The road ahead …

Thinking outside the box II

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$|\Psi\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

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DMRG

- **Determine** CI coefficients from correlations among orbitals

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Quantum Computing

- "**Learn**" the energy

$$\langle\Psi| \hat{H}_e |\Psi\rangle = \sum_k c_k \langle\Psi| P_k |\Psi\rangle$$

using an entangled set of qubits

$$|\Psi\rangle = \mathbf{U}(\vec{\theta}) |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

Quantum Chemistry on a Quantum Computer: Concepts and Challenges

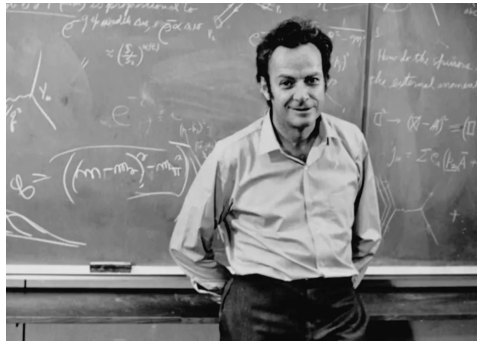
Some important references

- Quantum Chemistry in the Age of Quantum Computing
  Aspuru-Guzik *et al.,* Chem. Rev. **119***,* 10856 (2019)
- Quantum computational chemistry
  McArdle, Endo, Aspuru-Guzik, Benjamin, Yuan, Rev. Mod. Phys. **92**, 015003 (2020)
- An adaptive variational algorithm for exact molecular simulations on a quantum computer
  Grimsley, Economou, Barnes, Mayhall, Nat. Comm.**10**, 3007 (2019)
- Simulated Quantum Computation of Molecular Energies,
  Aspuru-Guzik, Dutoi, Love, Head-Gordon, Science **309**, 1704 (2005)
- Quantum chemistry, classical heuristics, and quantum advantage,
  Garnet Kin-Lic Chan, Faraday Discuss. **254**, 11 (2024)

The origins of quantum computing

Simulating quantum physics

Yuri Manin
1980



Richard Feynman
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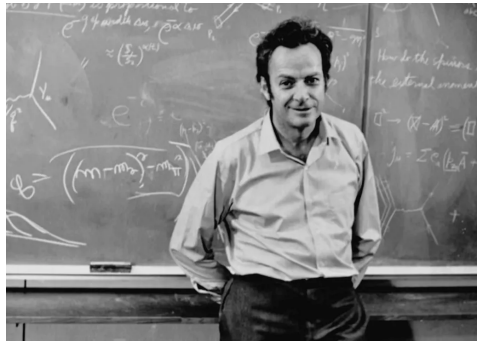


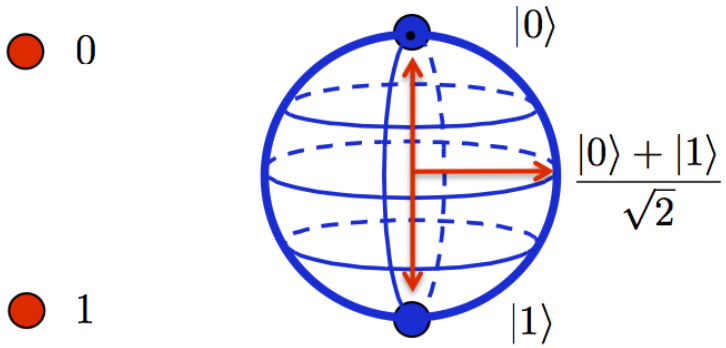
Richard Feynman
1982

Simulating some quantum mechanical effects on a classical computer is unfeasible

→ Use a quantum one!

The origins of quantum computing

Simulating quantum physics



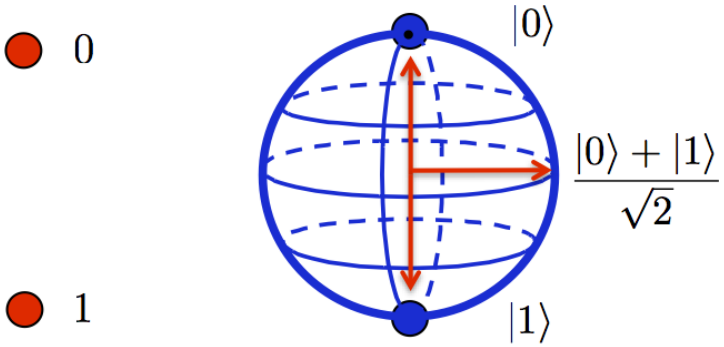
From **bits** to … → **qubits**

- Classical bit can be **either** in state $|0\rangle$ **or** state $|1\rangle$
- Qubit can be in a **superposition** of both states

$$|\psi\rangle = \alpha |0\rangle + \beta |1\rangle \equiv \alpha \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \beta \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

The origins of quantum computing

Simulating quantum physics



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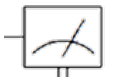
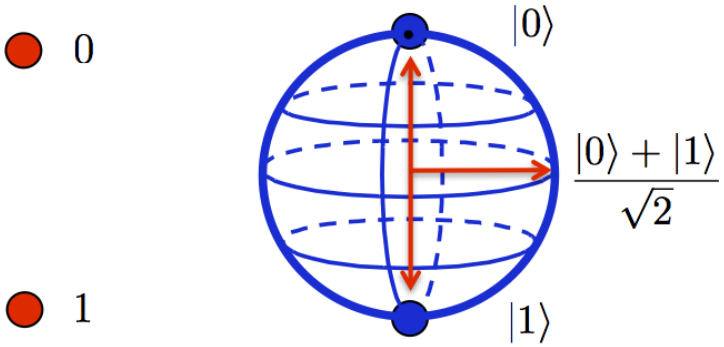
$$|\psi\rangle = |0\rangle \xrightarrow{\text{superposition}} |\psi\rangle = \alpha|0\rangle + \beta|1\rangle \xrightarrow{\text{quantum computation}} |\psi\rangle = \gamma|0\rangle + \delta|1\rangle$$



$$\rightarrow \begin{cases} |\psi\rangle = |0\rangle \\ |\psi\rangle = |1\rangle \end{cases}$$

The origins of quantum computing

Simulating quantum physics



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- Classical bit can be **either** in state $|0\rangle$ **or** state $|1\rangle$
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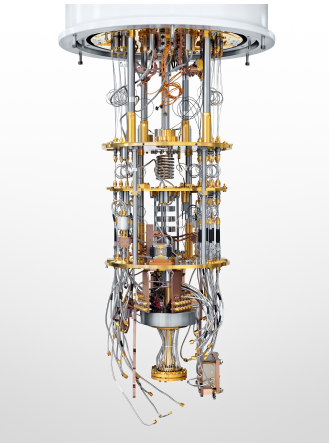
$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle \equiv \alpha\begin{bmatrix}1\\0\end{bmatrix} + \beta\begin{bmatrix}0\\1\end{bmatrix}$$

- Measuring the state of the qubit with probability P

$$P\left(|\psi\rangle = |0\rangle\right) = \gamma^2 \text{ and } P\left(|\psi\rangle = |1\rangle\right) = \delta^2$$

$|\psi\rangle = |0\rangle$ —**superposition**→ $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ —**quantum computation**→ $|\psi\rangle = \gamma|0\rangle + \delta|1\rangle$ → $|\psi\rangle = |0\rangle$ or $|\psi\rangle = |1\rangle$

Using a quantum computer
as a quantum physics simulator



Arbitrary state of its qubits

$$|\Psi\rangle = \sum_{\vec{f}} \alpha_{\vec{f}} |f_1 f_2 \dots f_M\rangle$$

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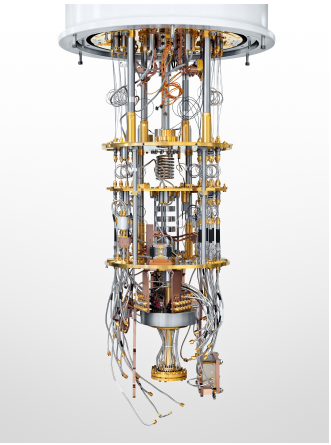

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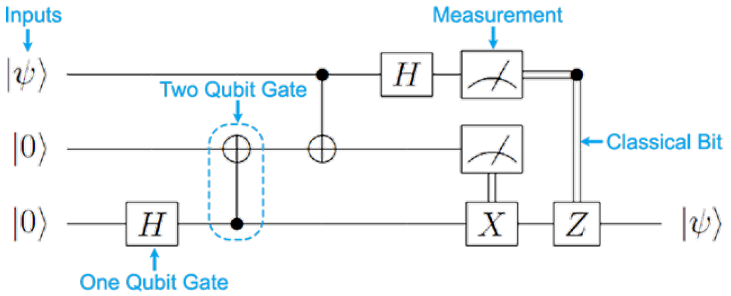
A universal quantum computer can solve problems beyond quantum simulation (e.g. factorisation)



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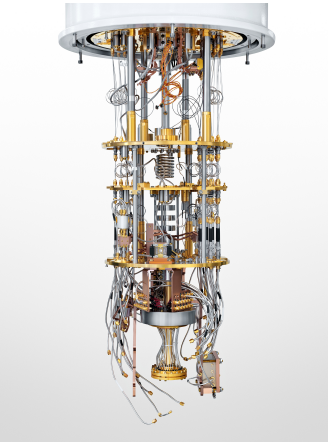

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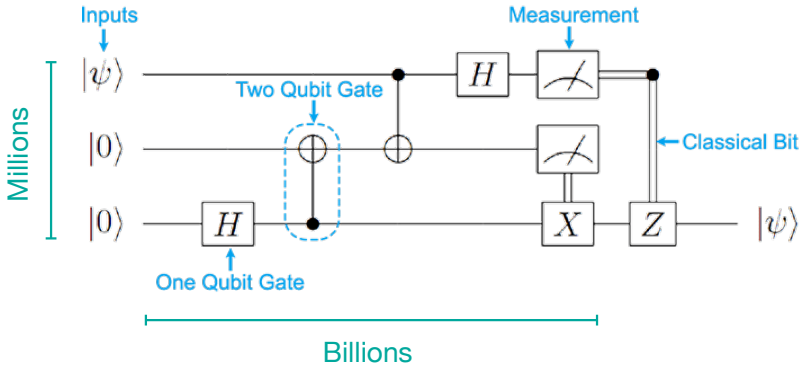

Quantum 5, 433 (2021)

Using a quantum computer
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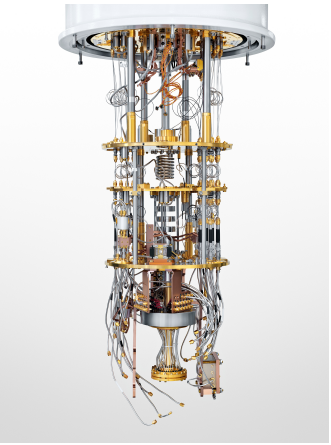

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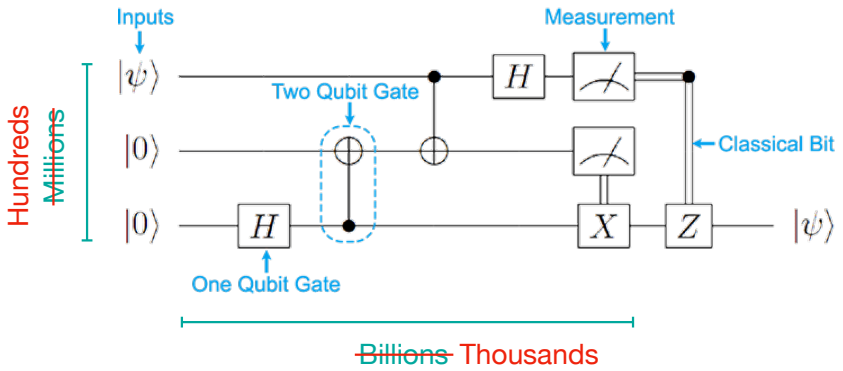

Quantum 5, 433 (2021)

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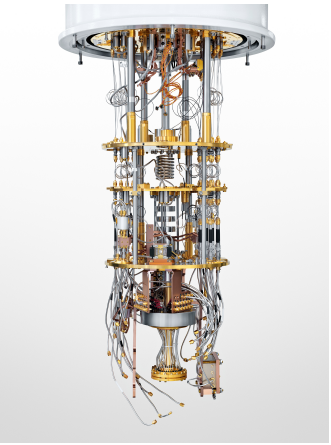

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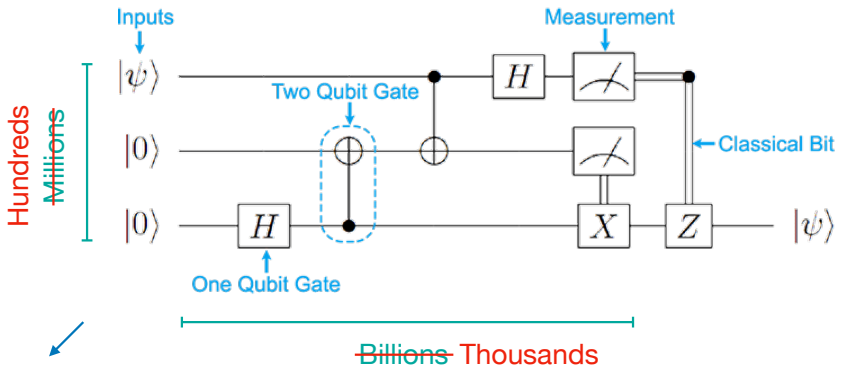


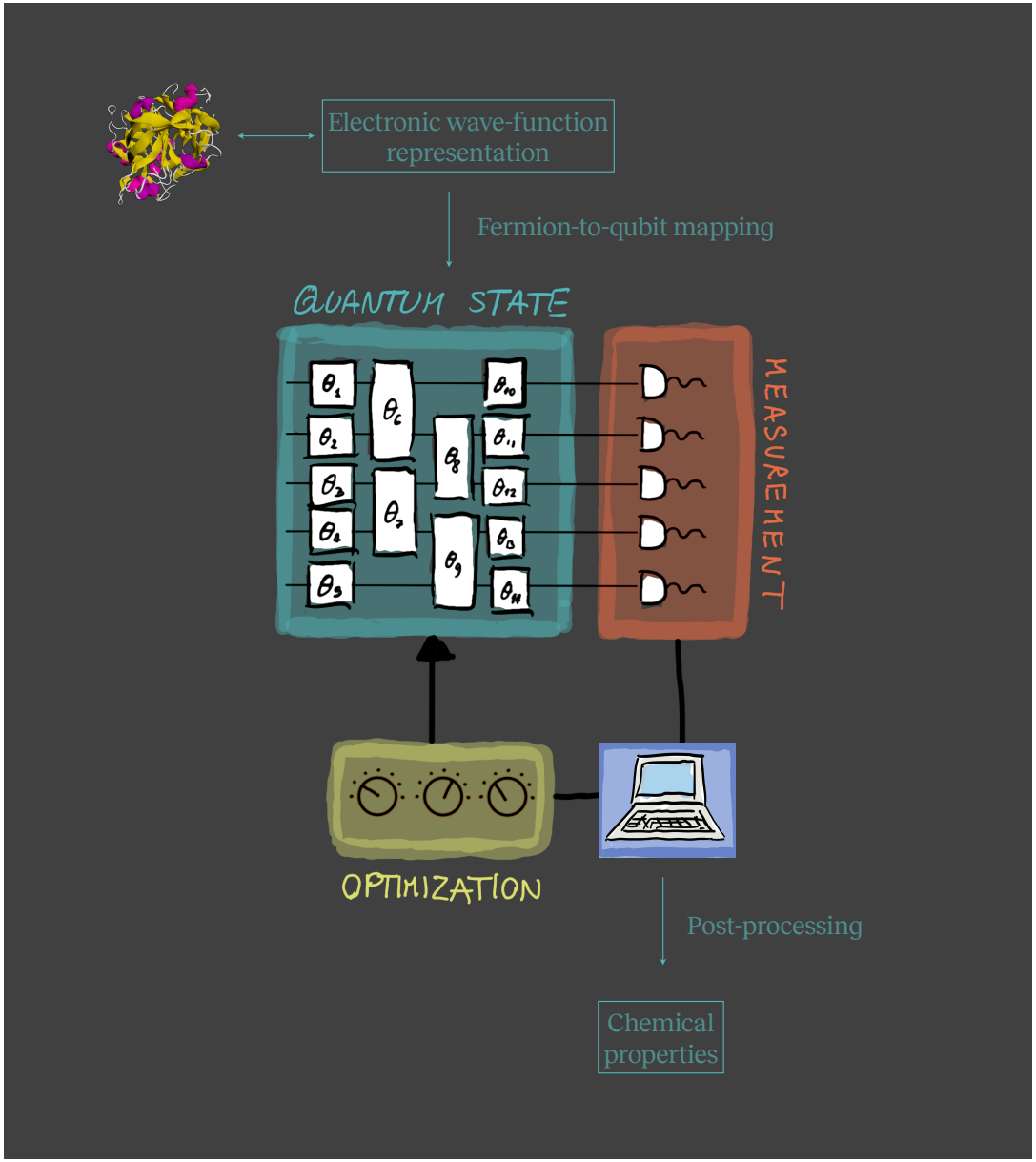
We are in the era of the Noisy/Early Fault Tolerant Quantum computers:
soon useful for simulation!

Quantum 5, 433 (2021)

Quantum computer technologies

Qubit Type	Pros/Cons	Select Players
Superconducting	***Pros***: High gate speeds and fidelities. Can leverage standard lithographic processes. Among first qubit modalities so has a head start. ***Cons***: Requires cryogenic cooling; short coherence times; microwave interconnect frequencies still not well understood.	rigetti, Google, IBM Q, QuTech, OQC, IQM, Quantum Circuits, Inc, 本源量子 Origin Quantum
Trapped Ions	***Pros***: Extremely high gate fidelities and long coherence times. Extreme cryogenic cooling not required. Ions are perfect and consistent. ***Cons***: Slow gate times/ operations and low connectivity between qubits. Lasers hard to align and scale. Ultra-high vacuum required. Ion charges may restrict scalability.	IONQ, AQT, QUANTINUUM, oxford ionics, Universal Quantum
Photonics	***Pros***: Extremely fast gate speeds and promising fidelities. No cryogenics or vacuums required. Small overall footprint. Can leverage existing CMOS fabs. ***Cons***: Noise from photon loss; each program requires its own chip. Photons don't naturally interact so 2Q gate challenges.	PsiQuantum, XANADU, QUIX QUANTUM, ORCA Computing
Neutral Atoms	***Pros***: Long coherence times. Atoms are perfect and consistent. Strong connectivity, including more than 2Q. External cryogenics not required. ***Cons***: Requires ultra-high vacuums. Laser scaling challenging.	ColdQuanta, QuEra Computing Inc., atom computing, PASQAL
Silicon Spin/Quantum Dots	***Pros***: Leverages existing semiconductor technology. Strong gate fidelities and speeds. ***Cons***: Requires cryogenics. Only a few entangled gates to-date with low coherence times. Interference/cross-talk challenges.	intel, Silicon Quantum Computing, diraq, QUANTUM MOTION, QUANTUM BRILLIANCE

Source: Quantum Computing Modalities - A Qubit Primer Revisited - The Quantum Leap (quantum tech.blog)

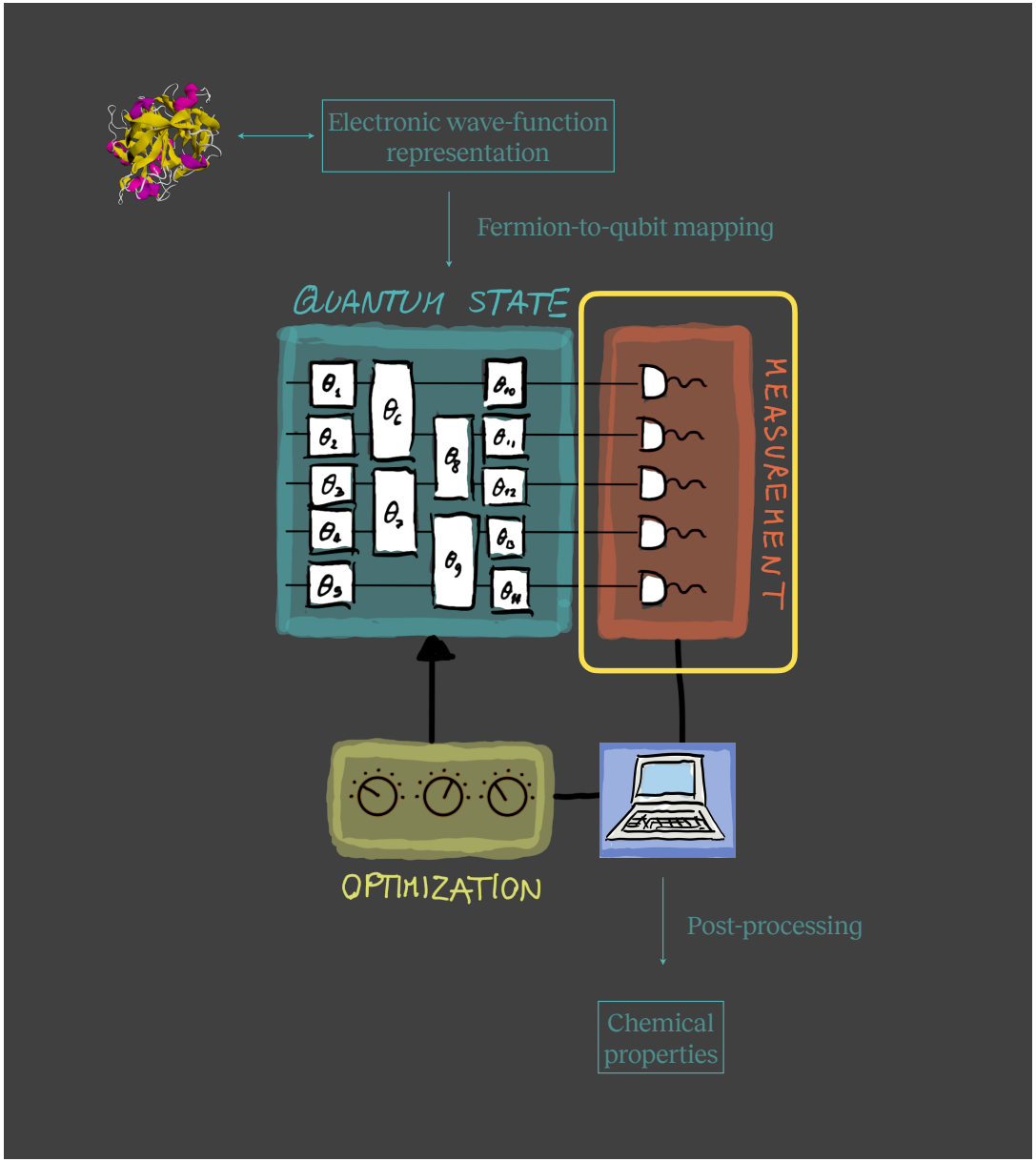


Quantum Computing for Quantum Chemistry in a Nutshell

The state of the quantum processor mathematically represents the state of the molecule

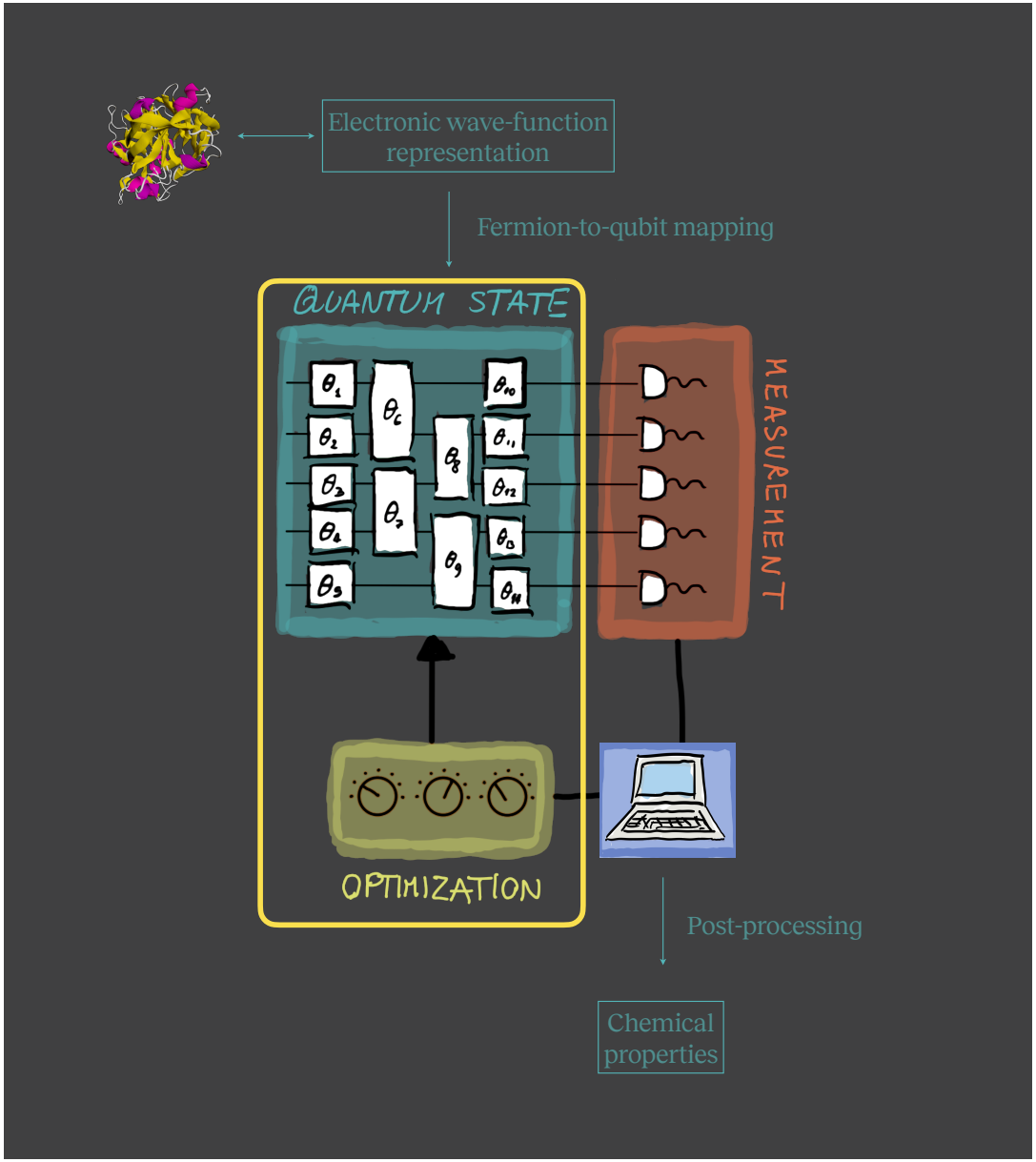
The goal is to find the state of the molecule for which the energy is minimal

The energy of the molecule needs to be measured



Challenges in near-term QC

1. Measurement stage is time-consuming
2. Hilbert space is a big space
3. Qubits are a scarce resource
4. Noise biases the results
5. Resource efficient/aware representation



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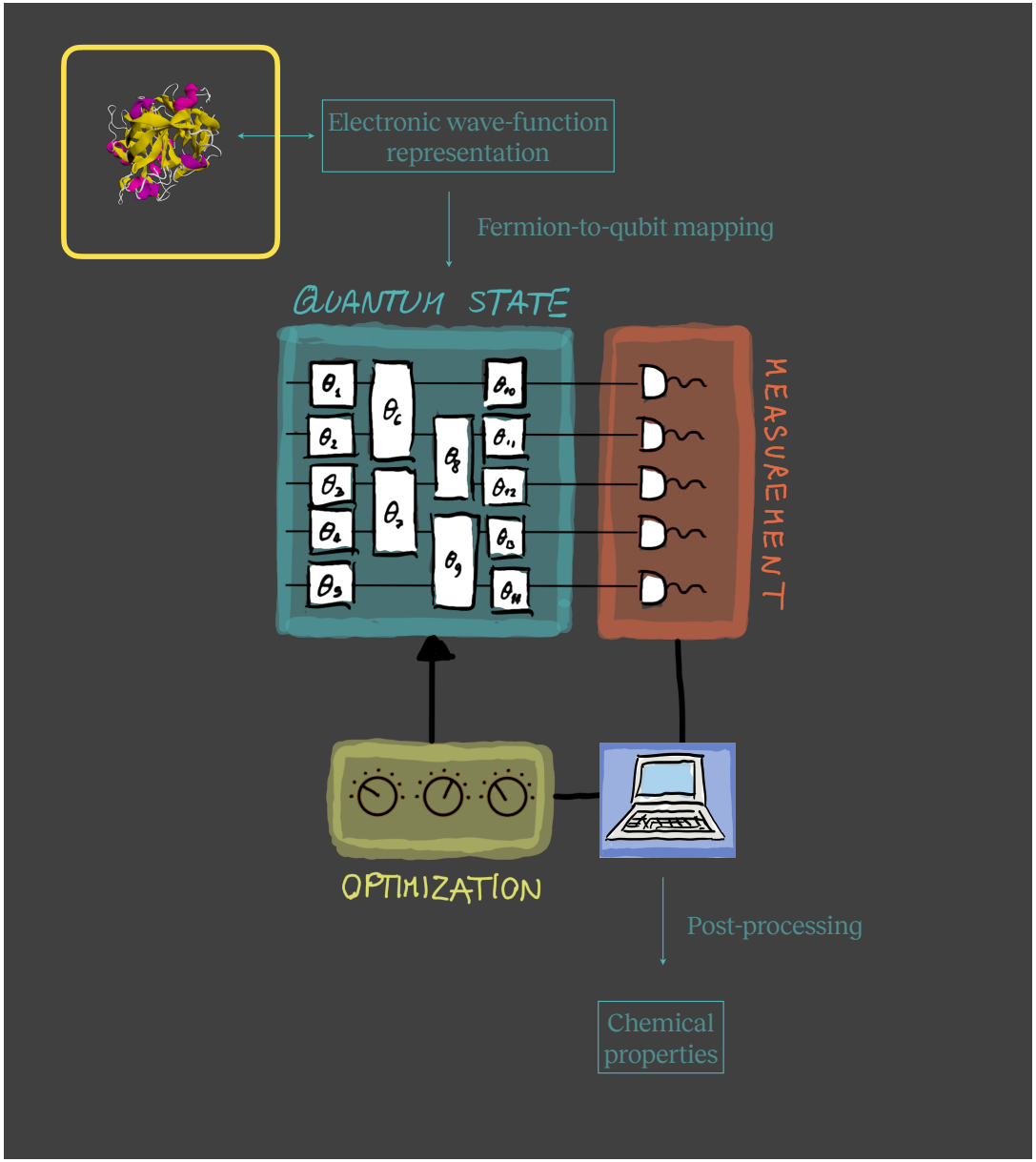

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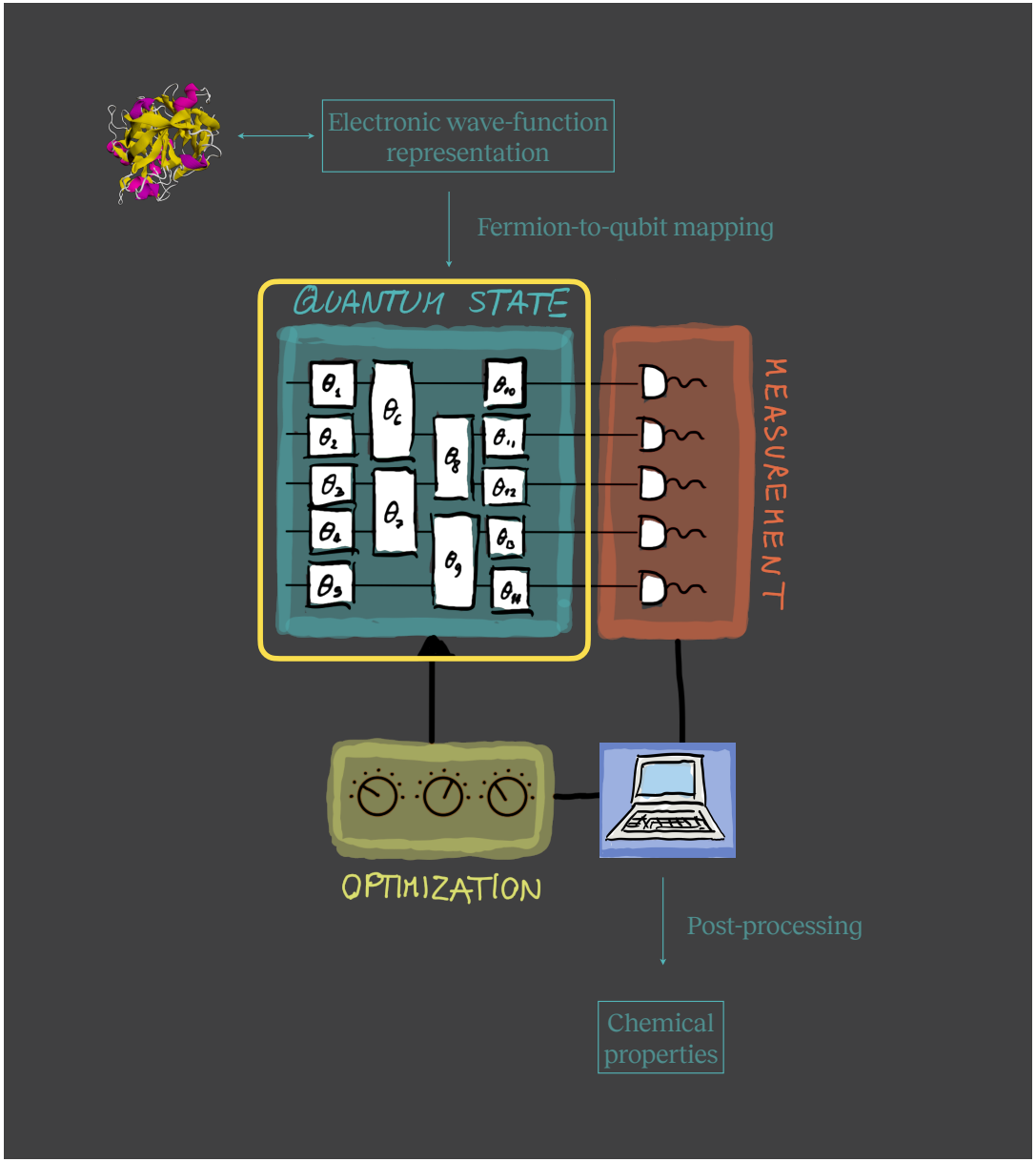

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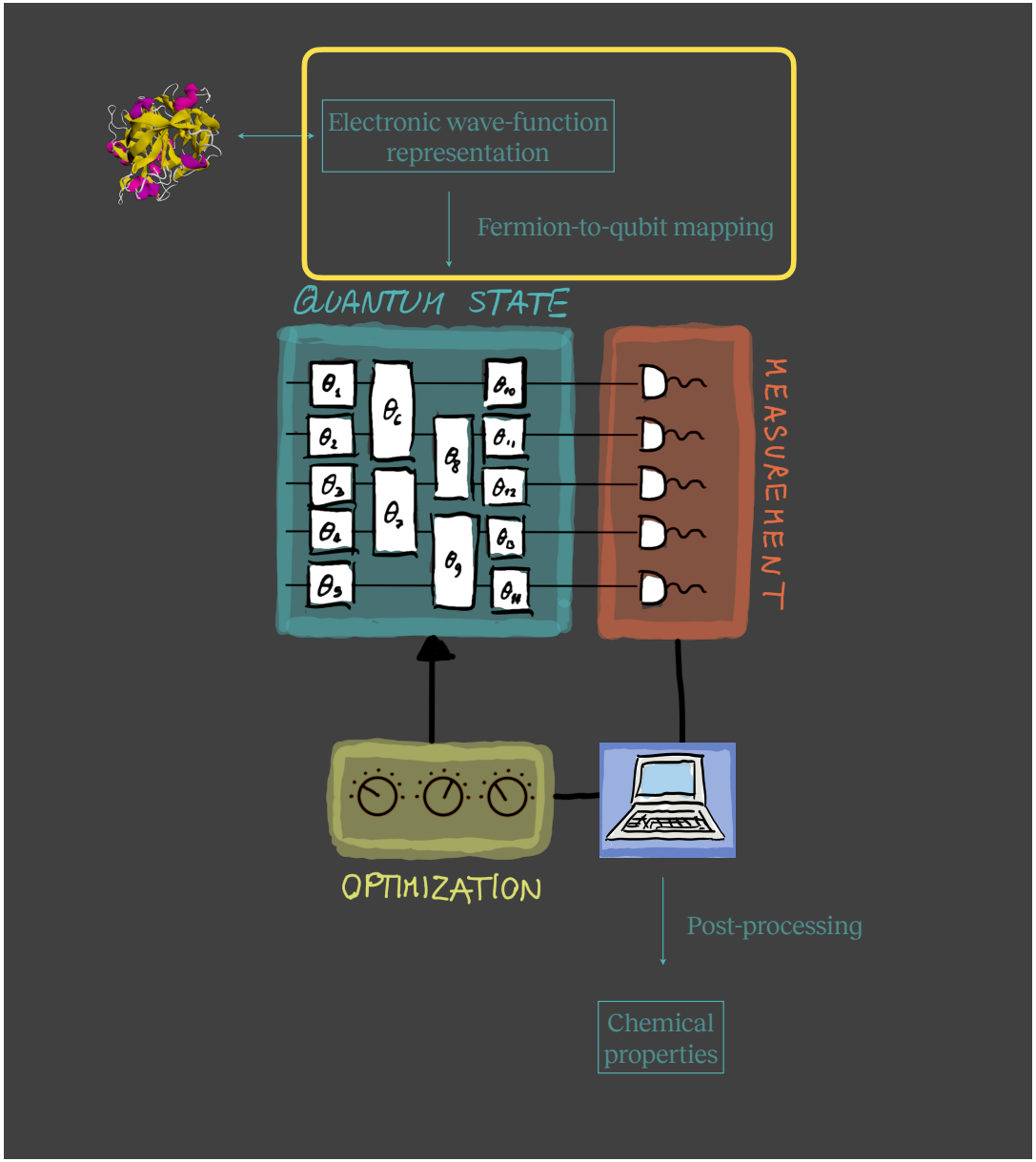

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Mapping “the problem” from fermion to qubit space

Mapping the problem from fermion to qubit space

General considerations

- *N*-electron wave function

$$|\Psi\rangle = \sum_{\zeta} c_{\zeta} \left|\Phi_{\zeta}\right\rangle \longrightarrow |\Psi\rangle$$

- Second-quantized Hamiltonian

$$\hat{H}_e = \sum_{p,q} h_{pq}\, \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} (pq\,|\,rs)\, \left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\right) \longrightarrow ?$$

- Fermions are indistinguishable particles, qubits are distinguishable
  —> we need to account for anti-commutation of fermionic operators in the map!

$$\{\hat{a}_p, \hat{a}_q\} = 0 \qquad \{\hat{a}_p^{\dagger}, \hat{a}_q^{\dagger}\} = 0 \qquad \{\hat{a}_p, \hat{a}_q^{\dagger}\} = \delta_{pq}$$

Mapping the problem from fermion to qubit space

N-electron wave function

$$|\Psi\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left| f_{M-1} \cdots f_1 f_0 \right\rangle$$

Exact for infinite *M*!

Mapping the problem from fermion to qubit space

N-electron wave function

$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\cdots f_1 f_0\right\rangle$$

Exact for infinite *M*!

- Trivial interaction of fermionic creation/annihilation operators on ON

$$\hat{a}_p^\dagger \left|f_{M-1}\cdots f_{p+1}\ 0\ f_{p-1}\cdots f_0\right\rangle = (-1)^{\sum_{s=0}^{p-1} f_s} \left|f_{M-1}\cdots f_{p+1}\ 1\ f_{p-1}\cdots f_0\right\rangle$$

$$\hat{a}_p^\dagger \left|f_{M-1}\cdots f_{p+1}\ 1\ f_{p-1}\cdots f_0\right\rangle = 0$$

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$$\hat{a}_p \left|f_{M-1}\cdots f_{p+1}\ 0\ f_{p-1}\cdots f_0\right\rangle = 0$$

Mapping the problem from fermion to qubit space

N-electron wave function

- Trivial translation of fermionic ON vector basis to qubit ON vector basis

$$\left|f_{M-1}\cdots f_1 f_0\right\rangle \longrightarrow \left|q_{M-1}\right\rangle\cdots\otimes\left|q_1\right\rangle\otimes\left|q_0\right\rangle \equiv \left|q_{M-1}\cdots q_1 q_0\right\rangle$$

- What about creation/annihilation operators for qubits?

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- We need a simple recipe for one-qubit creation and annihilation operators

$$\hat{Q}^{+}\left|1\right\rangle = 0 \qquad \hat{Q}^{+}\left|0\right\rangle = \left|1\right\rangle \qquad \hat{Q}^{-}\left|1\right\rangle = \left|0\right\rangle \qquad \hat{Q}^{-}\left|0\right\rangle = 0$$

with

$$\hat{Q}^{+} = \left|1\right\rangle\left\langle 0\right| \qquad \hat{Q}^{-} = \left|0\right\rangle\left\langle 1\right|$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

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$$\hat{Q}^{+}\left|1\right\rangle = 0 \qquad \hat{Q}^{+}\left|0\right\rangle = \left|1\right\rangle \qquad\qquad \hat{Q}^{-}\left|1\right\rangle = \left|0\right\rangle \qquad \hat{Q}^{-}\left|0\right\rangle = 0$$

with

$$\hat{Q}^{+} = \left|1\right\rangle\left\langle 0\right| \qquad\qquad \hat{Q}^{-} = \left|0\right\rangle\left\langle 1\right|$$

- They locally obey the fermionic anti-commutation relations

$$\left\{\hat{Q}^{+},\hat{Q}^{-}\right\} = \hat{Q}^{+}\hat{Q}^{-} + \hat{Q}^{-},\hat{Q}^{+} = \left|1\right\rangle\left\langle 1\right| + \left|0\right\rangle\left\langle 0\right| = I \qquad \left\{\hat{Q}^{+},\hat{Q}^{+}\right\} = \left\{\hat{Q}^{-},\hat{Q}^{-}\right\} = 0$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- We need a simple recipe for one-qubit creation and annihilation operators

$$\hat{Q}^+ |1\rangle = 0 \qquad \hat{Q}^+ |0\rangle = |1\rangle \qquad\qquad \hat{Q}^- |1\rangle = |0\rangle \qquad \hat{Q}^- |0\rangle = 0$$

with

$$\hat{Q}^+ = |1\rangle\langle 0| \qquad\qquad \hat{Q}^- = |0\rangle\langle 1|$$

- They locally obey the fermionic anti-commutation relations

$$\left\{\hat{Q}^+, \hat{Q}^-\right\} = \hat{Q}^+\hat{Q}^- + \hat{Q}^-, \hat{Q}^+ = |1\rangle\langle 1| + |0\rangle\langle 0| = I \qquad \left\{\hat{Q}^+, \hat{Q}^+\right\} = \left\{\hat{Q}^-, \hat{Q}^-\right\} = 0$$

BUT not for different qubits! (see exercise!)

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Better ansatz? Can we exploit the properties of Pauli matrices?

$$\hat{Q}^{+} = \left|1\right\rangle\left\langle 0\right| \equiv \frac{1}{2}\left(\sigma_x - i\sigma_y\right) = \frac{1}{2}\left(X - iY\right)$$

$$\hat{Q}^{-} = \left|0\right\rangle\left\langle 1\right| \equiv \frac{1}{2}\left(\sigma_x + i\sigma_y\right) = \frac{1}{2}\left(X + iY\right)$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why Pauli matrices and why are they a suitable choice?

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why are Pauli matrices a suitable choice?

Single-qubit quantum gates are 2×2 unitary matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Why are Pauli matrices a suitable choice?

Single-qubit quantum gates are 2×2 unitary matrices

—> Pauli matrices are 2×2 Hermitian (unitary) matrices

—> Pauli matrices are involutory: $\sigma_p^2 = \mathbf{1} \; \forall p \in [x, y, z]$

—> Pauli matrices anti-commute: $\left\{ \sigma_p, \sigma_q \right\} = 2I\delta_{pq} \qquad \forall p, q \in [x, y, z]$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

- Because of anti-commutation among Paulis, $\hat{Q}^{\pm}$ and σ_z anti-commute
- Represent action of fermionic operators $\hat{a}_p^{(\dagger)}$ for index p by acting with $\hat{Q}^{\pm}$ on qubit p and with σ_z on all qubits with index $q < p$ and with the identity $\mathbf{1}$ on the remaining qubits

Mapping the problem from fermion to qubit space

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$$\hat{a}_p^{\dagger} \equiv \mathbf{1}^{\otimes M-p-1} \otimes \hat{Q}_p^{+} \otimes \left[\sigma_z^{\otimes p}\right] = \frac{1}{2}\left(X_p \otimes \left[\sigma_z^{\otimes p}\right] - iY_p \otimes \left[\sigma_z^{\otimes p}\right]\right)$$

Mapping the problem from fermion to qubit space

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- Because of anti-commutation among Paulis, $\hat{Q}^{\pm}$ and σ_z anti-commute
- Represent action of fermionic operators $\hat{a}_p^{(\dagger)}$ for index p by acting with $\hat{Q}^{\pm}$ on qubit p and with σ_z on all qubits with index $q < p$ and with the identity $\mathbf{1}$ on the remaining qubits

$$\hat{a}_p^{\dagger} \equiv \mathbf{1}^{\otimes M-p-1} \otimes \hat{Q}_p^{+} \otimes \left[\sigma_z^{\otimes p}\right] = \frac{1}{2}\left(X_p \otimes \left[\sigma_z^{\otimes p}\right] - iY_p \otimes \left[\sigma_z^{\otimes p}\right]\right)$$

$$\hat{a}_p \equiv \mathbf{1}^{\otimes M-p-1} \otimes \hat{Q}_p^{-} \otimes \left[\sigma_z^{\otimes p}\right] = \frac{1}{2}\left(X_p \otimes \left[\sigma_z^{\otimes p}\right] + iY_p \otimes \left[\sigma_z^{\otimes p}\right]\right)$$

Mapping the problem from fermion to qubit space

Jordan-Wigner mapping

Major drawback of Jordan-Wigner mapping: **k-locality!**

k-locality: each term in the Hamiltonian acts non-trivially on at most k qubits

—> non-locality of “parity term $\left[\sigma_z^{\otimes p}\right]$” that appears in $\hat{a}_p^{(\dagger)}$ introduces a number of extra qubit operations which scale as $\mathcal{O}(M)$!

Example: how does it work for mapping $\hat{a}_6^\dagger$ for an $N = 10$ quit system?

Mapping the problem from fermion to qubit space

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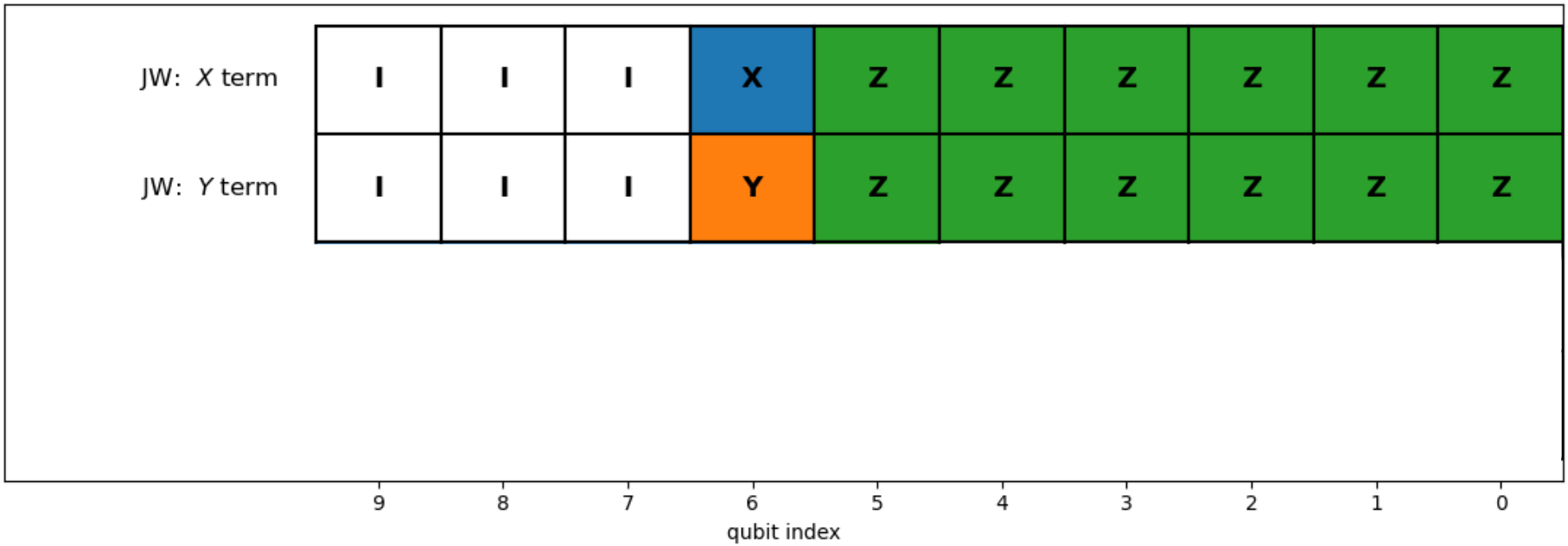

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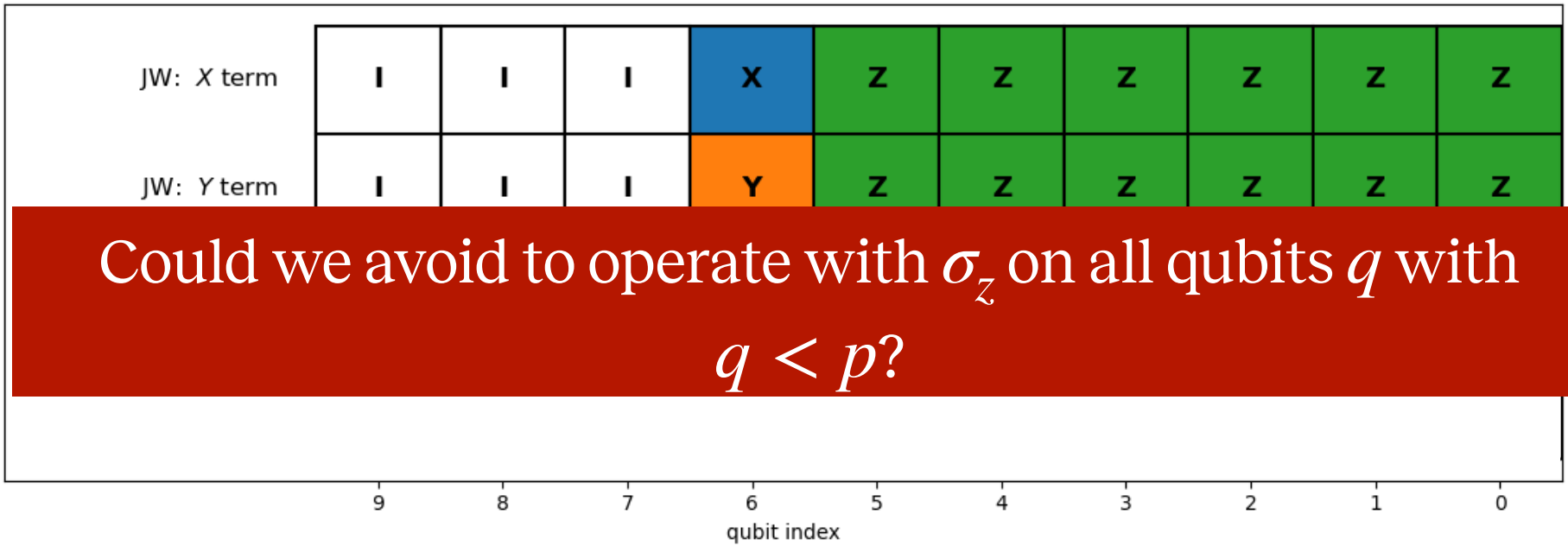

Could we avoid to operate with σ_z on all qubits q with $q < p$?

Mapping the problem from fermion to qubit space

Parity mapping

- Alternative idea to occupation number basis —> parity basis:

  Use qubit p to store the parity $\mathscr{P}$ of all occupied orbitals up to p

$$\mathscr{P}_p = \mod\left(\sum_{s=0}^{p} f_s\ ,\ 2\right)$$

- Parity of set of orbitals with $q < p$ determines whether $\hat{a}_p^{(\dagger)}$ introduces a phase of -1

  —> it suffices to only have σ_z acting on qubit $p-1$

Mapping the problem from fermion to qubit space

Parity mapping

- BUT: we cannot represent the creation or annihilation of a particle in qubit q_p with $\hat{Q}_p^{(\pm)}$ since q_p stores the parity of all orbitals with index $q \leq p$
- Representing for example $\hat{a}_p^\dagger$ in terms of $\hat{Q}_p^\pm$ depends on qubit $(p-1)$:
  - qubit $(p-1)$ is in state $|0\rangle$: act on qubit p with $\hat{Q}_p^+$
  - qubit $(p-1)$ is in state $|1\rangle$: act on qubit p with $\hat{Q}_p^-$

Mapping the problem from fermion to qubit space

Parity mapping

- Operator equivalent to $\hat{Q}^{\pm}$ in parity basis is $\hat{P}^{\pm}$ and a **two-qubit** operator!

$$\hat{P}_p^{\pm} \equiv \hat{Q}_p^{\pm} \otimes \left|0\right\rangle\left\langle 0\right|_{p-1} - \hat{Q}_p^{\mp} \otimes \left|1\right\rangle\left\langle 1\right|_{p-1}$$

$$= \frac{1}{2}\left(X_p \otimes Z_{p-1} \mp iY_p\right)$$

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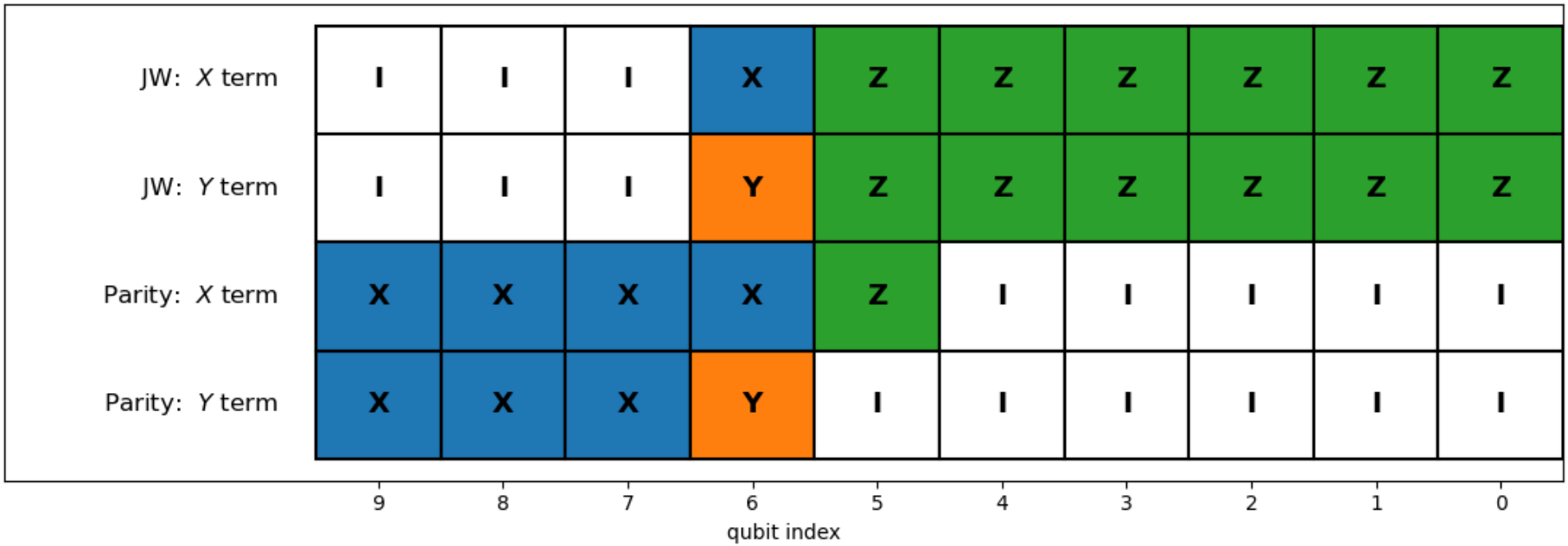

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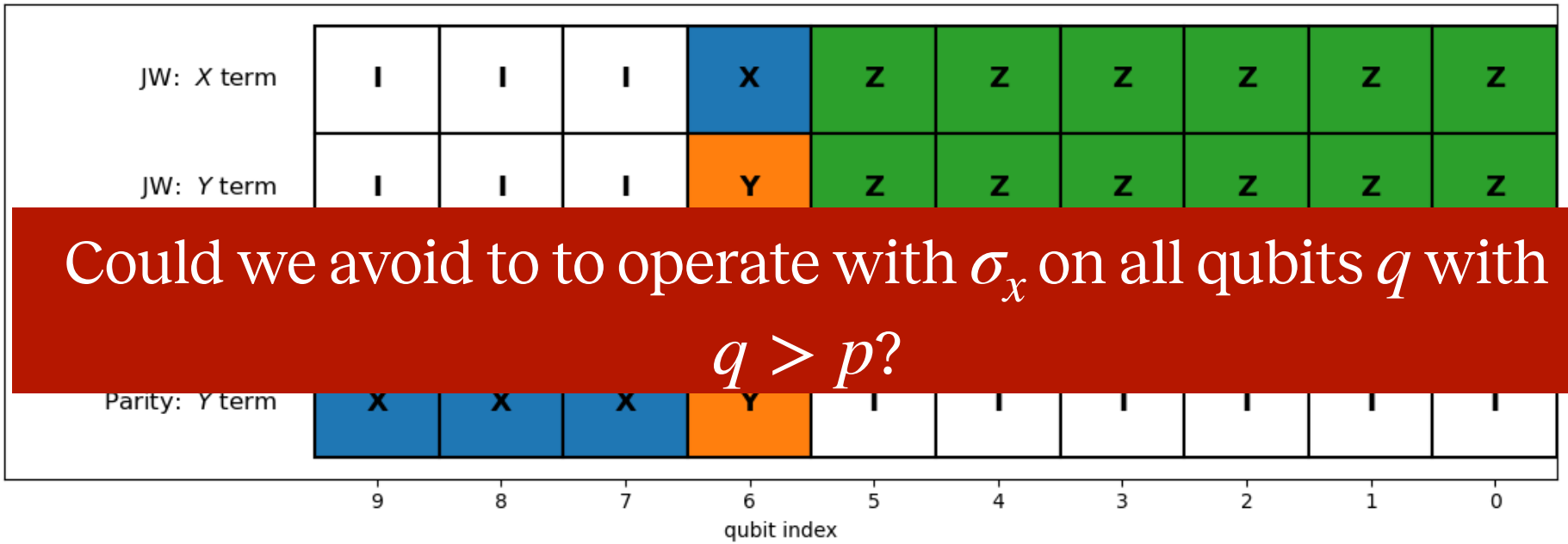

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Mapping the problem from fermion to qubit space

Notes on other mappings

- Major drawback of parity and J-W mapping: **k-locality which is also referred to as Pauli weight**

- Other more elaborate mappings exist which scale as $\mathcal{O}(\log_2 M)$ [Bravyi-Kitaev —> “combines ideas” of J-W and parity mappings] or even up to $\mathcal{O}(\log_3 M)$

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- Customised (tree-based) mappings tailored to QC hardware layout are also possible!

Bonsai Algorithm: Grow Your Own Fermion-to-Qubit Mappings

Aaron Miller[1,2,*], Zoltán Zimborás[1,3], Stefan Knecht[1,4], Sabrina Maniscalco[1], and Guillermo García-Pérez[1]

Show more

PRX Quantum **4**, 030314 – **Published 1 August, 2023**

Mapping the problem from fermion to qubit space

Notes on other mappings

- Common outcome of mappings: $\hat{H}_e$ is expressed as a sum of Pauli strings P_k

$$\hat{H}_e = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q \quad \longrightarrow \quad \hat{H}_e = \sum_k c_k P_k$$

Calculating the energy
on a quantum computer

- The Hamiltonian is given as a linear combination of Pauli strings

$\hat{H}_e = \sum_k c_k P_k$ ← Each term is a product of local operators $P_k = \otimes_{s=0}^{M-1} \sigma_{k_s,(s)}$

- We can calculate expectation values on the quantum computer

$$\left|\Psi\right\rangle = \sum_{\mathbf{f}} c_{\mathbf{f}} \left|f_{M-1}\cdots f_1 f_0\right\rangle \longrightarrow \left\langle\Psi\right| \hat{H}_e \left|\Psi\right\rangle = \sum_k c_k \left\langle\Psi\right| P_k \left|\Psi\right\rangle$$

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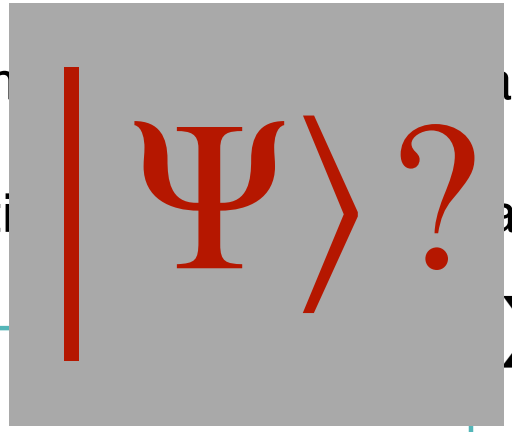

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Quantum algorithms for quantum chemistry: where the quantum computer sits

Variational Quantum Algorithms

"Wave function optimization done on the QPU"

- Need circuit that produces accurate energies
- Need to learn accurate noise model
- Exponential measurement overhead
- **risk**: noise, optimizer pathologies, depth limits
+ Provides a variational energy measured on the quantum computer
+ Tremendous research available

Fault-tolerant approaches

"Implement accurate quantum dynamics"

+ Systematic precision
- High resource costs
- Good initial wave function required (overlap!)
- **risk and cost drivers**: logical qubits, T gates, state prep

Quantum Boosted Classical Methods

"Use the QPU only where it adds information"

+ Exploit resource that is classically hard to produce
+ Highly accurate circuit is not required
+ No no-go theorems
- **risk**: sampling quality and bias control

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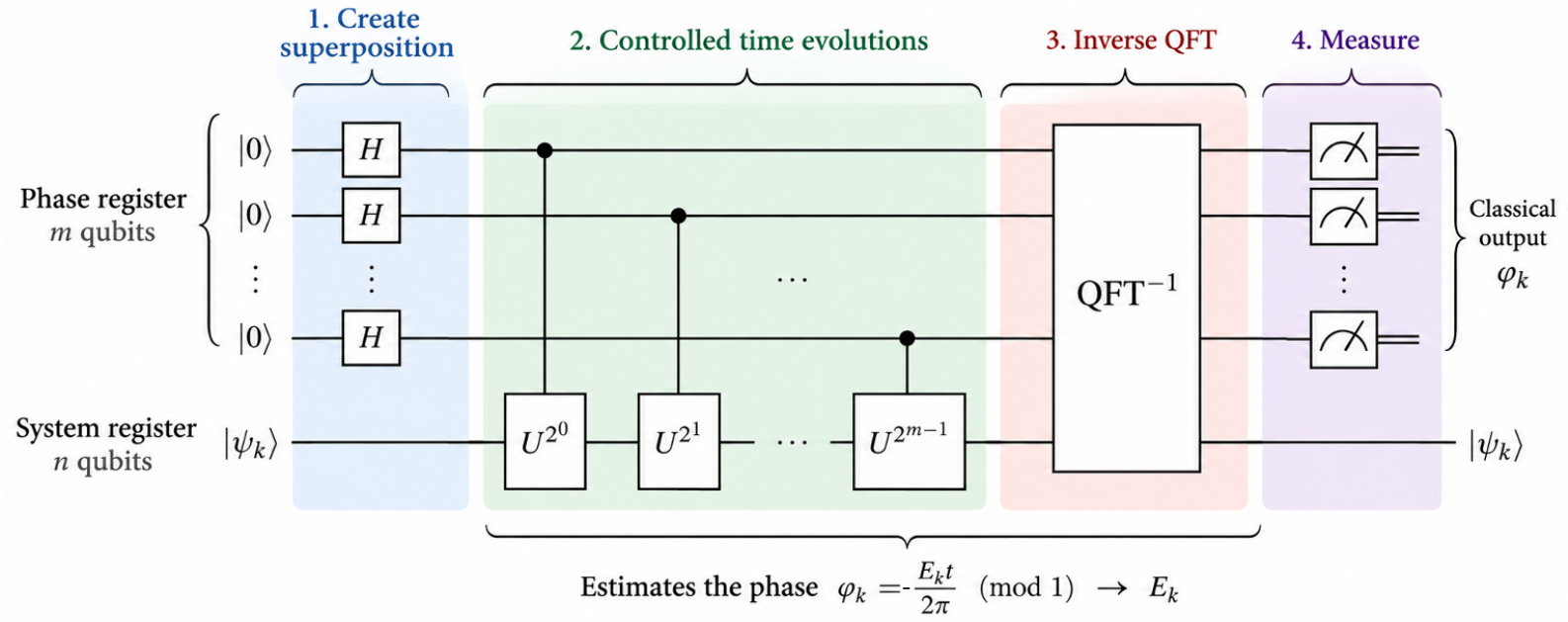
FT approaches: Quantum Phase Estimation in a Nutshell

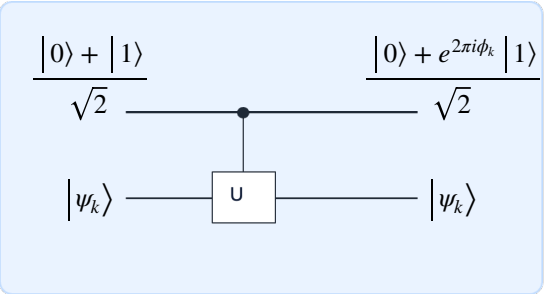
QPE converts the phase accumulated under time evolution into a digital estimate of an eigenvalue



- Requires system and register qubits
- Controlled unitaries and and (inverse) quantum fourier transformation (QFT) are costly operations
- reasonable initial state $|\psi_k\rangle$ required

FT approaches: Quantum Phase Estimation in a Nutshell

$$U\left|\psi_k\right\rangle = e^{2\pi i\phi_k}\left|\psi_k\right\rangle$$



Note that the eigenvector $\left|\psi_k\right\rangle$ does not change; the eigenvalue phase becomes a relative phase on the phase register.

-> **Phase kickback**

Suitable choice in chemistry: $U(t) = e^{-i\hat{H}t}$

$\left|\psi_k\right\rangle$ is an eigenstate

$$U^{2_j}\left|\psi_k\right\rangle = e^{2\pi i 2^j\phi_k}\left|\psi_k\right\rangle$$

The eigenstate stays unchanged; increasing powers of U amplify its unknown eigenphase so that QPE can resolve its binary digits

$\left|\psi\right\rangle$ is not an eigenstate but a superposition

$$\left|\psi\right\rangle = \sum_k c_k\left|\psi_k\right\rangle$$

QPE entangles phase and system registers; the probability of measuring ϕ_k occurs with probability $\approx \left|c_k\right|^2$.

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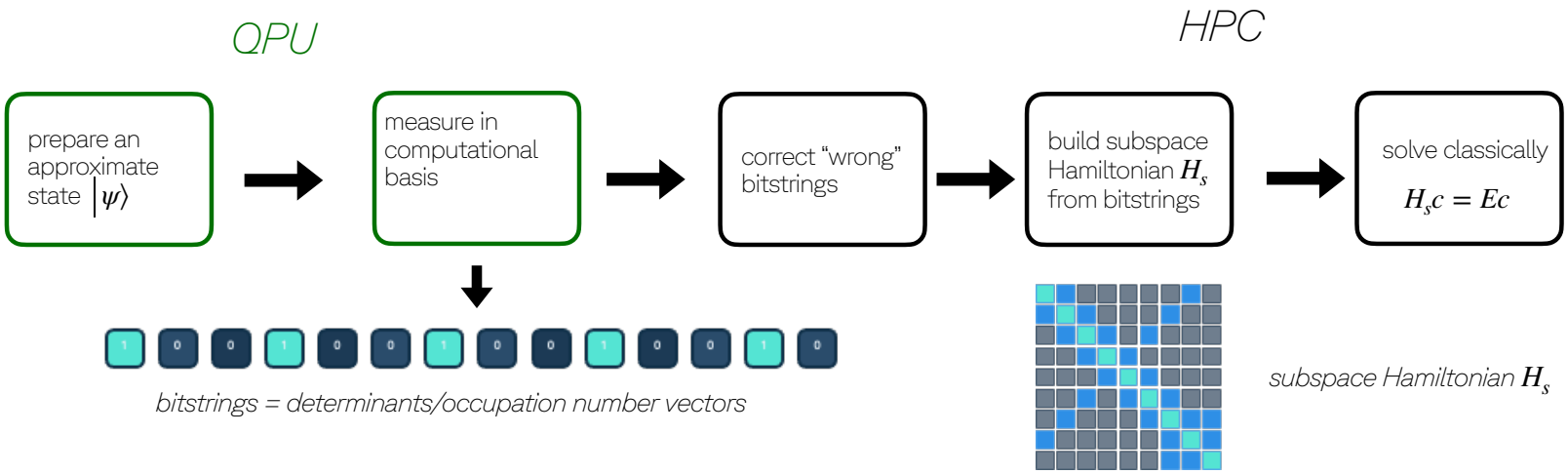
Quantum boosted approaches: Sample-based quantum diagonalization / quantum-selected CI as a prominent example

Use the QPU as a configuration generator while solving the eigenvalue problem in a compact classical subspace



core idea: bitstring samples reveal where the wavefunction has weight; selected CI recovers amplitudes, energies, and properties in that subspace.

Quantum boosted approaches: Sample-based quantum diagonalization / quantum-selected CI as a prominent example

Role of QPU

proposes a determinant list S by sampling $|\psi^2|$

Role of HPC

recover / batch and possibly expand the selected space S

diagonalize in S to obtain eigenvalues and eigenvectors $H_S C = EC$

Why could it be potentially useful?

✓ variational energies

✓ no noisy optimizer loop

✓ fewer measured observables

✓ system-tailored selected spaces

✓ cost set by |S|, not full FCI

Quantum boosted approaches: Sample-based quantum diagonalization / quantum-selected CI as a prominent example

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And why could it be potentially useless?

x Repeated samples: problem in discovering new bitstrings

x Ansatz dependence: S may miss energetically important bitstrings

x S may be less compact than spaces S' from classical SCI

x classical bottleneck: a large $|S|$ still means expensive Hamiltonian build and diagonalization

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SQD may be attractive when quantum samples contain information that classical selection cannot easily obtain. It remains elusive whether, for chemically accurate results, the sample cost + post-processing can (ever) beat mature classical selected-CI methods.

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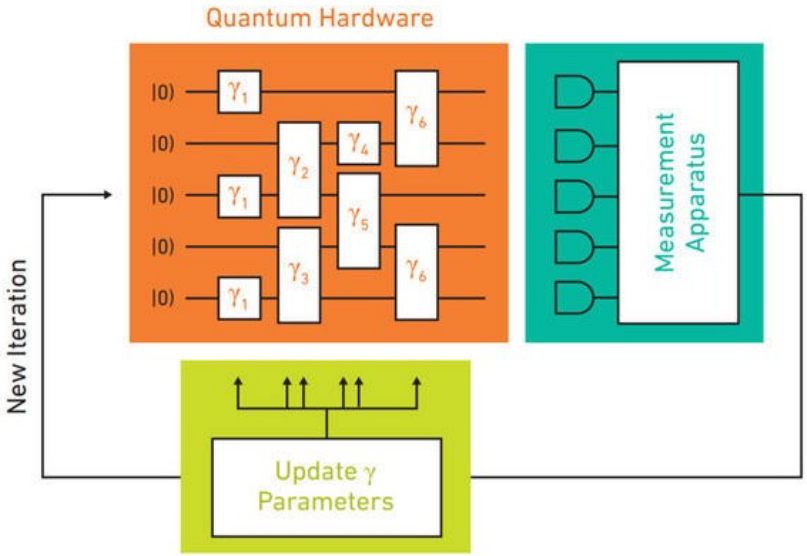
Variational optimisation with the Variational Quantum Eigensolver



Peruzzo *et al.*, *A variational eigenvalue solver on a photonic quantum processor*, Nature Communications **5**, 4213 (2014)

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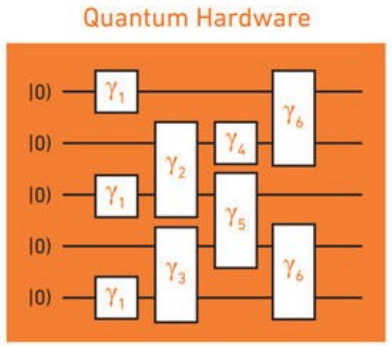
Solving the problem

The Variational Quantum Eigensolver

- Prepare *some* quantum state using a so-called variational form (ansatz)



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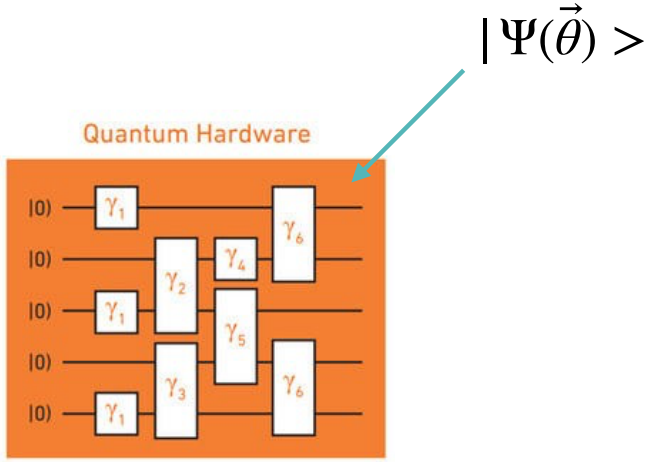

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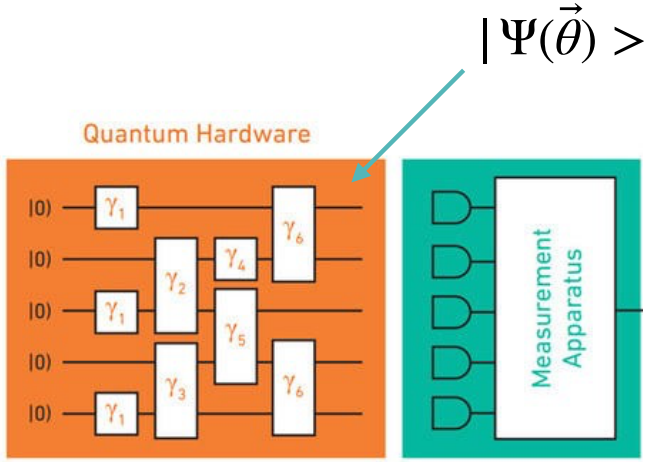
$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \right| \hat{H}_e \left| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$



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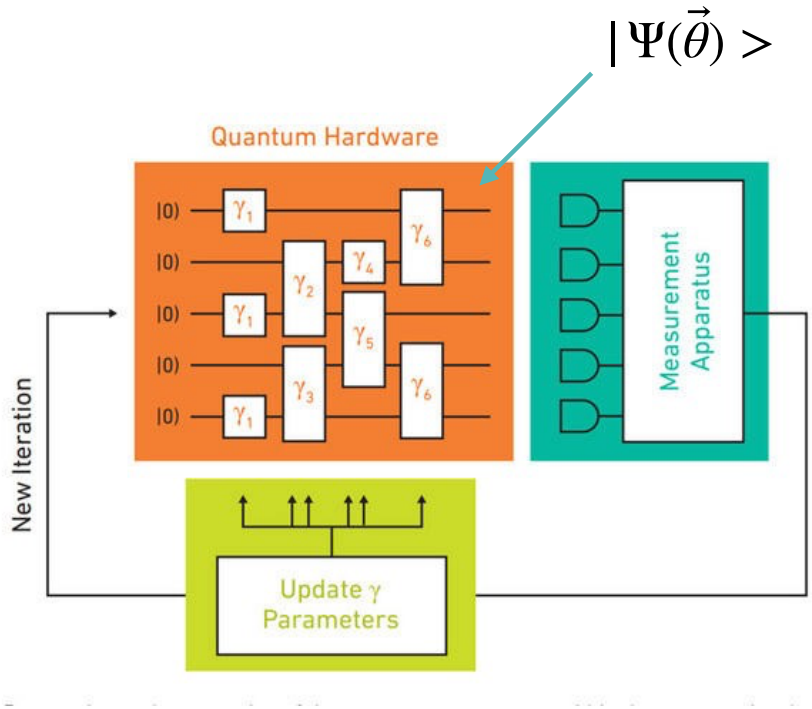
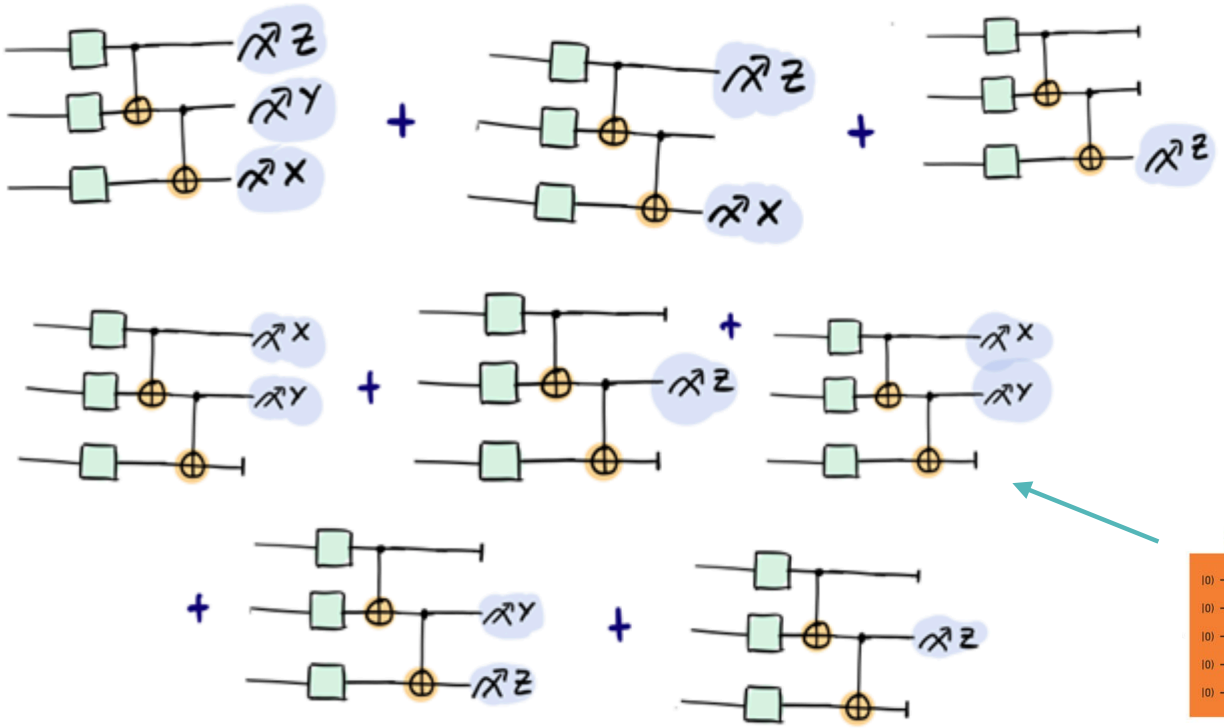
- Find the ground state variationally: minimising over the parameters $\{\vec{\theta}\}$



Measuring the energy
in a VQE simulation



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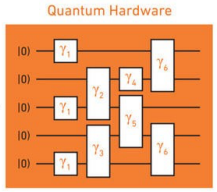
Every Pauli string evaluated independently through repeated measurements



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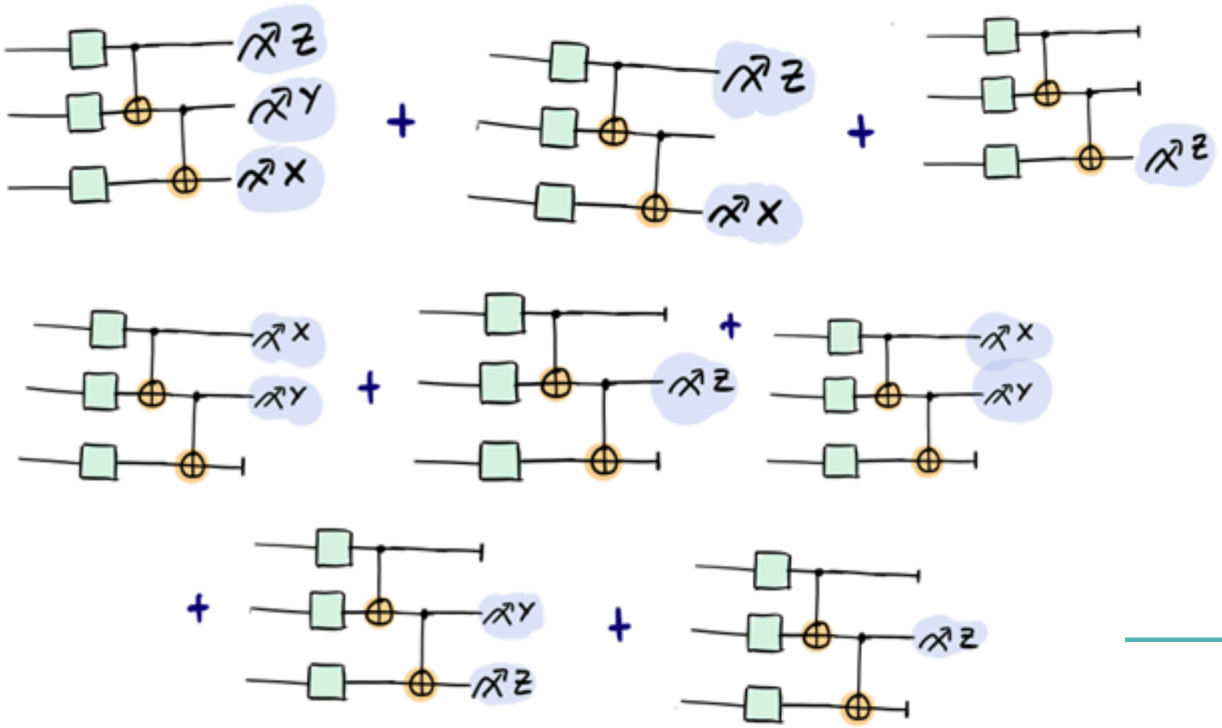

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Every Pauli string evaluated independently through repeated measurements

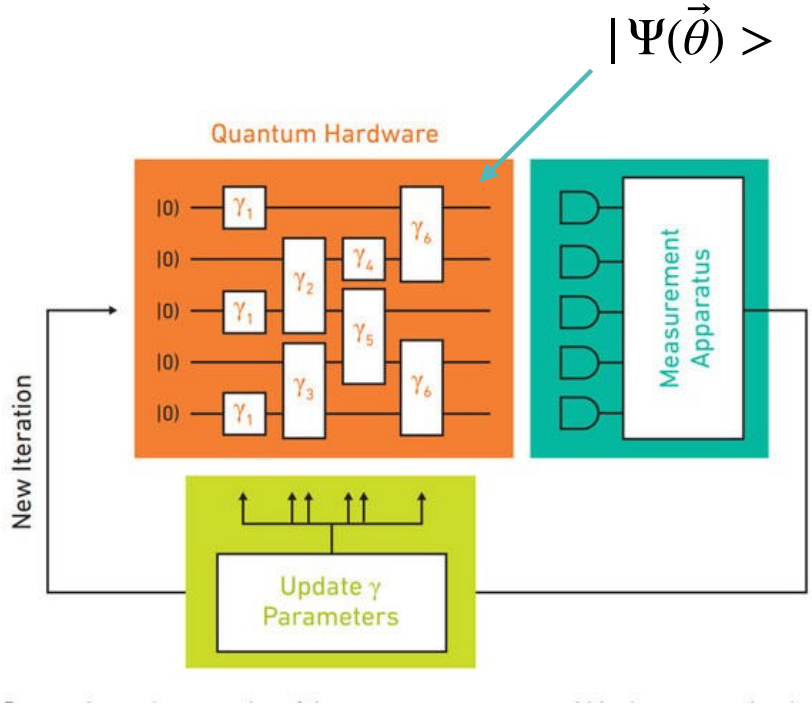
Repeat each many times to estimate the mean $\langle \Psi | P_k | \Psi \rangle$

Solving the problem?

The Variational Quantum Eigensolver

Sounds good, BUT

- How do we know the ansatz contains the ground state?
- How do we find the corresponding parameters?
- How efficient is the whole approach?
- What about the noise?



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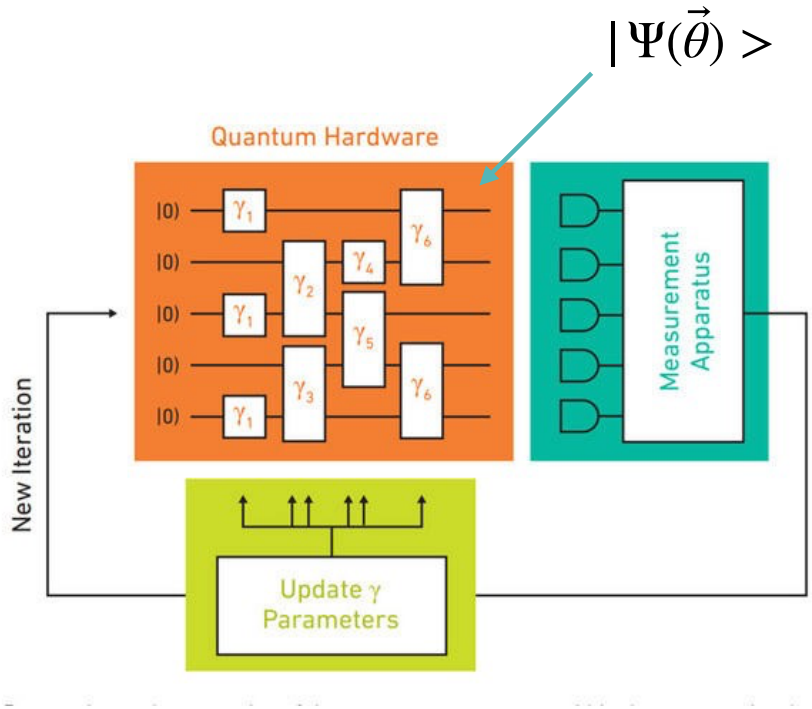
- There are mainly two broad strategies in circuit ansatz design
  - physically motivated ansätze
  - hardware heuristic ansätze
    —> parametrized circuits comprising single-qubit rotations and entangling blocks chosen to take advantage of specific quantum hardware capabilities



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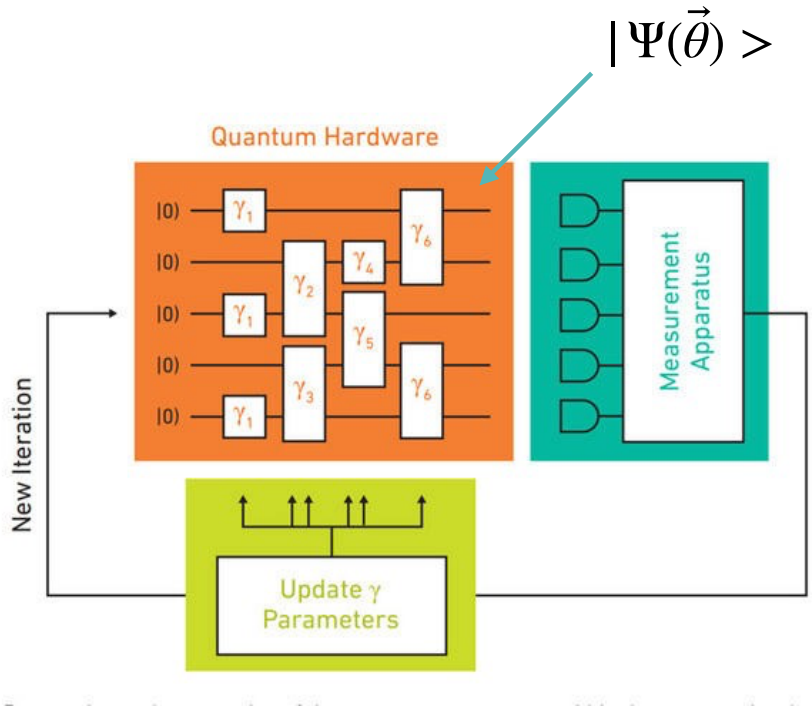

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The Variational Quantum Eigensolver
UCCSD ansatz

- UCCSD ansatz has the form

$$\left|\Psi_{\text{UCCSD}}\right\rangle = e^{\hat{T}_1+\hat{T}_2}\left|\Psi_{\text{ref}}\right\rangle \quad \text{with}$$

$$\hat{T}_1 = \sum_{i,a} \hat{\tau}_i^a = \sum_{i,a} \tau_i^a (a_a^\dagger a_i - a_i^\dagger a_a)$$

$$\hat{T}_2 = \sum_{i,j,a,b} \hat{\tau}_{ij}^{ab} = \sum_{i,j,a,b} \tau_{ij}^{ab} (a_a^\dagger a_b^\dagger a_i a_j - a_j^\dagger a_i^\dagger a_b a_a)$$

- Commonly approximation: Trotterize unitary to first order

$$\left|\Psi_{\text{tUCCSD}}\right\rangle = \prod_{c\in\{ia\}} e^{\hat{\tau}_c} \prod_{d\in\{ijab\}} e^{\hat{\tau}_d} \left|\Psi_{\text{ref}}\right\rangle$$

—> Low-order trotterized form may fail to reach chemical accuracy
—> Large number of exponential factors prohibits preparation on quantum processors

The Variational Quantum Eigensolver

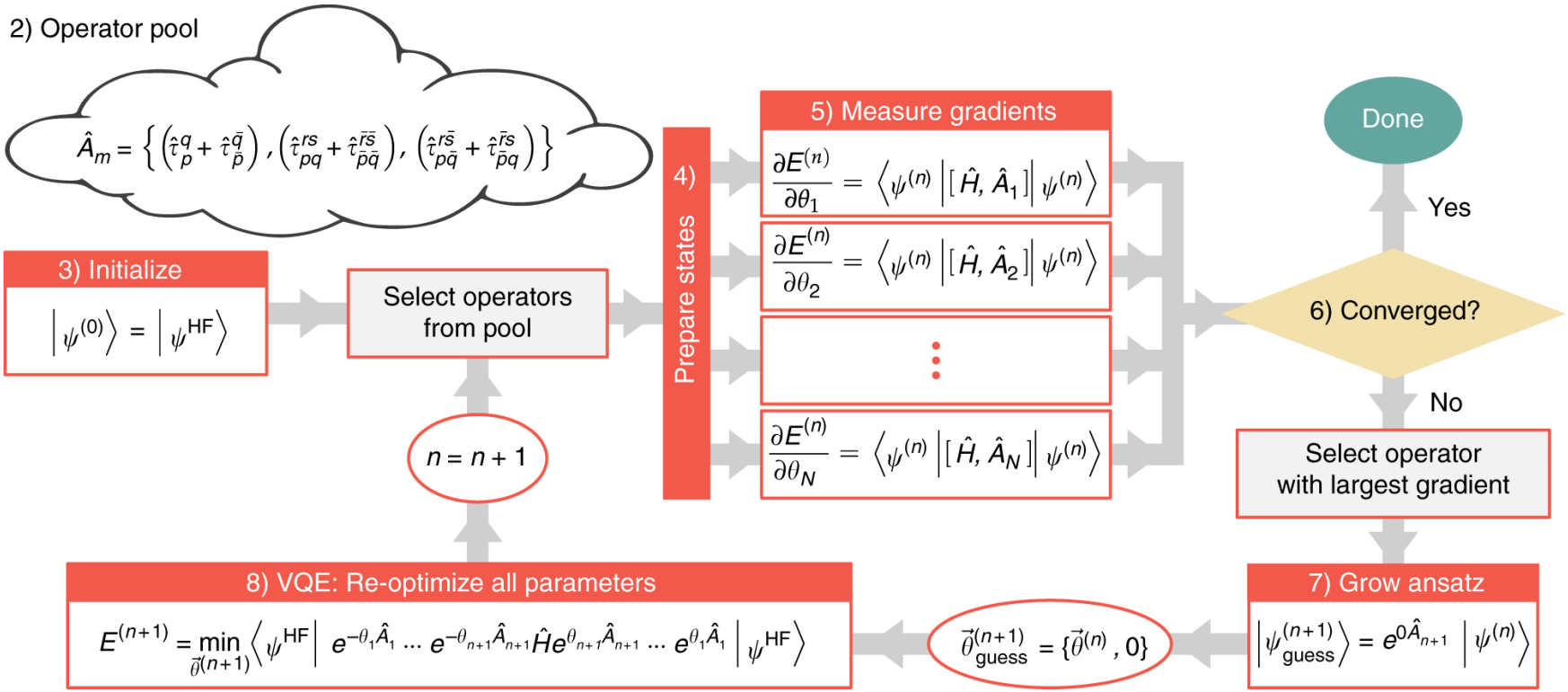
ADAPT-VQE ansatz

- The ADAPT-VQE algorithm grows ansätze by appending one unitary at a time to a trial state
- Requires to
  - a priori define an operator pool $\mathscr{P} = \{P_i\}$, a collection of antihermitian generators —> $\hat{\tau}_i^a$ and $\hat{\tau}_{ij}^{ab}$ in UCCSD
  - choose a reference state calculate (HF or anything reasonable)

$$\left.\frac{\partial E}{\partial \theta_i}\right|_{\theta_i=0} = \left[\frac{\partial}{\partial \theta_i}\left\langle \Psi^{(k)} \right| e^{-\theta_i P_i} H e^{\theta_i P_i} \left| \Psi^{(k)} \right\rangle\right]\Bigg|_{\theta_i=0} = \left\langle \Psi^{(k)} \right| [H, P_i] \left| \Psi^{(k)} \right\rangle$$

- The operator with the largest gradient norm is appended to the ansatz

Choosing an ansatz - ADAPT-VQE



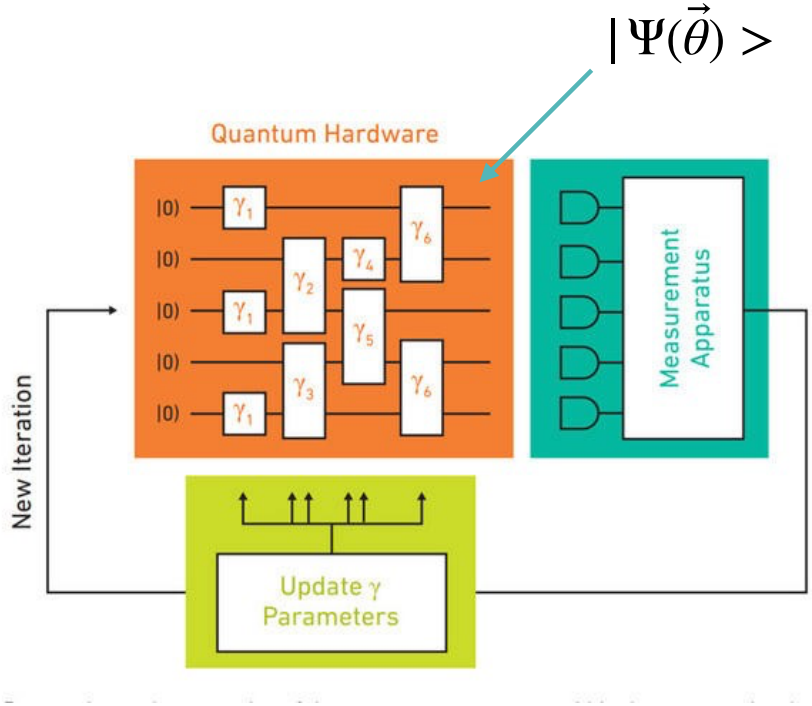
Nat. Comm., 10, 3007 (2019)

Solving the problem?

The Variational Quantum Eigensolver

Sounds good, BUT

- How do we know the ansatz contains the ground state?
- How do we find the corresponding parameters?
- How efficient is the whole approach?
- What about the noise?



$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \middle| \hat{H}_e \middle| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

Solving the problem?

The Variational Quantum Eigensolver

Identifying challenges towards practical quantum advantage through resource estimation: the measurement roadblock in the variational quantum eigensolver

Jérôme F. Gonthier,[1] Maxwell D. Radin,[1] Corneliu Buda,[2]
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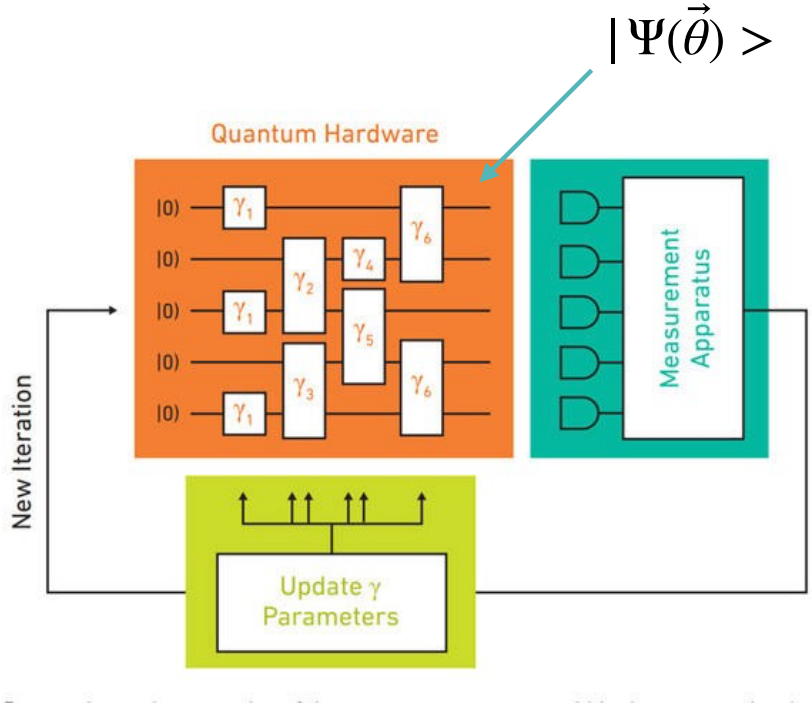
Molecule	H_2O	CO_2	CH_4	CH_4O	C_2H_6	C_2H_4	C_2H_2	C_2H_6O	C_3H_8	C_3H_6	C_3H_4
N_{el}	8	16	8	14	14	12	10	20	20	18	16
N_q	104	208	104	182	182	156	130	260	260	234	208
$K \cdot 10^{-3}$	1.9	16	1.6	8.4	8.5	6.6	3.1	24	16	23	18
$M \cdot 10^{-9}$	3.9	32	3.2	17	17	13	6.2	48	31	46	36
t (days)	2.3	39	1.9	18	18	12	4.6	71	47	62	44

TABLE IV. Estimated runtimes t in days for a single energy evaluation using the number of measurements M from extrapolated

arXiv: 2012.04001



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Solving the problem?

The Variational Quantum Eigensolver

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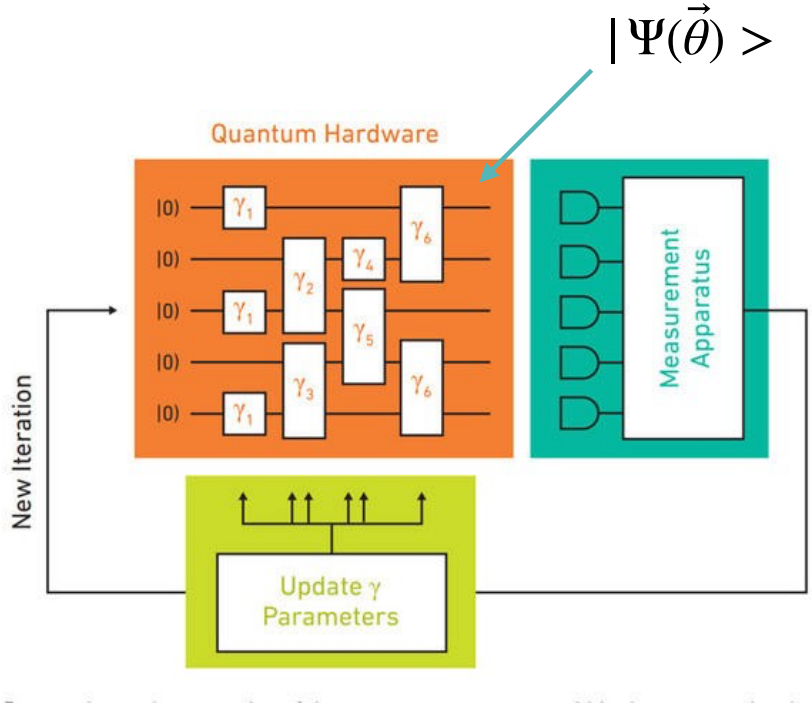


$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \right| \hat{H}_e \left| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

Efficient measurement strategies are required!

Noise mitigation is crucial!

Molecular properties / Dynamical correlation

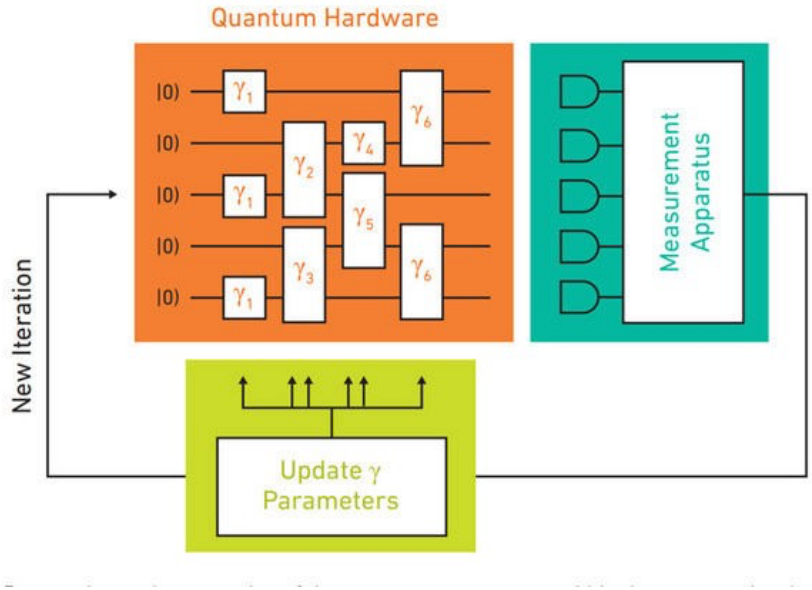
The Variational Quantum Eigensolver

- Expectation values of one-electron $\hat{O}_1$ and two-electron $\hat{O}_2$ operators can be straightforward obtained from optimal VQE

$$\left\langle \hat{O}_1 \right\rangle = \sum_{pq} o_{pq} \left\langle \hat{a}_p^\dagger \hat{a}_q \right\rangle$$

$$\left\langle \hat{O}_2 \right\rangle = \sum_{pqrs} o_{pqrs} \left\langle \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \right\rangle$$

- Higher-order RDMs …
  —> CASPT2/NEVPT2, response theory, …
- *quantum* equation-of-motion …
- …



$$\langle E \rangle = \left\langle \Psi(\vec{\theta}) \middle| \hat{H}_e \middle| \Psi(\vec{\theta}) \right\rangle \geq E_{\text{ground}}$$

CONCLUSION

Quantum computers without algorithms are useless machines

With proper algorithms we can make quantum computers work

Which algorithms will make “the race” remains unclear, but there is no substantial reason to await the FT are of quantum computing

We barely scratched the surface of quantum algorithms for quantum chemistry...