

Compute the Energy of  
Molecular Hydrogen ( $\text{H}_2$ )

# Molecular Hamiltonian in Second Quantization

- We use the Born-Oppenheimer approximation to separate nuclear and electronic degrees of freedom.
- Nucleus-nucleus interactions are treated with classical Coulombic potential, added to the electronic energy.
- Molecular Hamiltonian consists of one-particle and two-particle terms.

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

$$h_{pq} = \langle \phi_p | \frac{\nabla_r^2}{2} - \sum_I \frac{Z_I}{|R_I - r|} | \phi_q \rangle$$

$$h_{pqrs} = \langle \phi_p(r_1) \phi_q(r_2) | \frac{1}{|r_1 - r_2|} | \phi_s(r_2) \phi_r(r_1) \rangle$$

# Unitary Coupled-Cluster Wave Function Ansatz

- Choose trial wave function as unitary transformation of some reference wave function with

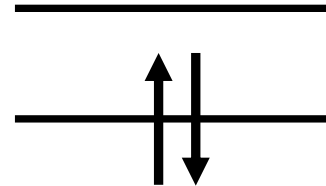
$$|\psi\rangle = e^{\hat{T}-\hat{T}^\dagger} |\psi_0\rangle$$

$$\hat{T} = \sum_i \theta_i \hat{g}_i$$

- $|\psi_0\rangle$  is the reference, often chosen as the Hartree-Fock solution, consisting of Hartree-Fock orbitals and electron occupations.
- $g_i$  is some “generator” that moves electrons around (can be written in the form of second quantization)

# H<sub>2</sub> Molecule with a Minimal Basis

- Minimal basis (STO-3G): each H atom is modeled with an s-type orbital, giving rise to a two-spatial-orbital two-electron system
- The HF reference has two electrons occupying the lowest energy molecular orbital



- In the UCC wave function ansatz, excitation operators create all possible configurations arising from the HF orbital space to be used to expand the UCC wave function
- Spin-symmetry can be enforced to reduce the number of configurations

# Hamiltonian in Qubit Basis

- Represent the Hamiltonian in the basis of qubits
  - There are several ways to do this. The most used approaches are the **Jordan-Wigner (JW)** transformation and the **Bravyi-Kitaev (BK)** transformation
- Using the BK-transformed Hamiltonian & exploiting symmetries, the Hamiltonian can be represented by only **two** qubits.

$$H = g_0 \mathbb{1} + g_1 Z_0 + g_2 Z_1 + g_3 Z_0 Z_1 + g_4 Y_0 Y_1 + g_5 \boxed{X_0 X_1}$$

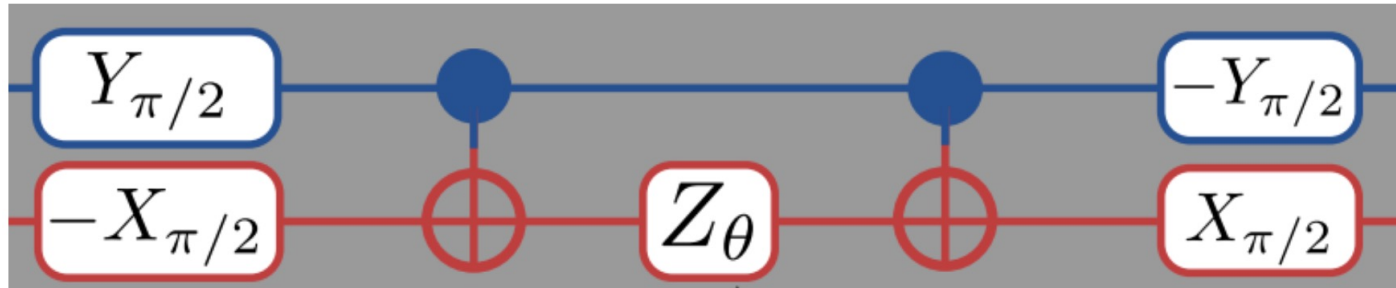
Pauli matrices

- Coefficients  $g_i$  are related to integrals obtained from a Hartree-Fock calculation. The magnitudes of  $g_i$  depend on the bond distance and the type of atomic orbital used.

# UCC Wave Function in Qubit Basis

- $H_2$  molecule with a minimal basis set has two spatial orbitals and two electrons. Enforcing the spin symmetry to be singlet, the wave function ansatz in qubit representation is

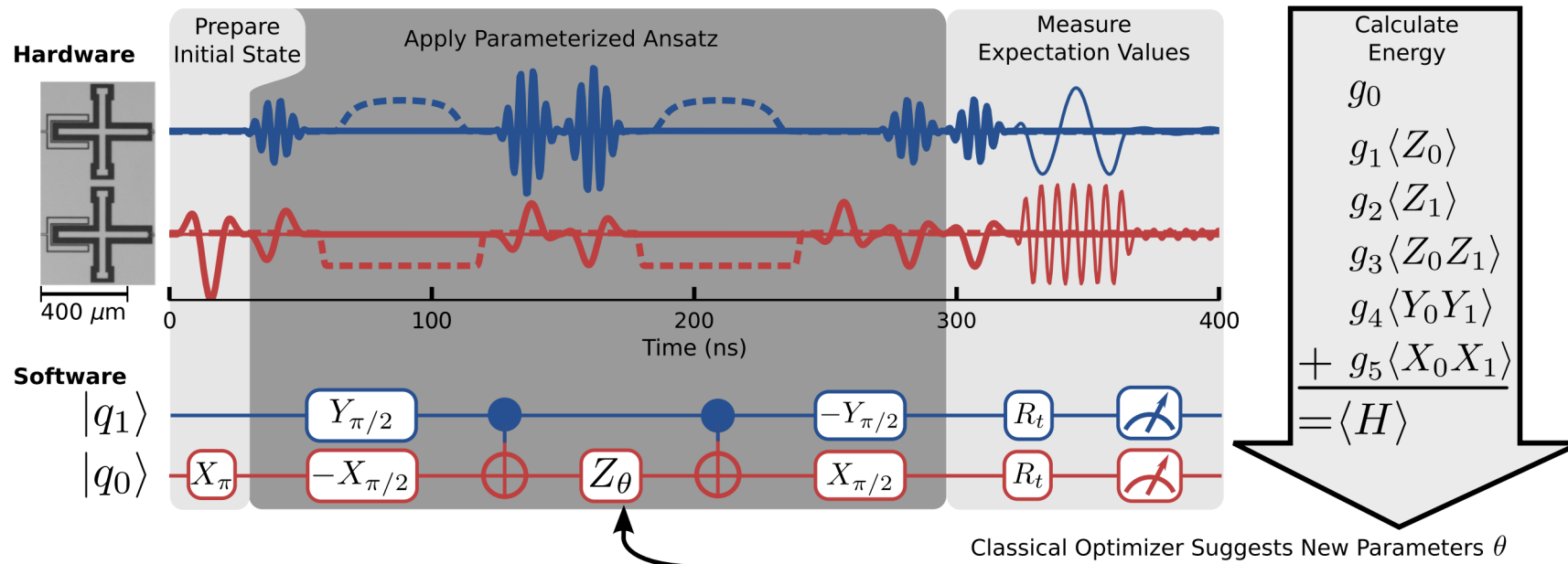
$$|\psi(\theta)\rangle = e^{-i\theta X_0 Y_1} |01\rangle$$



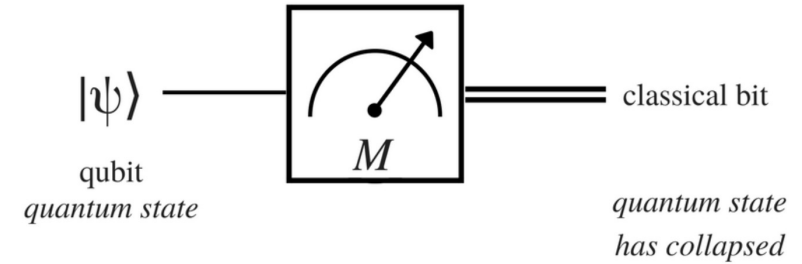
# Quantum Measurements

- The expectation value of the energy of a wave function can be obtained from measurements of physical operations

$$\begin{aligned}
 & \langle \psi(\{\theta\}) | H | \psi(\{\theta\}) \rangle \\
 &= \langle 01 | e^{-i\theta X_0 Y_1} (H) e^{-i\theta X_0 Y_1} | 01 \rangle \\
 &= \langle 01 | e^{-i\theta X_0 Y_1} (g_0 + g_1 \mathbf{Z}_0 + g_2 \mathbf{Z}_1 + g_3 \mathbf{Z}_0 \mathbf{Z}_1 + g_4 \mathbf{Y}_0 \mathbf{Y}_1 + g_5 \mathbf{X}_0 \mathbf{X}_1) e^{-i\theta X_0 Y_1} | 01 \rangle
 \end{aligned}$$



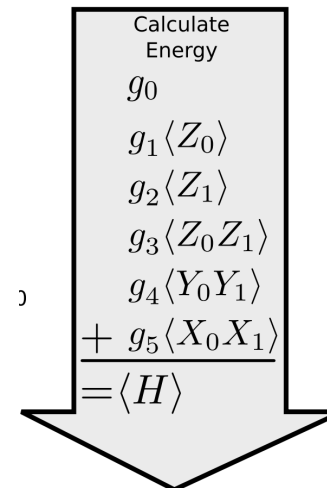
# Let's measure the energy!



- ✓ Experimentally, the "only" measurements we can make are those which probe the final quantum state of the qubits
- ✓ Is quantum measurement deterministic or probabilistic?
  - ✓ qubit states are quantum states. Wave function distribution of a quantum state is probabilistic
  - ✓ statistical average of many qubit measurements is needed to compute the expectation value of a quantum operation

$$\langle Z_0 \rangle = \frac{\sum_i^N Z_0^i}{N}$$

$N$ =number of shots





# Variational Principle

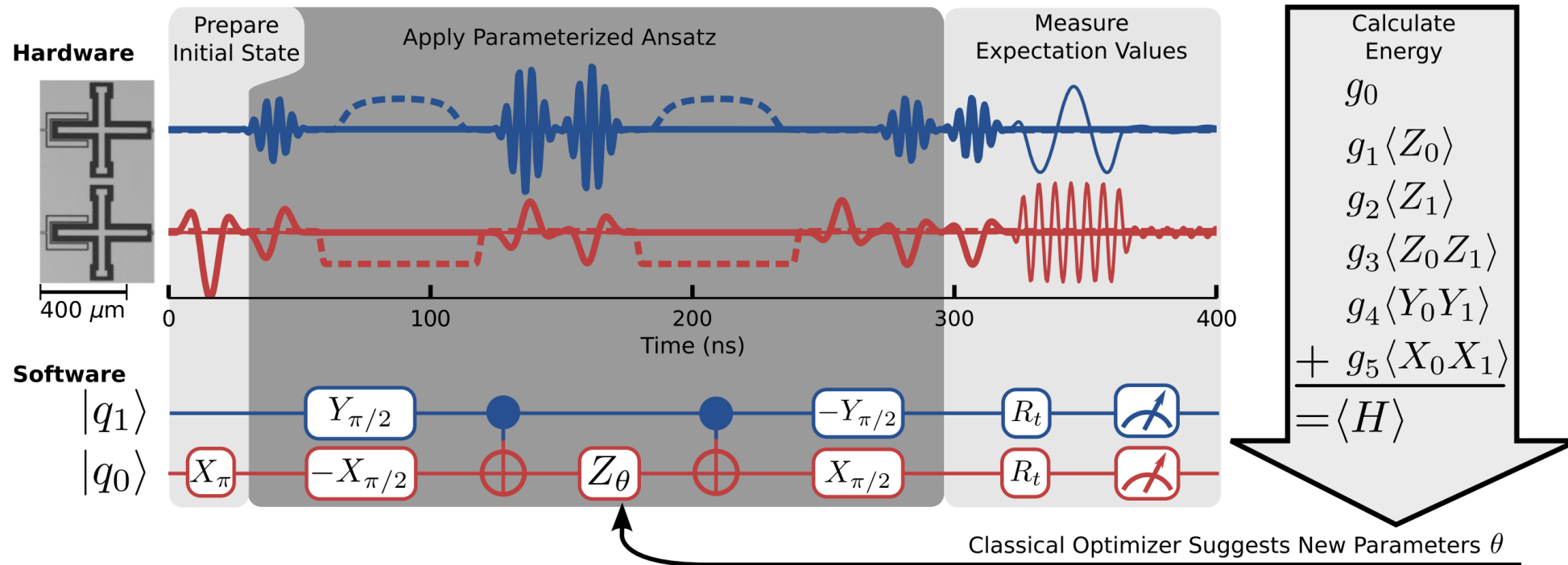
- The exact many-body wave function is unknown
- There are many ways to find the optimal wave function, all based on the variational principle

$$\frac{\langle \psi(\{\theta\}) | H | \psi(\{\theta\}) \rangle}{\langle \psi(\{\theta\}) | \psi(\{\theta\}) \rangle} \geq E_0$$

- Optimizing variational parameters can lead to the optimal wave function and the ground state energy which is bound from below by the true energy.

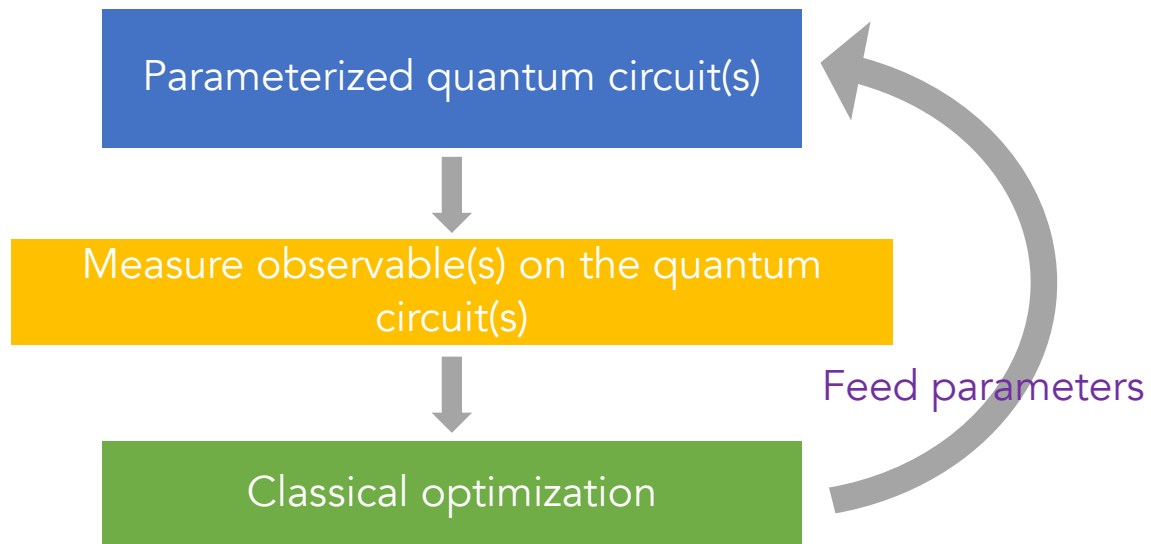
# Variational Quantum Eigensolver

- By performing (inefficient) classical simulations of the circuit, we can identify the theoretically optimal value of  $\theta$  at each  $R$ .



# Variational Quantum Eigensolver

- Hybrid: parameterized quantum circuits + classical optimization
- Optimize an objective function, e.g. the ground state energy



McClean, Romero, Babbush, et al. New J. Phys. 18, 023023 (2016)  
Cerezo, Arrasmith, Babbush, et al. Nat. Rev. Phys. 3, 625-644 (2021)

# Homework #1: Compute Energy using Linear Algebra

1. Find parameters in Table 1 of O'Malley, Peter JJ, et al. Physical Review X 6.3 (2016): 031007.

- We will provide you with the numerically exact full CI results

TABLE I. Hamiltonian coefficients for Eq. (1) and parameters for the PEA experiment for each value of  $R$ .

$R$	$\mathbb{1}$	$Z_0$	$Z_1$	$Z_0Z_1$	$X_0X_1$	$Y_0Y_1$	$t_0$	Ordering	Trotter error
0.20	2.8489	0.5678	-1.4508	0.6799	0.0791	0.0791	1.500	$Z_0 \cdot X_0X_1 \cdot Z_1 \cdot Y_0Y_1$	0.0124
0.25	2.1868	0.5449	-1.2870	0.6719	0.0798	0.0798	1.590	$Z_0 \cdot Y_0Y_1 \cdot Z_1 \cdot X_0X_1$	0.0521
0.30	1.7252	0.5215	-1.1458	0.6631	0.0806	0.0806	1.770	$X_0X_1 \cdot Z_0 \cdot Y_0Y_1 \cdot Z_1$	0.0111
0.35	1.3827	0.4982	-1.0226	0.6537	0.0815	0.0815	2.080	$Z_0 \cdot X_0X_1 \cdot Z_1 \cdot Y_0Y_1$	0.0368

1. Follow <https://joshuagoings.com/2020/08/20/VQE/> and code the linear algebra version of VQE (Note: this tutorial utilizes unitary transformations to map n-qubit to a single qubit measurement)
2. Find the optimal  $\theta$  value for the bond length of your choice. Submit your results including bond length, optimal  $\theta$  value, and the ground state energy.

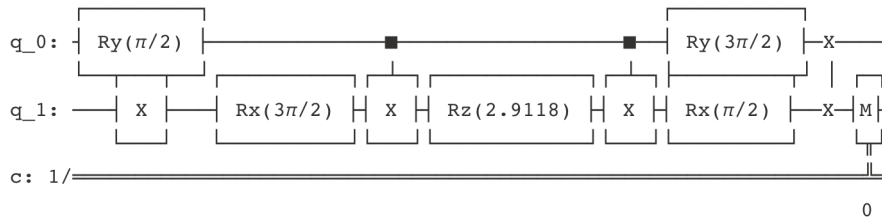
# Homework #2: Compute Energy with Quantum Measurements on QPUs

1. Follow the example for the  $g_1$  term and code quantum measurements using simulators
2. Use the optimal  $\theta$  value for the bond length of your choice
3. Compare your result obtained from simulator to the exact numerical result from your previous homework
4. Run your code using IonQ qpus with 200, 500, 1000, and (possibly 5000) shots, respectively. **Submit your results, including the  $\theta$  value and the ground state energy for each run.**

# Real Circuit for $g_1$

```
#####  
# g1  
# <I1 Sz0>  
circuit = QuantumCircuit(2, 1)  
circuit.name = "H2 ST0-3G"  
circuit.x(1)  
circuit.ry(np.pi/2,0)  
circuit.rx(3*np.pi/2,1)  
circuit.cx(0,1)  
circuit.rz(2.9118489,1)  
circuit.cx(0,1)  
circuit.ry(3*np.pi/2,0)  
circuit.rx(np.pi/2,1)  
#U = SWAP  
circuit.swap(0,1)  
  
circuit.measure([1], [0])  
  
print(circuit)  
✓ <1 sec
```

⇒ We fix the parameter  $\theta$  temporarily



Python

Copy

```
simulator_backend = provider.get_backend("ionq.simulator")
```

You can also change the backend to "ionq.qpu"

Python

Copy

```
qpu_backend = provider.get_backend("ionq.qpu")
```

You can change the number of shots to any value

Python

Copy

```
# Submit the circuit to run on Azure Quantum  
qpu_job = qpu_backend.run(circuit, shots=1024)  
job_id = qpu_job.id()  
print("Job id", job_id)  
  
# Monitor job progress and wait until complete:  
job_monitor(qpu_job)  
  
# Get the job results (this method also waits for the Job to complete):  
result = qpu_job.result()  
print(result)
```

# Homework #3: Variational Quantum Eigensolver

1. Code the variational quantum eigensolver for your quantum measurement program
2. Start with a random (yet reasonable  $\theta$  value), use your VQE code to find the optimal  $\theta$  value
3. Submit your complete code to Prof. Xiaosong Li and Dr. Linghua Zhu.

# Background: VQE

➤ Variational Principle:  $\frac{\langle \psi(\vec{\theta}) | H | \psi(\vec{\theta}) \rangle}{\langle \psi(\vec{\theta}) | \psi(\vec{\theta}) \rangle} \geq E_{gs}$

- $|\psi(\vec{\theta})\rangle$  is our parameterized state, created by a chosen ansatz (quantum circuit)

✓ Second quantized Hamiltonian  
→

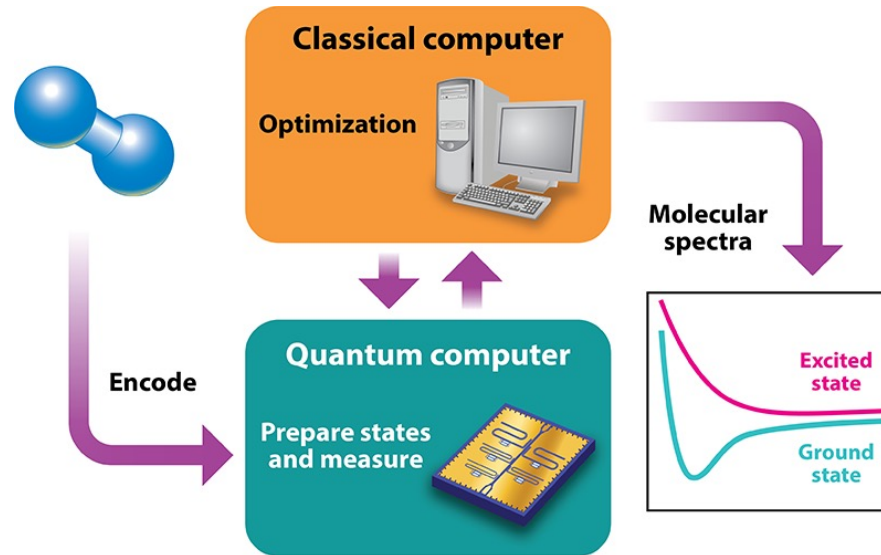
$$H = \sum h_{ij} \hat{a}_i^\dagger \hat{a}_j + h_{ijkl} \hat{a}_i \hat{a}_j \hat{a}_k^\dagger \hat{a}_l^\dagger$$

✓ Mapping to Qubit Hamiltonian →

$$H = \sum h_{\alpha}^i \sigma_{\alpha}^i + \sum h_{\alpha\beta}^{ij} \sigma_{\alpha}^i \sigma_{\beta}^j + \sum h_{\alpha\beta\gamma}^{ijk} \sigma_{\alpha}^i \sigma_{\beta}^j \sigma_{\gamma}^k + \dots$$

➤ **Advantages:**

- Extended to multiple qubits to calculate more complex problem
- Suitable for noisy intermediate-scale quantum devices



✓ Parameter optimization  $\vec{\theta}$

Image from  
Physics 11, 14 (2018)

✓ Store states  $|\psi(\vec{\theta})\rangle$  & Measure expected energy value  
 $\langle E \rangle_{\vec{\theta}}$

McClean., et al. *New J. Phys.* 18, 023023 (2016)  
Colless., et al. *Phys. Rev. X* 8.1 (2018): 011021  
Kandala., et al. *Nature* 549.7571 (2017):242  
O'Malley, et al. *Phys. Rev. X* 6.3 (2016): 031007