Simulating molecular properties on a quantum computer

Bruno Senjean

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Supervisors: Tom O'Brien (Leiden), Luuk Visscher (Amsterdam)

Exponential wall problem in Quantum Chemistry

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Electronic Schrödinger Equation:

$$\hat{H}|\Psi_j\rangle = E_j|\Psi_j\rangle$$

Second Quantized Hamiltonian (finite basis of M orbitals):

$$\hat{H} = \sum_{pq}^{M} h_{pq}\hat{a}_p^\dagger \hat{a}_q + \frac{1}{2}\sum_{pqrs}^{M}(pq|rs)\hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q$$

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Fock space with spanned by 2^M many-particle states

$$|\Psi\rangle = \sum_{i}^{2^M} c_i|\Phi_i\rangle$$

Hamiltonian matrix of size $2^M \times 2^M$

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Alternatives:

- **Truncate the number of many-particle states (CISD, CCSD(T), CAS, SCI, ...)**
- **Quantum Monte Carlo**
- **Reduced quantities (density, 1RDM, Green's function)**
- **Embedding**

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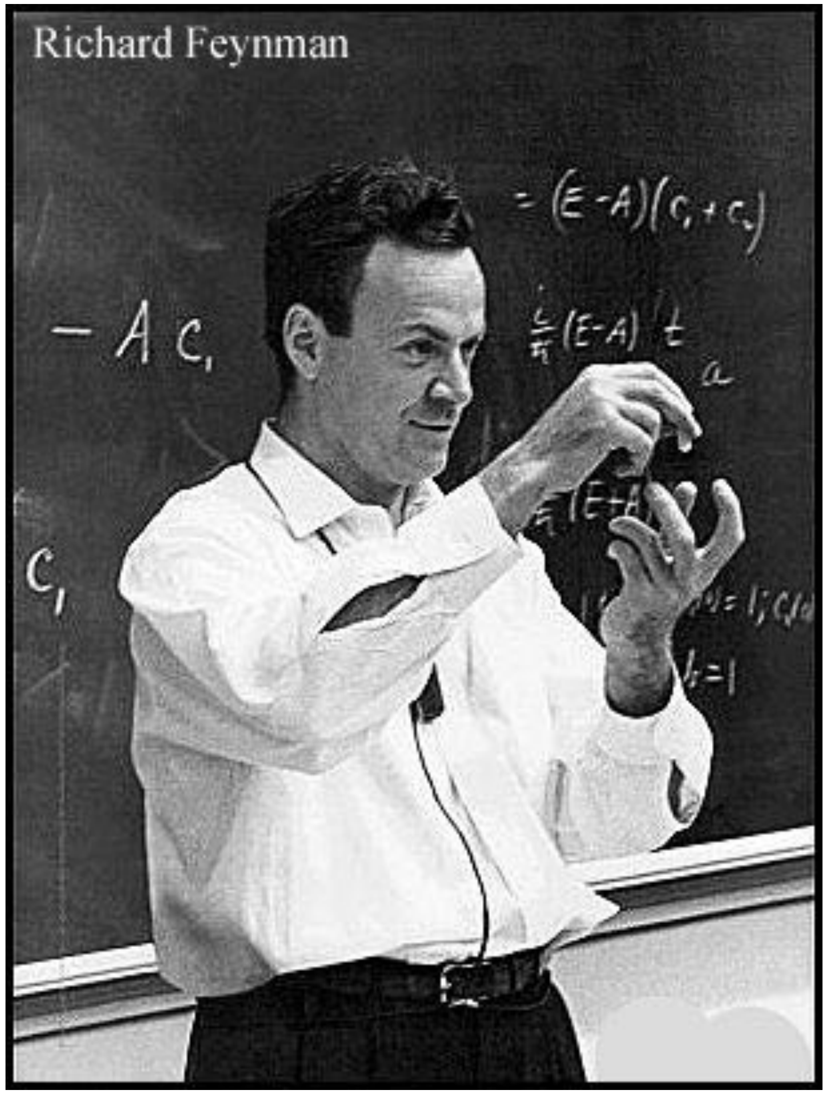
- **Embe…**

But can we do FCI in polynomial time ?

Quantum Computers: Origins



Richard Feynman 1981:

"Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy"

Arute *et al.*, Nature (2019)

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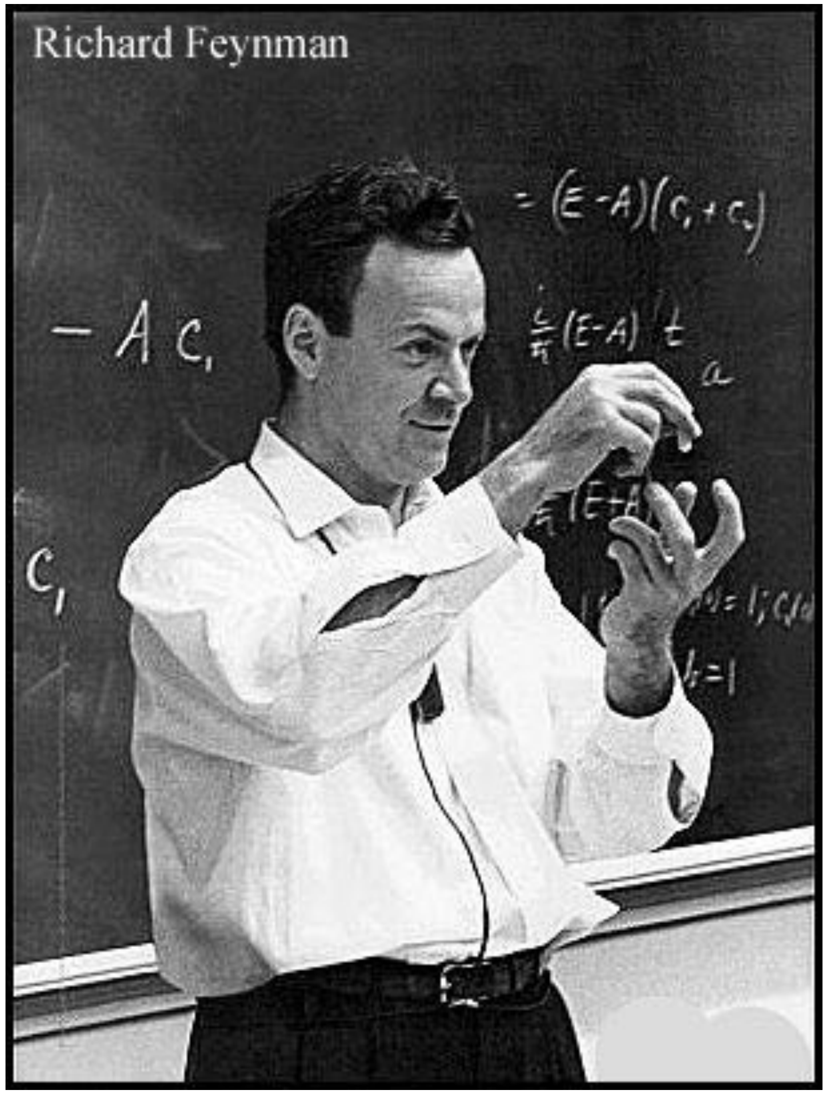

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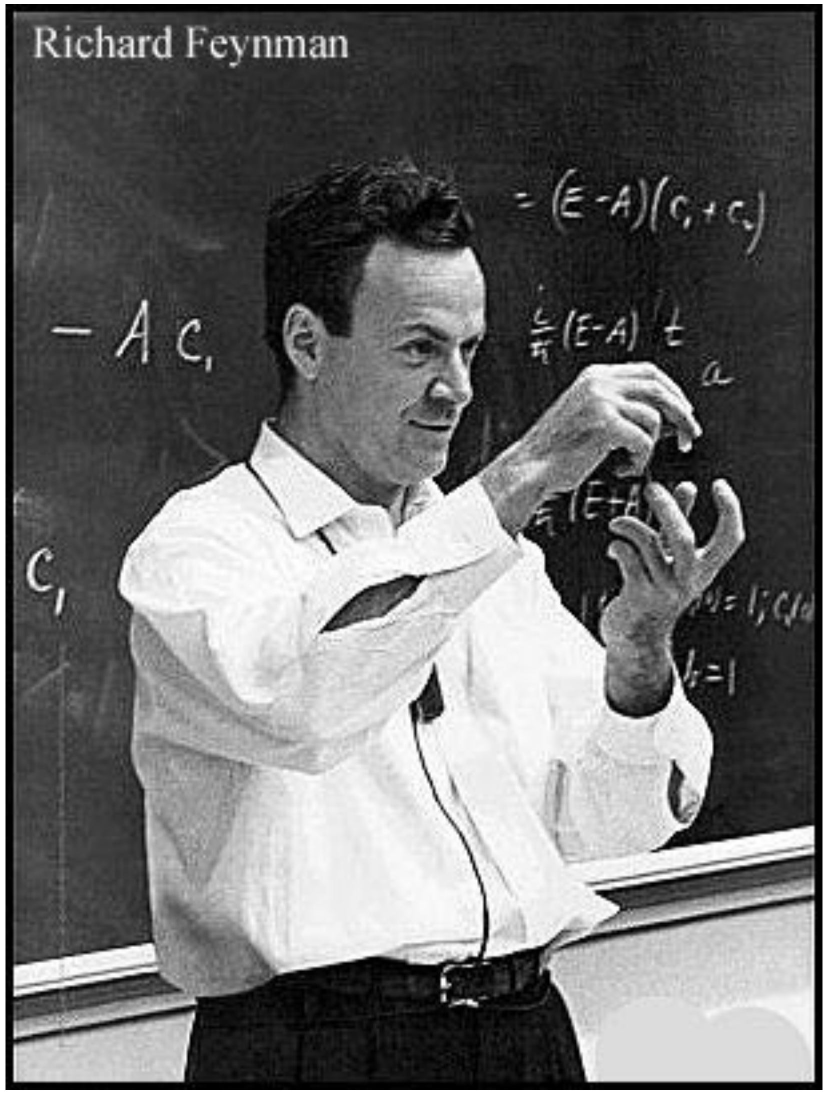
50th birthday of the Laboratoire de Chimie Quantique de Strasbourg:

Alain Dedieu and Jean-Marie Lehn gave historical conferences about the state of the art of quantum chemistry at the time...
using PUNCH CARDS !

Arute *et al.*, Nature (2019)

Quantum Computers: Origins



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October 23, 2019: Google claims quantum advantage on 53-qubit device.

For a particular problem:
Sampling the output distribution of random quantum circuits

Arute *et al.*, Nature (2019)

Quantum Computers: Exponential speed-up

Replace classical bit (either 0 or 1) with qubit (superposition of $|0\rangle$ and $|1\rangle$)

M-qubit state is a superposition of 2^M states

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Example with 3 qubits:

$$|\Psi\rangle = \frac{1}{\sqrt{8}}\left(|000\rangle + |001\rangle + |010\rangle + |011\rangle + |100\rangle + |101\rangle + |110\rangle + |111\rangle\right)$$

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Example with 5 qubits:

$$|\Psi\rangle = \frac{1}{\sqrt{32}}\Big(|00000\rangle + |00001\rangle + |00010\rangle + |00011\rangle + |00100\rangle + |00101\rangle + |00110\rangle + |00111\rangle + |01000\rangle + |01001\rangle + |01010\rangle + |01011\rangle + |01100\rangle + |01101\rangle + |01110\rangle + |01111\rangle + |10000\rangle + |10001\rangle + |10010\rangle + |10011\rangle + |10100\rangle + |10101\rangle + |10110\rangle + |10111\rangle + |11000\rangle + |11001\rangle + |11010\rangle + |11011\rangle + |11100\rangle + |11101\rangle + |11110\rangle + |11111\rangle\Big)$$

Quantum Corollary to Moore's law:
double power for every additional qubit

Quantum Circuits

Example: 3-qubit state

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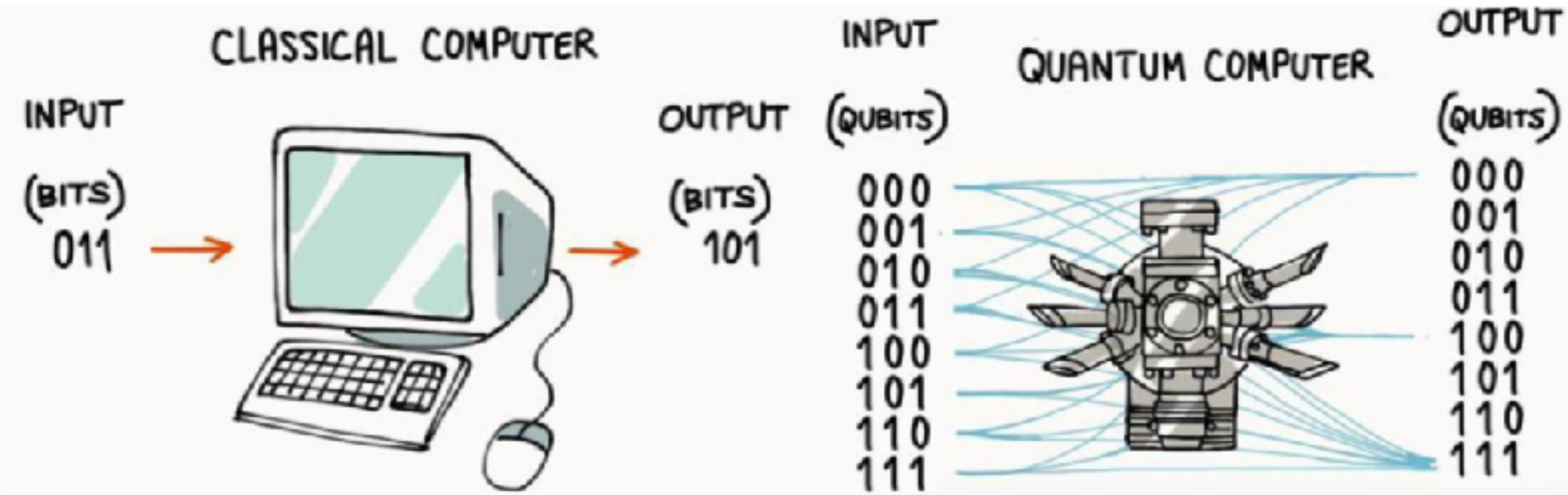

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M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information

Quantum Circuits

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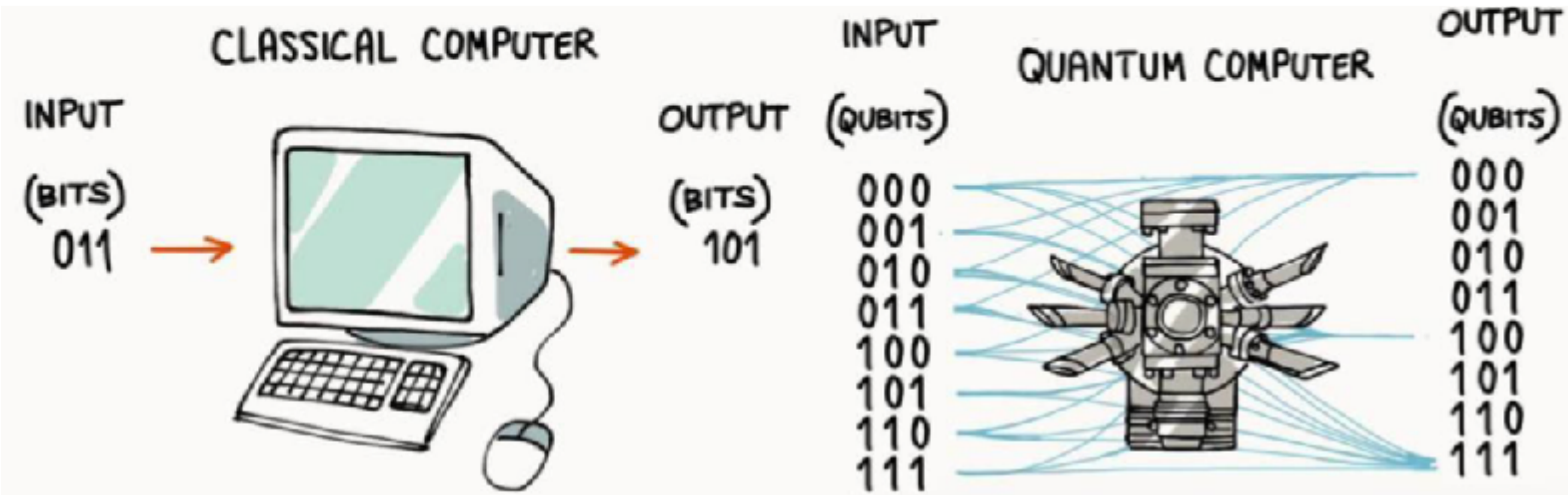

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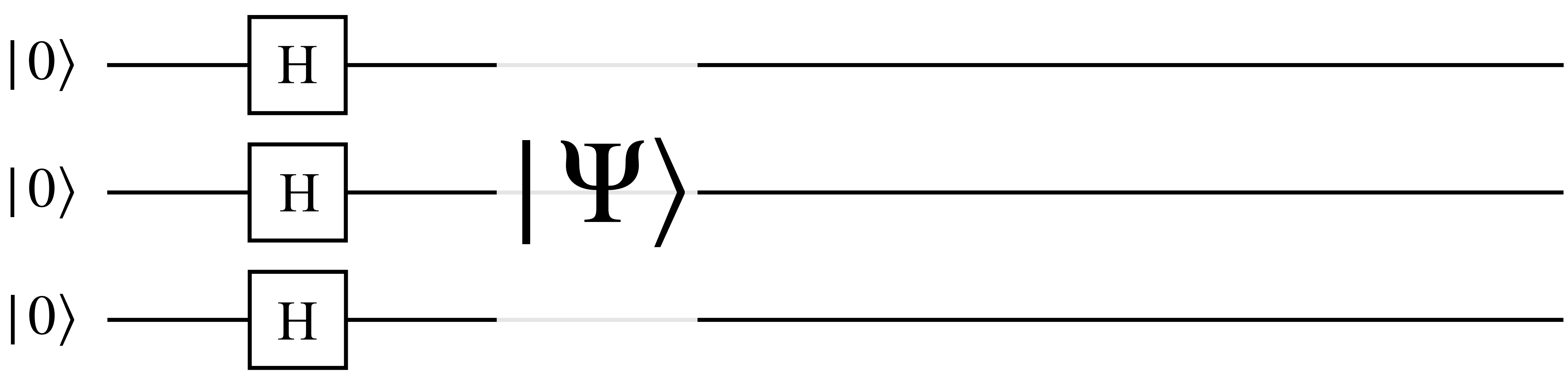

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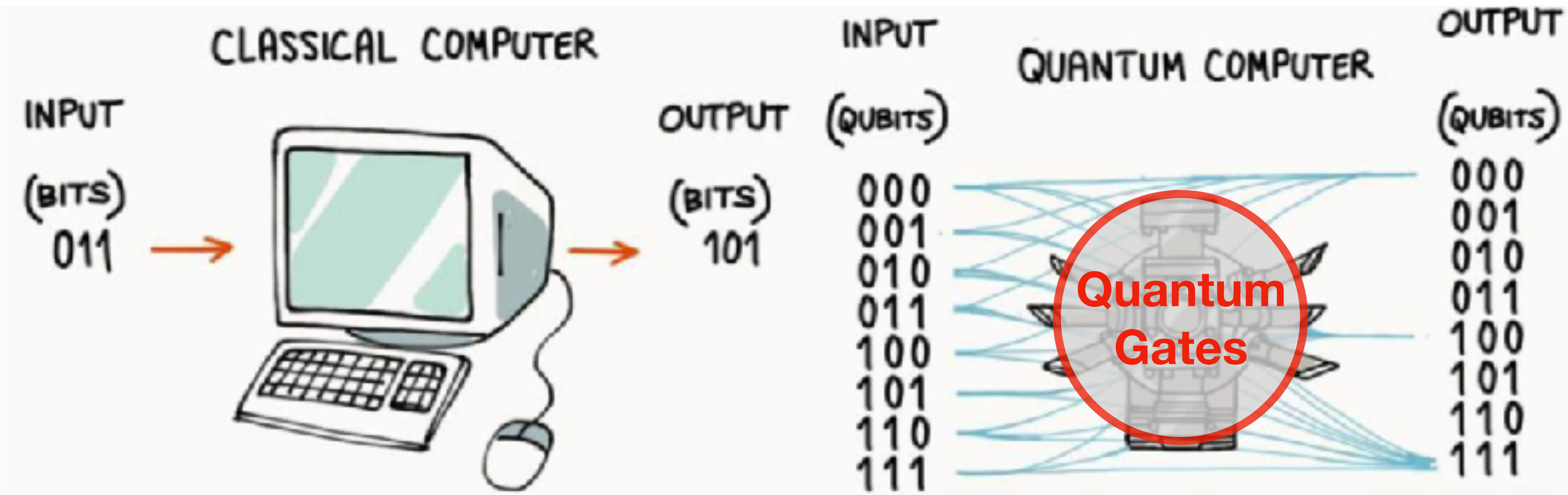
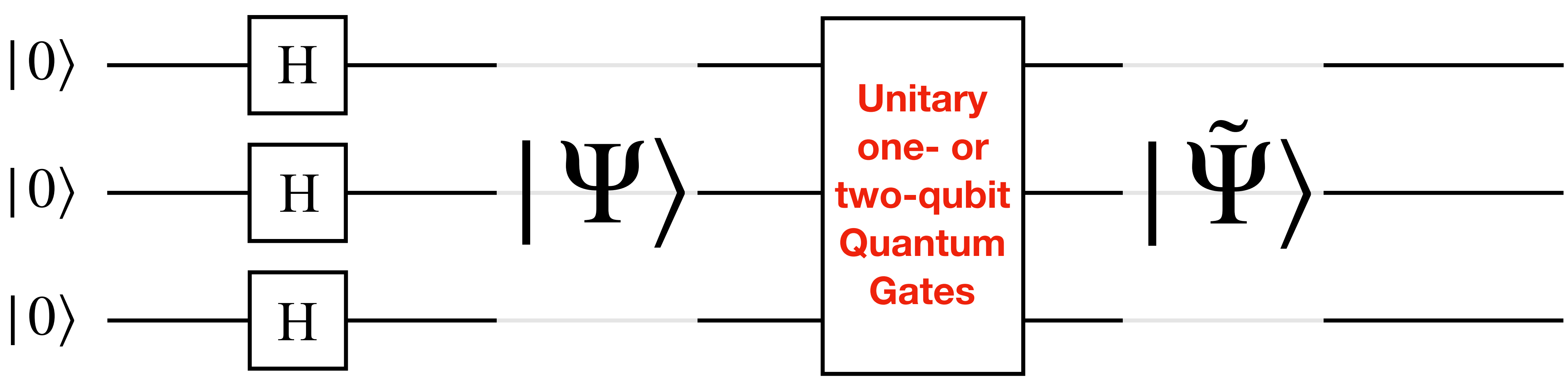


$$|\Psi\rangle \longrightarrow |\tilde{\Psi}\rangle$$



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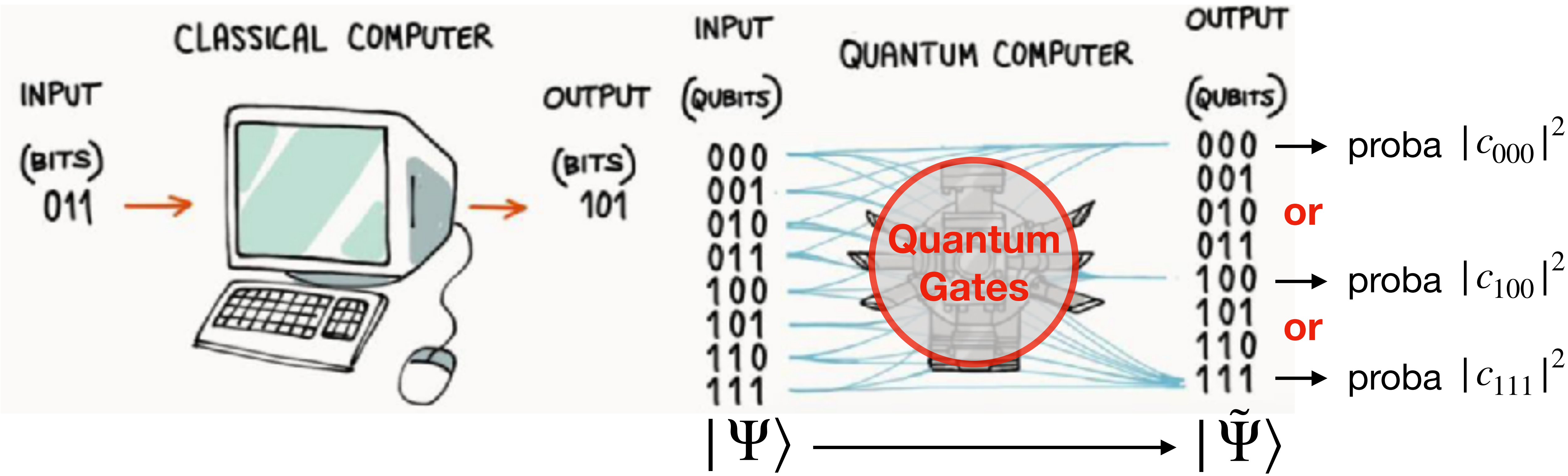

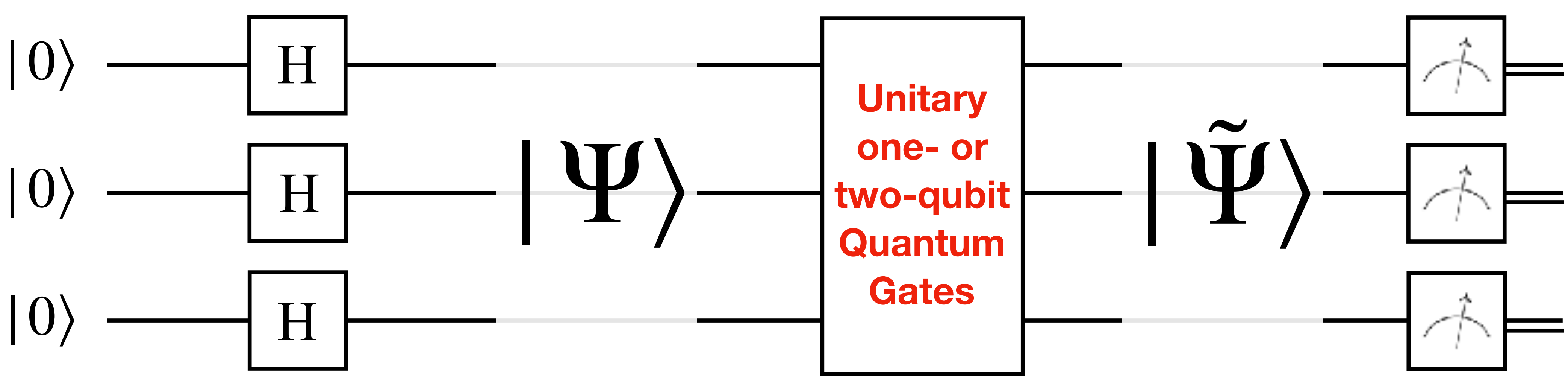

M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information

Quantum Chemistry and Quantum Computer

https://github.com/bsenjean/Openfermion-Dirac

Quantum Chemistry and Quantum Computer

Encode the spin-orbital occupation into the qubit state:

$$|\Psi\rangle = \sum_{n_1 \ldots n_i \ldots n_M} C_{n_1 \ldots n_i \ldots n_M} |n_1 \ldots n_i \ldots n_M\rangle \qquad |n_1 \ldots n_M\rangle = \left(\hat{c}_1^\dagger\right)^{n_1} \ldots \left(\hat{c}_M^\dagger\right)^{n_M} |\text{vac}\rangle$$

$|0\rangle$ and $|1\rangle$ → unoccupied/occupied spin-orbital → M **spin-orbitals** $\equiv$ M **qubits**

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$|0\rangle$ and $|1\rangle$ → unoccupied/occupied spin-orbital → **M spin-orbitals ≡ M qubits**

Mapping the second quantized Hamiltonian into a qubit Hamiltonian:

$$\hat{H} = \sum_{pq}^{M} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs}^{M} (pq|rs) \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q = \sum_{i=1}^{M^4} h_i \hat{P}_i \qquad \hat{P}_i \in \{I, X, Y, Z\}^{\otimes M}$$

Jordan-Wigner transformation

$$\hat{a}_i^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \otimes \ldots \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{i-1} \otimes \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}_i \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_{i+1} \otimes \ldots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_M$$

$$\hat{a}_i = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \otimes \ldots \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{i-1}}_{Z^{\otimes i-1}} \otimes \underbrace{\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}_i}_{\frac{X \pm iY}{2}} \otimes \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_{i+1} \otimes \ldots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_M}_{I^{\otimes M-i}}$$

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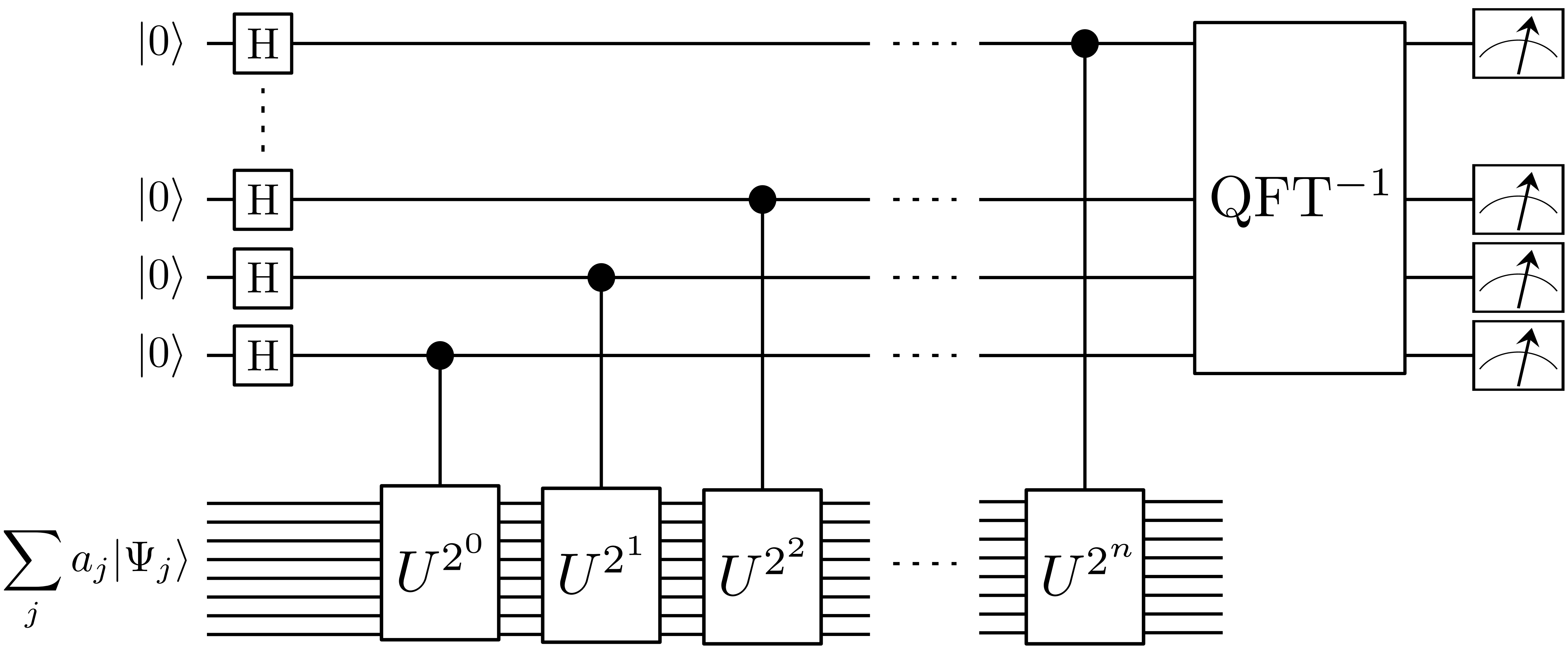
Quantum Phase Estimation (QPE)

Goal: Estimate the phase $E_j t$ of the unitary operator $U = e^{\mathrm{i}\hat{H}t}$ with $e^{\mathrm{i}\hat{H}t}|\Psi_j\rangle = e^{\mathrm{i}E_j t}|\Psi_j\rangle$ with precision given by the number of ancilla qubits

Two qubit registers: one encoding the state and the other composed of ancilla qubits

Start with Hartree-Fock !

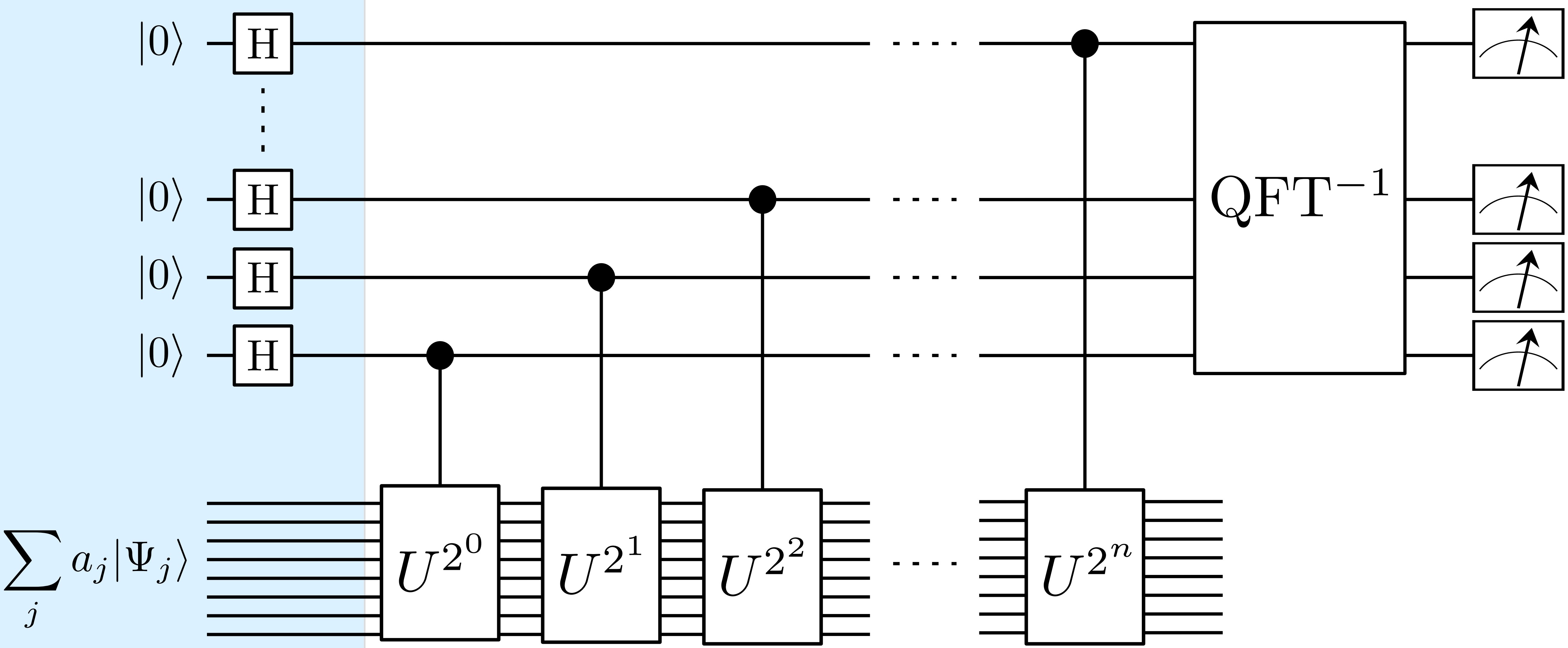


Quantum Phase Estimation (QPE)

Hadamard gates to create Superposition

$$\frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right) \otimes \ldots \otimes \frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right) \otimes \sum_j a_j |\Psi_j\rangle$$

$$= \frac{1}{\sqrt{2^n}} \sum_{k=0}^{2^n-1} |k\rangle \sum_j a_j |\Psi_j\rangle$$

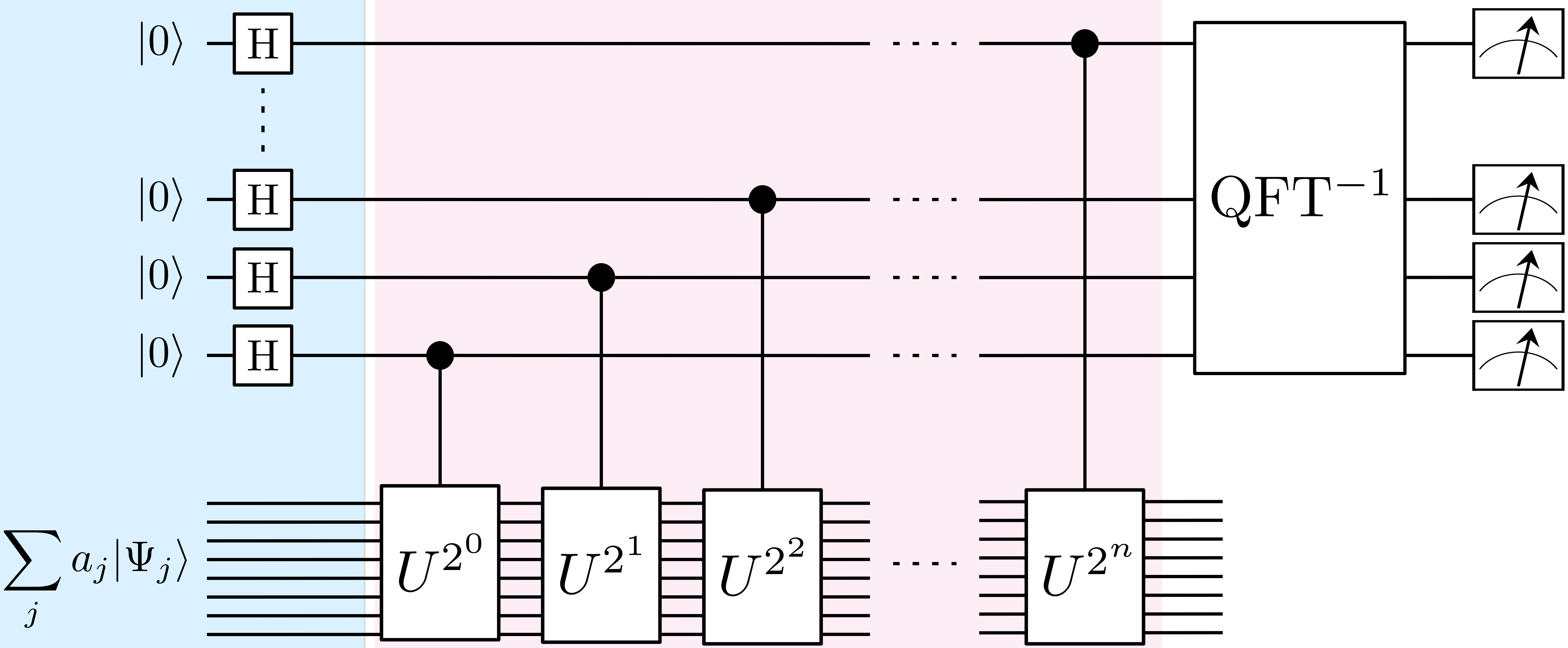


Quantum Phase Estimation (QPE)

Hadamard gates to create Superposition

Controlled-Unitaries leading to

$$\frac{1}{\sqrt{2^n}} \sum_{k=0}^{2^n-1} \sum_{j} a_j e^{iE_j t k} \,|k\rangle\, |\Psi_j\rangle$$



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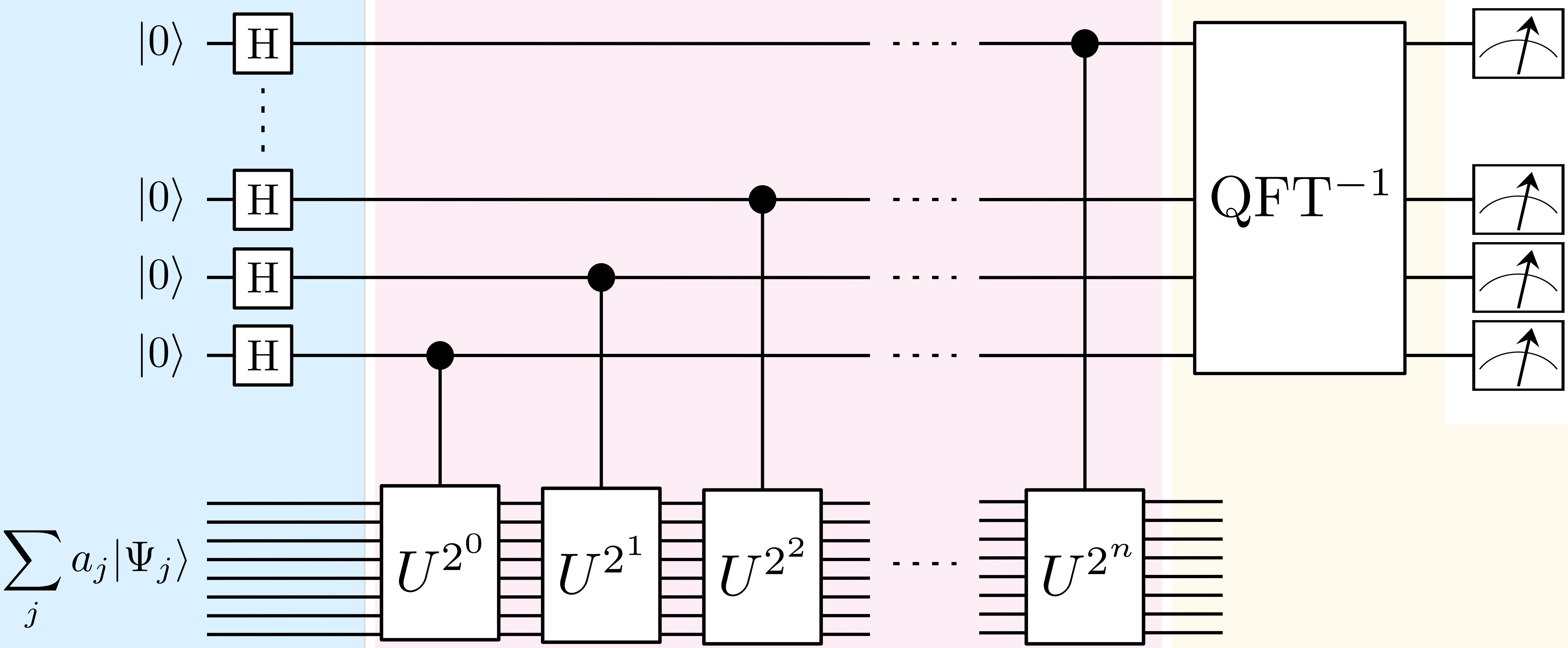
$$\frac{1}{\sqrt{2^n}} \sum_{k=0}^{2^n-1} \sum_j a_j e^{\mathrm{i}E_j tk} |k\rangle |\Psi_j\rangle \longrightarrow \sum_j a_j |E_j t\rangle |\Psi_j\rangle$$

Inverse Quantum Fourier Transform



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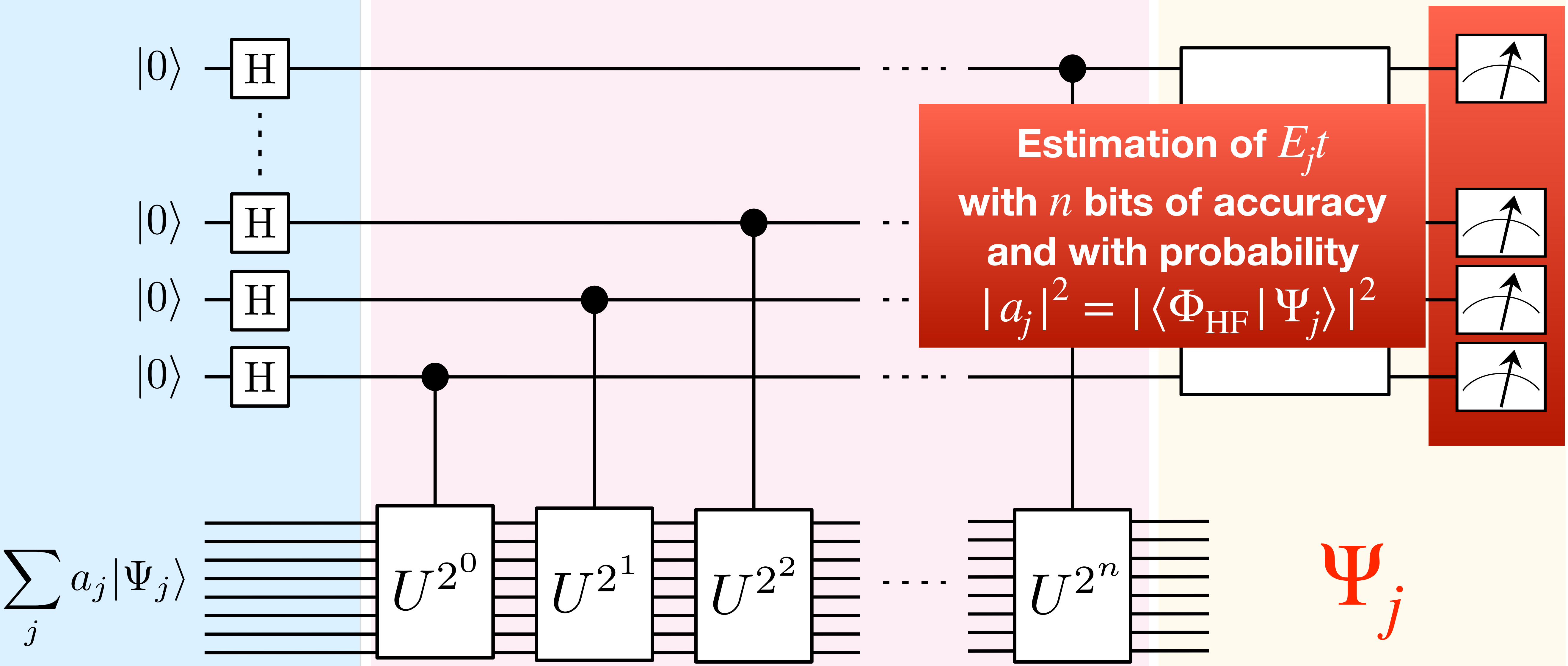

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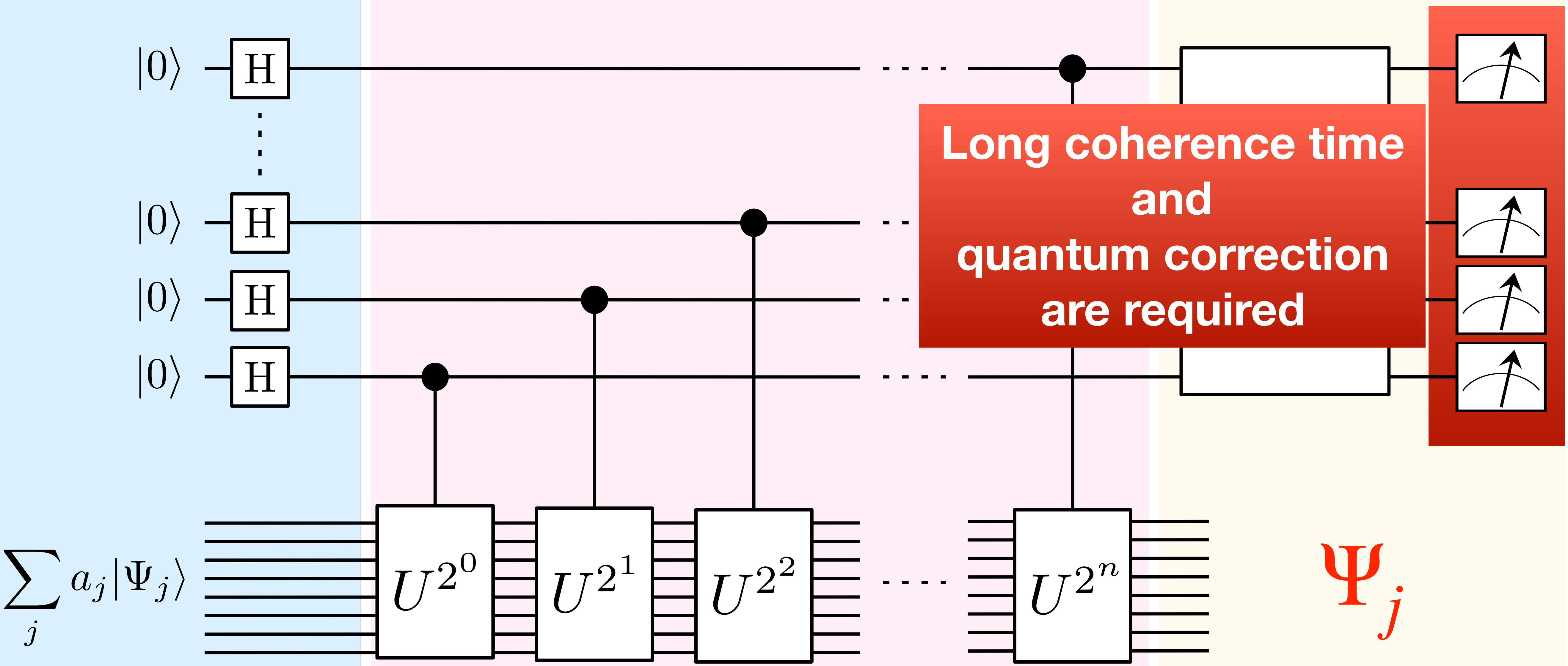

Variational Quantum Eigensolver (VQE)

Classical Device

Quantum Device

Variational principle:

$$E_0 = \min_{\vec{\theta}} \langle \Psi(\vec{\theta}) | \hat{H} | \Psi(\vec{\theta}) \rangle$$

A. Peruzzo *et al.* Nat. Commun. 5, 4213 (2014).

Variational Quantum Eigensolver (VQE)

Classical Device

Mean-Field calculation

Second quantized Hamiltonian

Transformation to qubit Hamiltonian

$$\hat{H} = \sum_i h_i \hat{P}_i$$

Initialize parameters $\overrightarrow{\theta}$

Quantum Device

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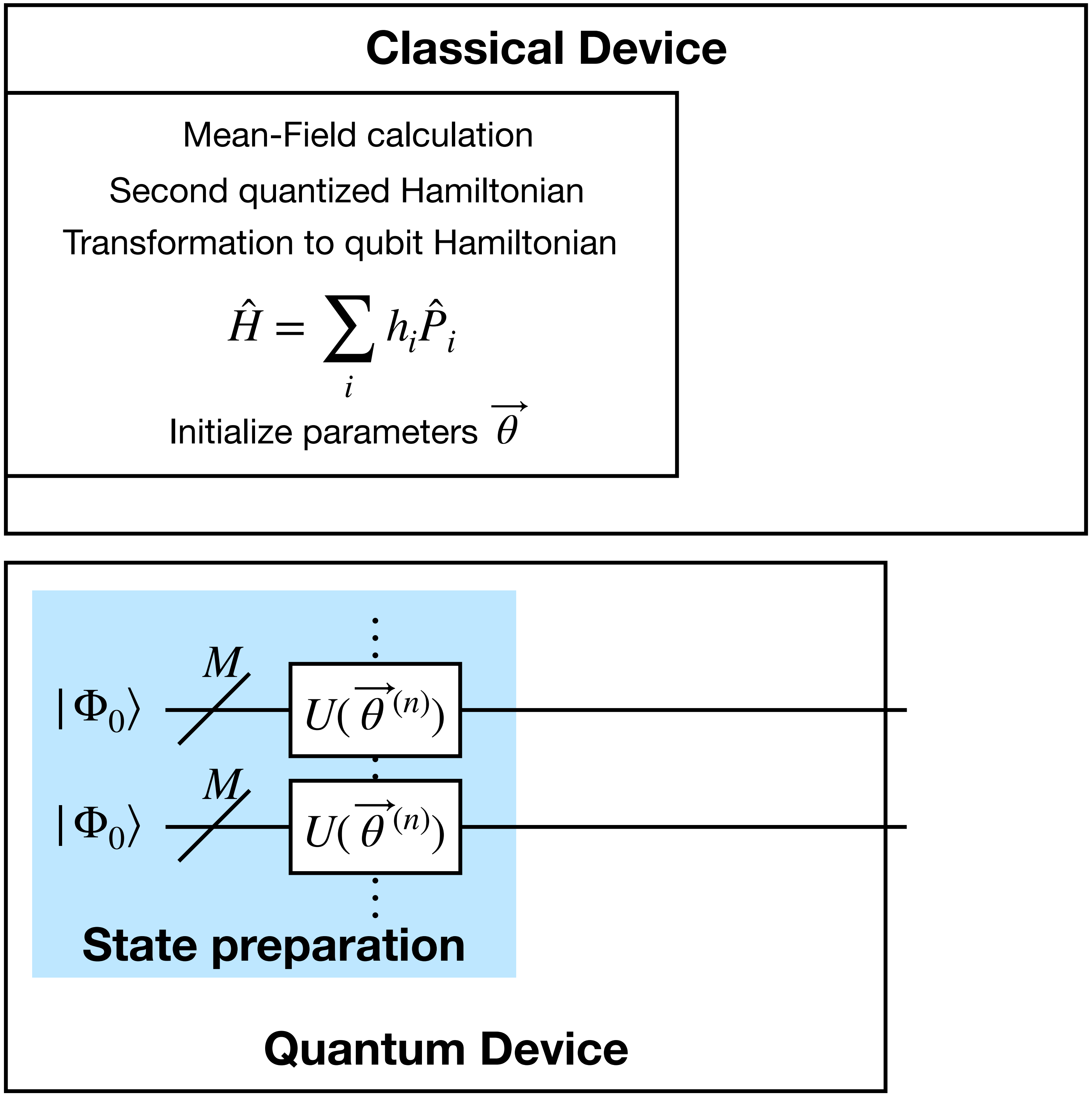

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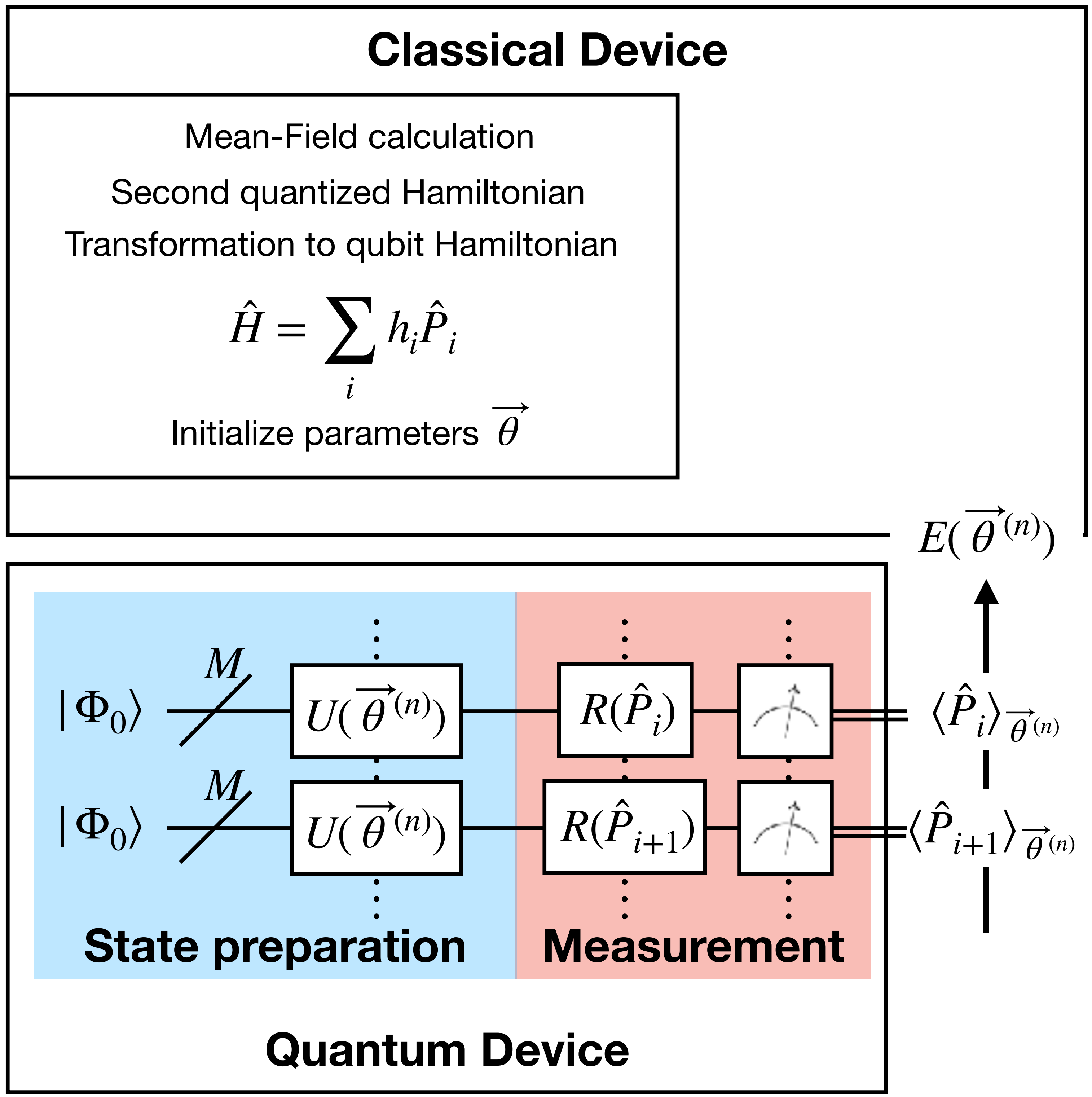

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Measurement:

$$P\left(\sum_i m_i = 1 \bmod 2 \,\middle|\, R(\hat{P}) \right) = \frac{1}{2}\left(1 - \langle \hat{P} \rangle\right)$$

$$E(\vec{\theta}) = \sum_i h_i \langle \hat{P}_i \rangle_{\vec{\theta}}$$

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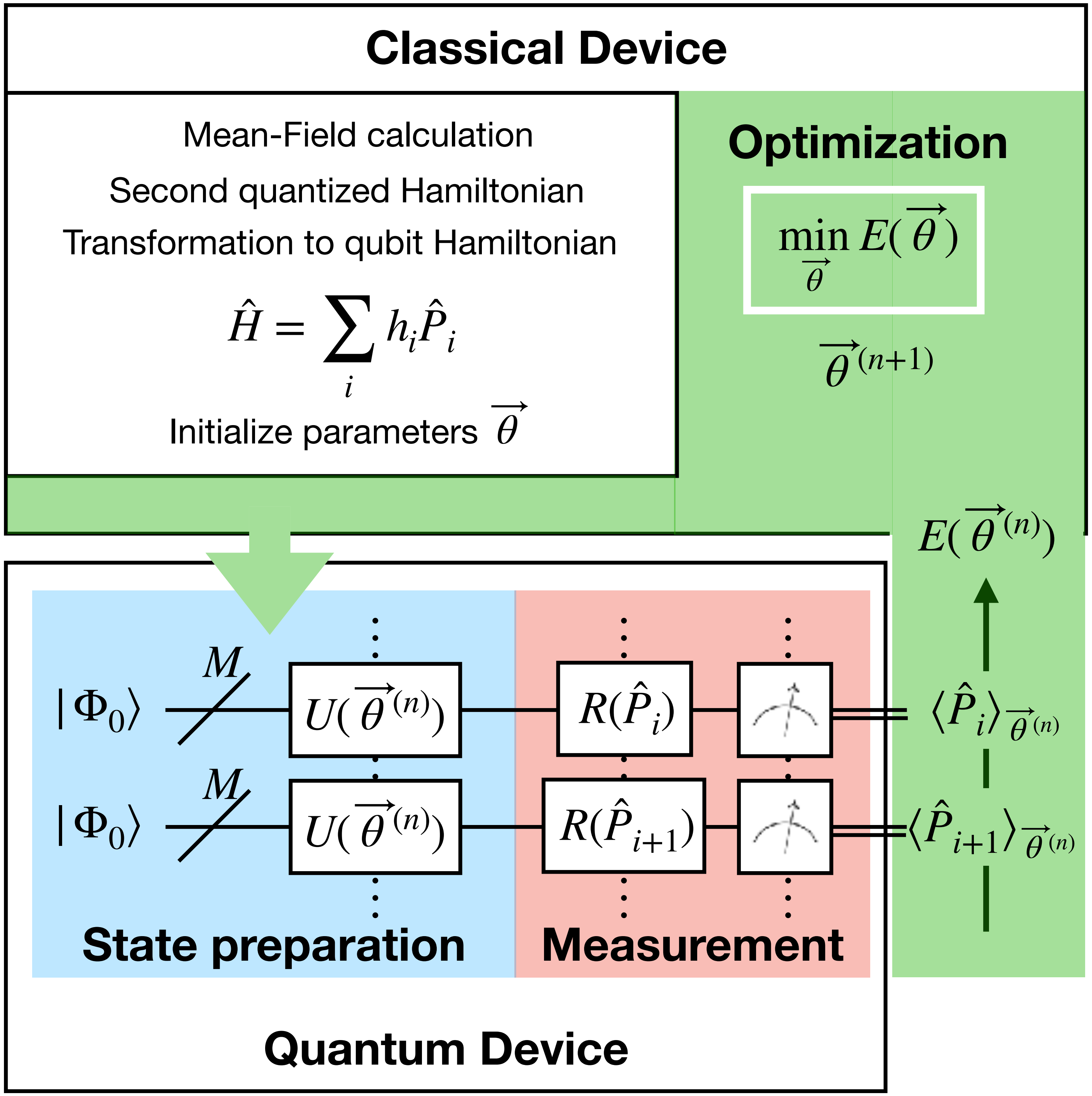

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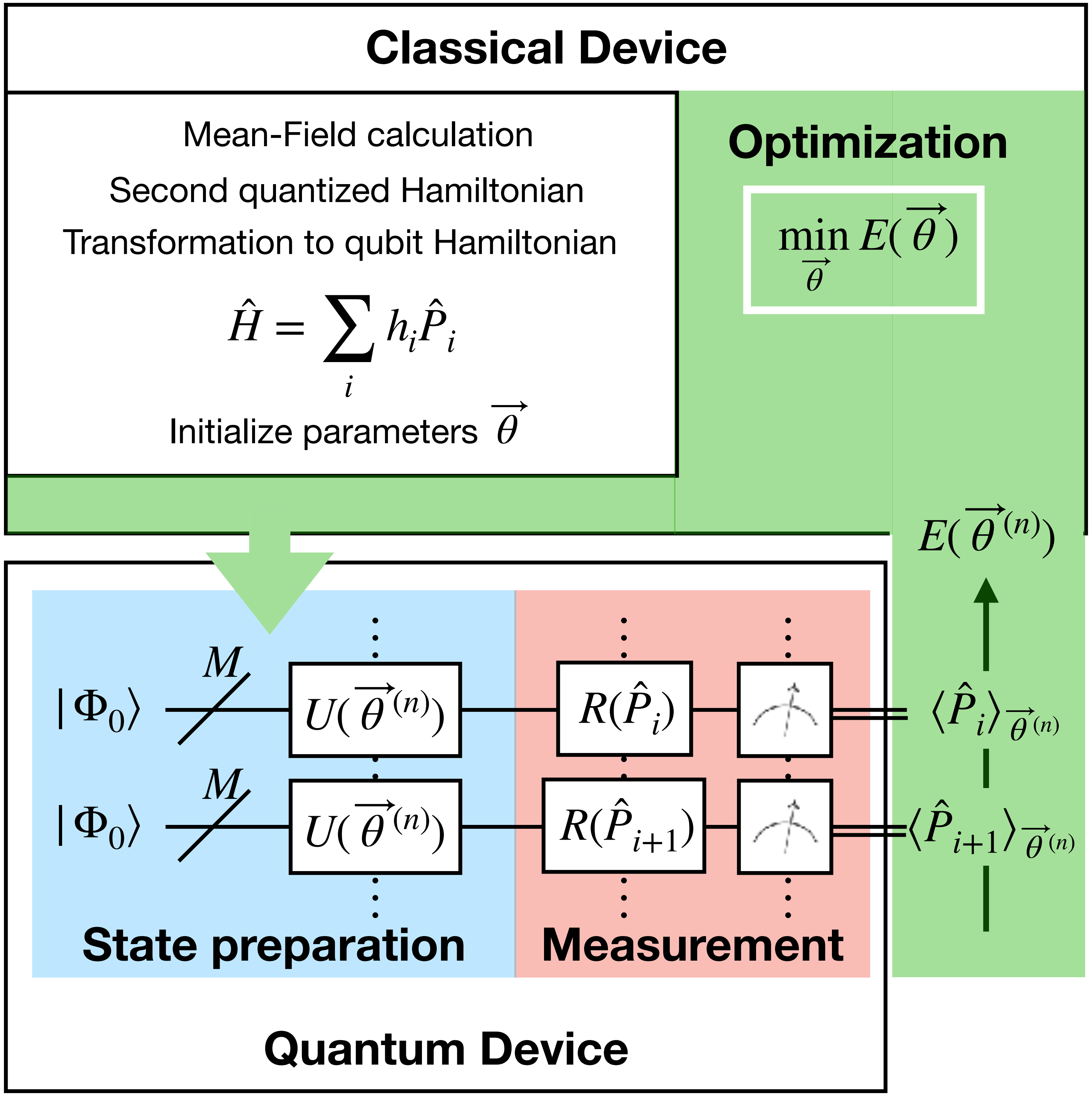

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Geometry Optimization, H_2 (minimal basis)

T. E. O'Brien, **BS** *et al.* npj Quantum Inf **5**, 113 (2019) ; O'Malley *et al.* PRX **6**, 031007 (2016)

Geometry Optimization, H_2 (minimal basis)

First-order derivative: Hellmann-Feynman theorem

$$\frac{\partial E_0}{\partial \lambda} = \langle \Psi_0 | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_0 \rangle \longrightarrow \sum_i \underbrace{\frac{\partial h_i}{\partial \lambda}}_{\text{classically}} \underbrace{\langle \Psi_0 | \hat{P}_i | \Psi_0 \rangle}_{\text{VQE}}$$

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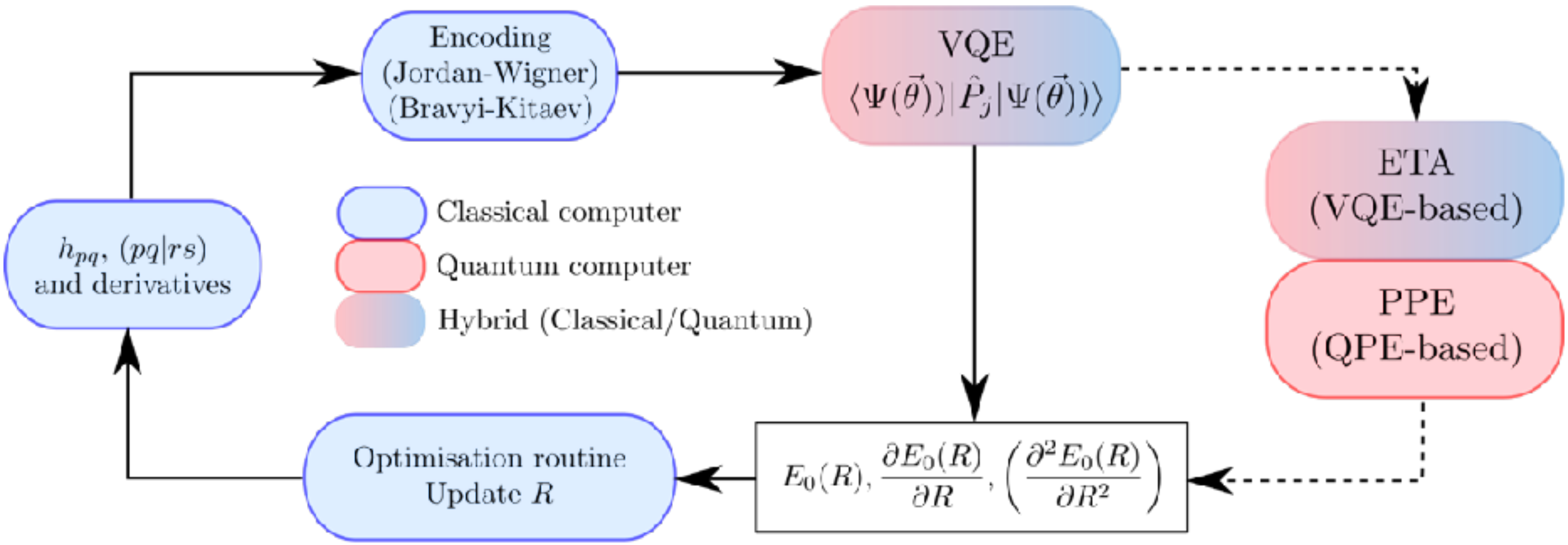

$$\hat{H}_{H_2} = f_0 + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 X_0 Z_1 X_2 + f_6 Y_0 Z_1 Y_2$$
$$+ f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 + f_6 X_0 Z_1 X_2 Z_3 + f_6 Y_0 Z_1 Y_2 Z_3 + f_7 Z_0 Z_1 Z_2 Z_3$$

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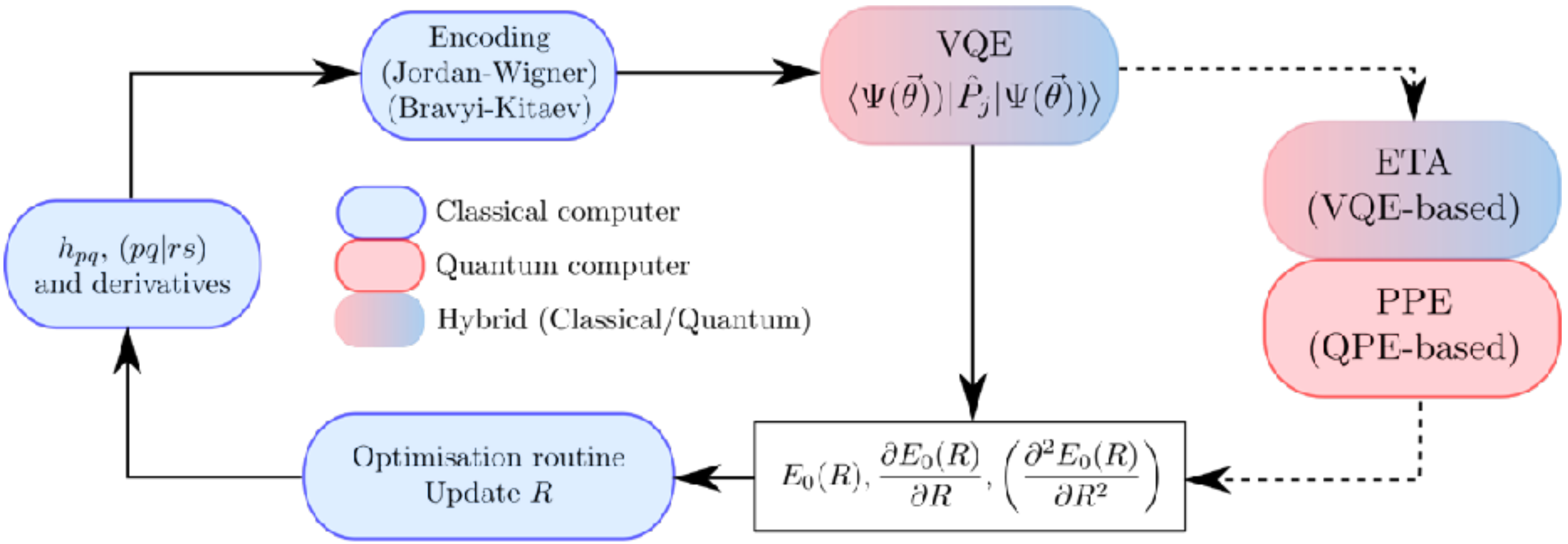
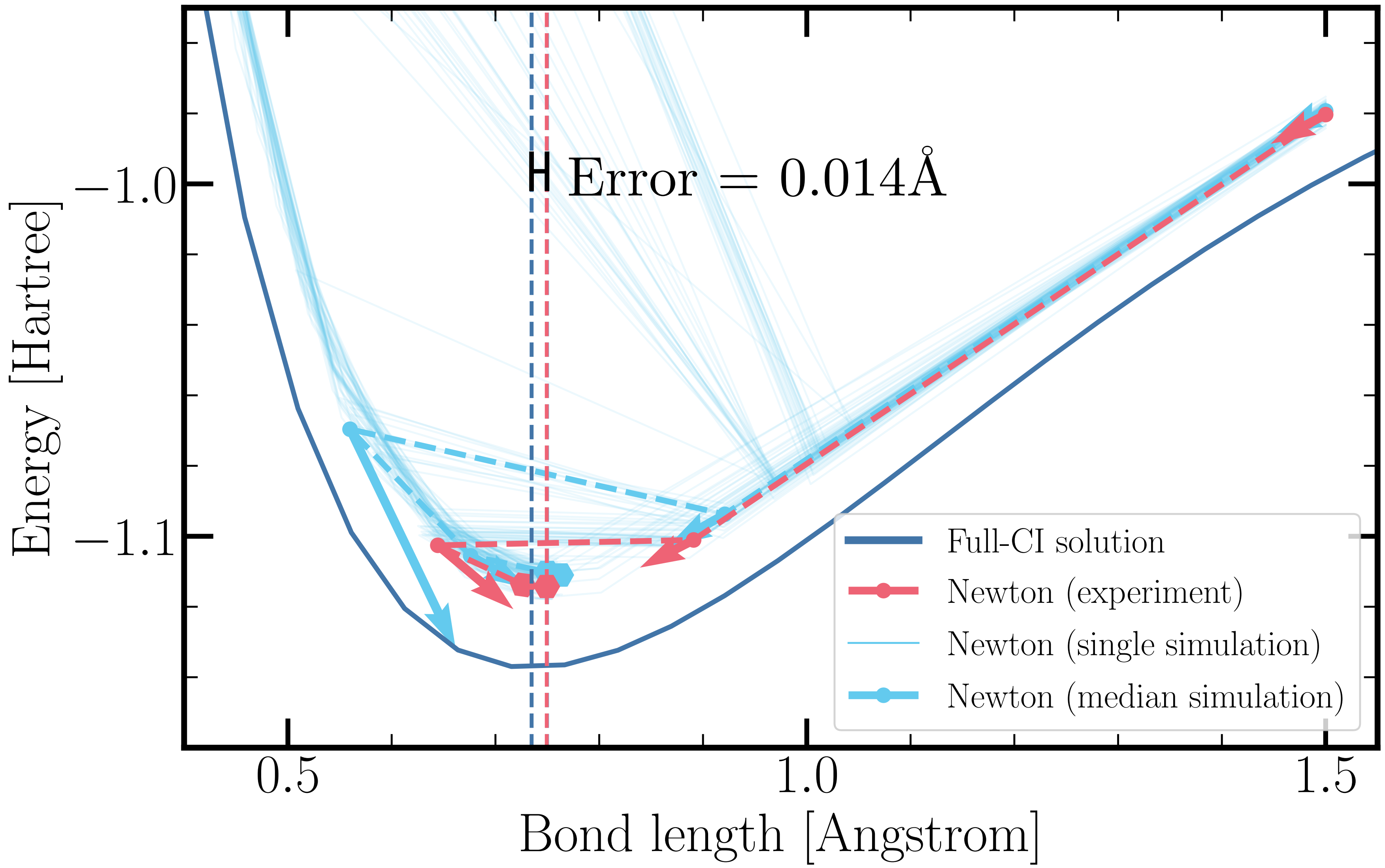


$$\hat{H}_{H_2} = g_0 + g_1 Z_0 + g_2 Z_1 + g_3 Z_0 Z_1 + g_4 X_0 X_1 + g_5 Y_0 Y_1$$

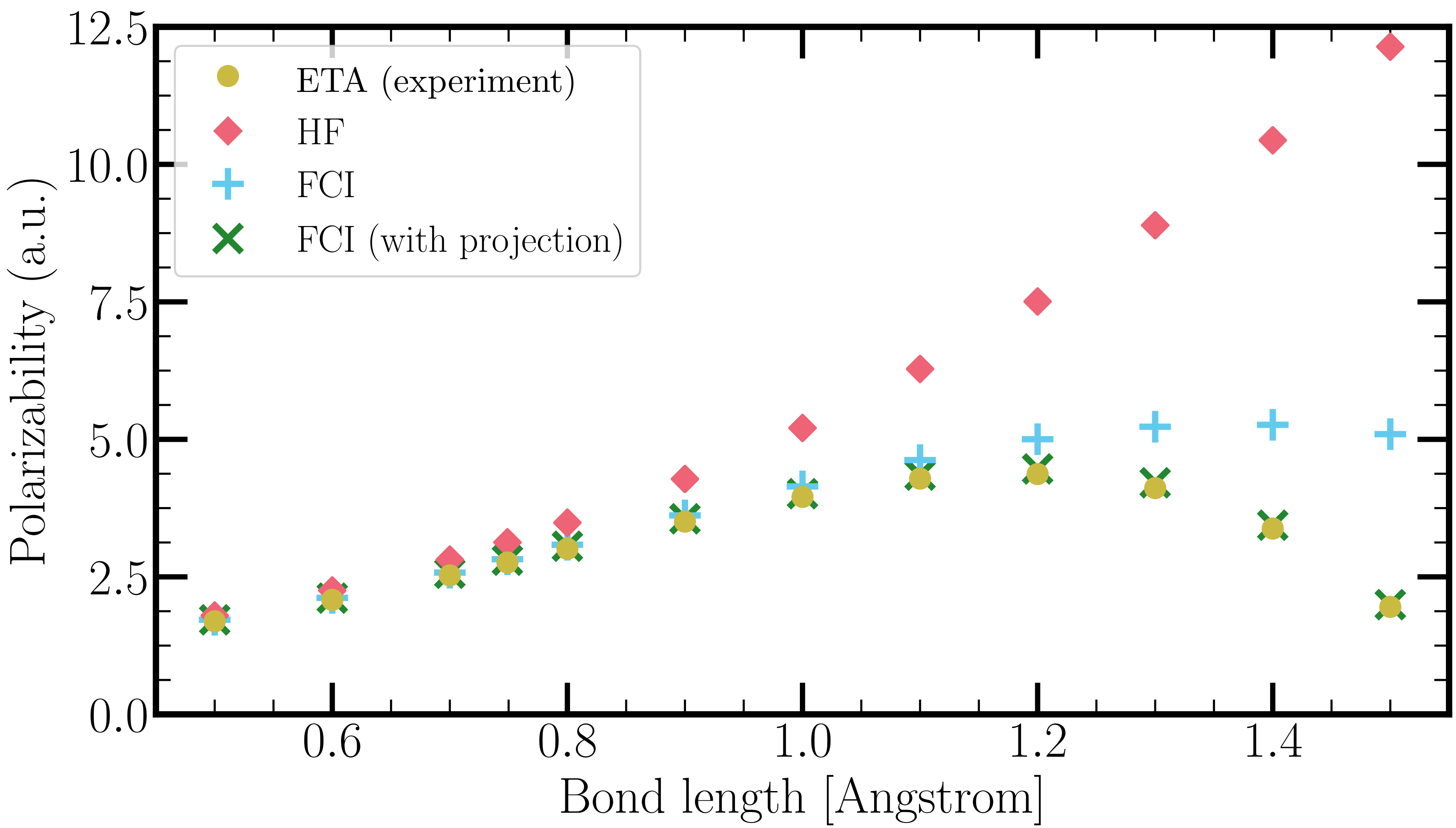
T. E. O'Brien, **BS** *et al.* npj Quantum Inf **5**, 113 (2019) ; O'Malley *et al.* PRX **6**, 031007 (2016)

Geometry Optimization on H_2



T. E. O'Brien, **BS** *et al.* npj Quantum Inf **5**, 113 (2019)

Polarizability of H_2



Dipole moment operator breaks symmetry,

transformation to two-qubit no longer valid

T. E. O'Brien, **BS** *et al.* npj Quantum Inf **5**, 113 (2019)

Perspectives

Quantum advantage is now a question of "when" and not "if"...

1. Find new algorithms for near-term/long-term quantum computers:

   Excited states, Hybrids (embedding ? CASSCF?)

2. Optimize existing algorithms:

   measurements, ansatz, ancillas...

3. Quantum Chemistry side:

   Better embedding methods, Basis set error ... E. Giner teaser ... :)

4. But:

   Cannot copy data (hard drives), and not always advantageous

So much things to do... :)

Acknowledgments

- Tom O'Brien
- Luuk Visscher
- Saad Yalouz
- Xavier Bonet-Monroig
- Francesco Buda
- Carlo Beenakker (and group)
- Leo DiCarlo (and group)

Acknowledgments

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- **Leo DiCarlo (and group)**

And you for your kind attention

and Happy New Year!