = -tr(\rho_i \log \rho_i)$
- $S(2)_{ij} = -tr(\rho_{ij}log \rho_{ij})$

#### qubit wavefunction

density matrix

reduced density matrix for qubit *i* Von Neumann one-qubit entropy

Von Neumann two-qubit entropy

$$I_{ij} = \frac{1}{2} [S(1)_i + S(1)_j - S(2)_{ij}] (1 - \delta_{ij})$$

Quantum mutual information capture the correlation between the two qubits. If the state of the qubit *i* is know,  $I_{ij}$  measure the information obtained on qubit *j*.

#### System:

- $H_2O$  molecule
- Sto-3g basis set
- Jordan-Wigner mapping
- Qubits {0,1,2,3,4,5} = spin orbitals
- Qubits {6,7,8,9,10,11} = spin orbitals



- correlations are concentrated on a smaller number of qubits pairs (as expected in |NO) basis)
- The same results can be obtained for the other molecules under consideration (H<sub>2</sub>, LiH, HF, BeH<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>)



(a) VQE state in HF molecular orbitals





(b) WAHTOR state in converged molecular orbitals



(d) Groundstate in converged molecular orbitals



	H $0.0 \ 0.0 \ 0.0$					
$BeH_2$	Be $0.0 \ 0.0 \ 1.334$	sto-3g	12	45.40	45.42	$ HF\rangle \equiv  NO\rangle$
	H 0.0 0.0 2.668					

Whats happen if  $|NO\rangle \equiv |HF\rangle$ ? WAHTOR algorithm does not optimize



(a) VQE state in HF molecular orbitals



(b) WAHTOR state in converged molecular orbitals

 $|W\rangle \equiv |NO\rangle \equiv |HF\rangle$ 









(c) Groundstate in HF molecular orbitals



(e) Groundstate in natural molecular orbitals

### CONCLUSIONS

Wevefunction-Adapted Hamiltonian Through Orbital Rotations (WAHTOR)

- Improve the VQE results escaping from the local minima
- Ansatz are composed by a lower number of quantum gates
- Invariance of the results respect to the ansatz topology
- Hamiltonian parameters are optimized using analytic derivatives
- For small molecules (H<sub>2</sub>, LiH, BeH<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>) WAHTOR converge to the natural orbitals, correlations are concentrated on a smaller number of qubits pairs

### SU(N) FERMIONIC SYSTEMS



(Picture from ref. [9])

[7] Rapp A, Zaránd G, Honerkamp C and Hofstetter W," Color superfluidity and 'baryon' formation ´ in ultracold fermions", Phys. Rev. Lett. 98 160405.

[8] F. Scazza, C. Hofrichter, M. H"ofer, P. De Groot, I. Bloch, and S. F"olling, "Observation of two-orbital spin-exchange interactions with ultracold su(n)-symmetric fermions", Nature Physics 10, 779 (2014).

[9] M. Consiglio et al, "Variational quantum eigensolver for SU(N) fermions", J. Phys. A: Math. Theor. 55 265301 (2022).

### Hubbard-like Hamiltonian with SU(3) fermions

VQE









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Group experience: molecular modelling of biomolecules, electronic structure for strongly correlated systems, high-performance computing and quantum computing





**Thanks to:** Celestino Angeli (Univ. Ferrara)

**Current collaborations:** IBM-Zurich (Switzerland) Algorithmiq (Finland)

Improved Accuracy on Noisy Devices by Nonunitary Variational Quantum Eigensolver for Chemistry Applications

JCTC 2021 10.1021/acs.jctc.1c00091

Wave Function Adapted Hamiltonians for Quantum Computing JCTC 2022 https://doi.org/10.1021/acs.jctc.1c01170