# VQE

## Variational Quantum Eigensolver

1、Electronic Structure Problem

2、First / Second Quantization

3、Fermion - Qubit.

4、Overall Workflow.

5. Demo.

# 1. Electronic Structure Problem

Time-dependent Shrodinger Equation.

(H)-(H) $\hat{H}\Psi(\vec{r},\vec{R},t) = i\hbar\frac{\partial}{\partial t}\Psi$

$\vec{r}$: electron
$\vec{R}$: nulei

Isolated, non-relativistic.

If $\hat{H}$ is time-independent:

$$\Psi = \sum_k C_k \Psi_k(\vec{r},\vec{R}) e^{-iE_k t/\hbar}$$

where $\hat{H}\Psi_k = E_k \Psi_k$

$Ax = \lambda x$ ; $E_k$: e-values
$\Psi_k$: e-vectors

Curse of Dimensionality:

(H)-(H); $\Psi = f(\vec{r_1}, \vec{r_2}, \vec{R_1}, \vec{R_2})$; 12-D; $10^{12}$

Protein: $\Psi \sim 10^5 D$; $10^{100000}$

Born-Oppenheimer Approx. ($M_n >> M_e$)

$$H\Psi(\vec{r}, \vec{R}) = E\Psi$$

$$H = \underbrace{T_n + V_{nn}}_{\text{offset}} + \underbrace{T_e + V_{ne} + V_{ee}}_{H_e(\vec{r}|\vec{R})}$$

$$T_e = -\frac{1}{2}\sum_{1}^{N_e} \nabla_i^2 \; ; \; V_{ne} = -\sum_{i}^{N_e}\sum_{1}^{N_n} \frac{Z_k}{|\vec{r}_i - \vec{R}_k|}$$

$$V_{ee} = \sum_{i>j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \; ; \; m_e = \hbar = e = 1$$

$$H_e \Psi_e(\vec{r}|\vec{R}) = E_e \Psi$$

Electronic Structure Problem.

## 2. First / Second Quantization.

Molecular Orbitals: One-electron Picture

mean-field.

$$\Phi(\vec{r}|\vec{R}) \approx \prod_{i}^{N_e} \Phi_i(\vec{r}_i|\vec{R})$$

— ↓ ↑ ⇅ STO-3G

⇅ ↑ ↓ —

# Basis Wavefunction (Slater Determinants)

$$\Psi(\vec{x}_1, \cdots, \vec{x}_n) = \frac{1}{\sqrt{n!}} \left| \Phi_i(\vec{x}_j) \right|$$

$\Phi_i \rightarrow$ orbital

$\vec{x}_j \rightarrow (\vec{r}_j, \sigma_j)$

$\sigma_j \downarrow$ spin.

## 2-electron Example

$$\Psi_{ij}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_i(x_1) & \phi_i(x_2) \\ \phi_j(x_1) & \phi_j(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}} (\phi_i(x_1)\phi_j(x_2) - \phi_i(x_2)\phi_j(x_1))$$

$$\Psi_{ij}(x_1, x_2) = -\Psi_{ij}(x_2, x_1) \quad \text{(Basis)}$$

$$\Phi(\vec{x}_1, \vec{x}_2) = \sum_{i>j=1}^{N_0} C_{ij} \Psi_{ij}(\vec{x}_1, \vec{x}_2)$$

## Fock or occupation space:

$$\Phi = \sum_{\bar{n}} C_{\bar{n}} |n_1, \cdots, n_{N_0}\rangle, \quad n_i \in \{0, 1\}$$

2-electron case

$$\Phi = \sum_{i<j} C_{ij} |0 \cdots 1_i \cdots 1_j \cdots 0\rangle$$

## First Quantization

$$\hat{H}\Phi(\vec{r}_1, \vec{r}_2) = \sum_{i>j=1}^{N_o} C_{ij} \hat{H} \Psi_{ij} = \sum_{i>j=1}^{N_o} \tilde{C}_{ij} \Psi_{ij}$$

Anti-symmetry enforced in the wave-function

## Second Quantization

$$\hat{a}_i^{+} | n_1 \cdots n_i \cdots n_{N_o} \rangle = \delta_{n_i,0} (-1)^{\sum_{j<i} n_j} | n_1 \cdots n_i+1 \cdots n_{N_o} \rangle$$

Anti-symmetry enforced in the properties of operators

First Quantization (Hamiltonian)

Slater-Condon Rules. $\quad \downarrow$ span $\{\phi_i(x_i)\}$

$$h_{pq} = \langle \phi_p | T_e + V_{ne} | \phi_q \rangle$$

$$= \int d\vec{x}\, \phi_p^*(\vec{x}) \left(-\frac{1}{2}\nabla^2 - \sum_{1}^{N_n} \frac{Z_k}{|\vec{r} - \vec{R}_k|}\right) \phi_q(\vec{x})$$

$$h_{pqrs} = \langle \phi_p \phi_q | V_{ee} | \phi_r \phi_s \rangle$$

$$= \iint d\vec{x}_1 d\vec{x}_2 \frac{\phi_p^* \phi_q^* \phi_r \phi_s}{|\vec{r}_1 - \vec{r}_2|}$$

$$\hat{H} = \sum_{i}^{N_e} \sum_{pq}^{N_o} h_{pq} |\phi_p^i\rangle\langle\phi_q^i| + \frac{1}{2} \sum_{i \neq j}^{N_e} \sum_{pqrs}^{N_o} h_{pqrs} |\phi_p^i \phi_q^j\rangle\langle\phi_r^i \phi_s^j|$$

Second Quantization (Hamiltonian)

$$\hat{H} = \sum\sum h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum\sum h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

Fermion-qubit mapping

Fock or occupation space:

$$\Phi = \sum_{\bar{n}} C_{\bar{n}} |n_1, \cdots, n_{N_o}\rangle, \quad n_i \in \{0, 1\}$$

$|0\rangle_j$ jth orbit not occupied

$|1\rangle_j$ jth orbit is occupied.

$$\hat{a}_j^\dagger \sim |1\rangle\langle 0|_j = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \frac{X_j - iY_j}{2}$$

to enforce anti-symmetry $\otimes Z_0 \otimes Z_1 \otimes \cdots \otimes Z_{j-1}$

# Parity Encoding

$|00\rangle_{j}\,;\ |11\rangle_{j-1\,j}$ j th orbit not occupied.

$|10\rangle_{j}\,;\ |01\rangle_{j-1\,j}$ j th orbit is occupied.

| string | parity |
|---|---|
| 0010 | 1 |
| 0110 | 0 |
| 1111 | 0 |
| 1110 | 1 |

$$\hat{a}_j^{\dagger} = |01\rangle\langle 00|_{j-1,j} - |10\rangle\langle 11|_{j-1,j}$$

$$= \frac{Z_{j-1} \otimes X_j + iY_j}{2} \otimes X_{j+1} \otimes \cdots \otimes X_{n-1}$$

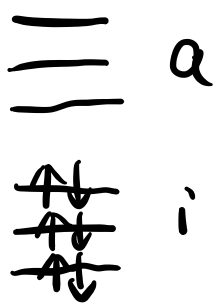
$$\hat{H} = \sum_{a} \omega_a \hat{P}_a \,; \quad P = \{I, X, Y, Z\}^{\otimes n}$$

$$E_0 \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E_{VQE} = \min_{\theta} \sum_{a} W_a \langle 0 | U^{\dagger}(\theta) \hat{P}_a U(\theta) | 0 \rangle$$

# Unitary Coupled Cluster

$$\hat{U} = \exp\left( \sum_{n} \hat{T}_n - \hat{T}_n^{\dagger} \right)$$




$$\hat{T}_1 = \sum_{ia} \theta_{ia} a_a^\dagger a_i$$

$$\hat{T}_2 = \sum_{ijab} \theta_{ijab} a_a^\dagger a_b^\dagger a_i a_j$$

$$\hat{U}_{SD} = \exp\left(\sum_{1}^{2} \hat{T}_n - \hat{T}_n^\dagger\right)$$

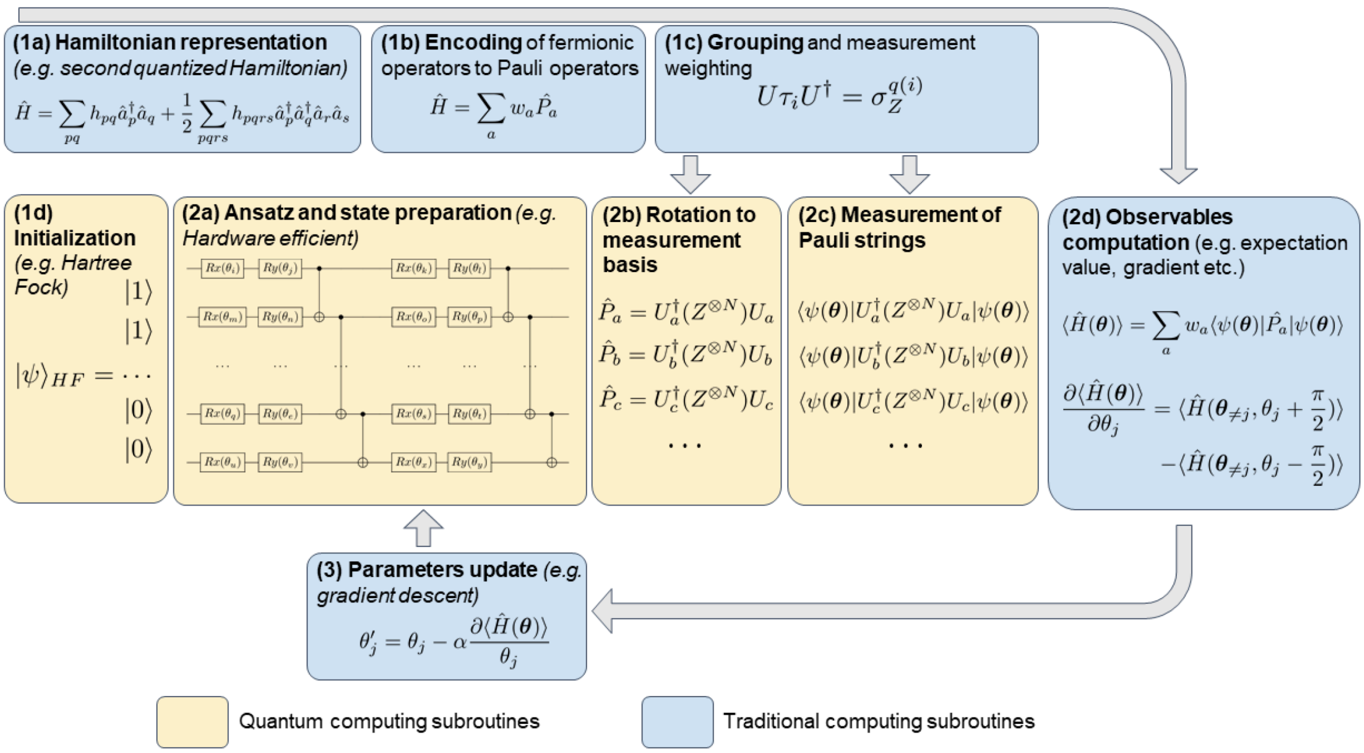
$$K_i^a = a_a^\dagger a_i - a_i^\dagger a_a$$

$$K_{ij}^{ab} = a_a^\dagger a_b^\dagger a_i a_j - a_j^\dagger a_i^\dagger a_b a_a$$

$$\hat{U}_{SD} \approx \left(\prod_{ia} e^{\theta_{ia} K_i^a / k} \prod_{ijab} e^{\theta_{ij}^{ab} K_{ij}^{ab} / k}\right)^k$$

Captures the essense of the electron correlations in the molecular.

Variational quantum eigensolver: review and best practices




# $\theta$s 100    Design of Ansatz

# Iterations 100    Optimizer

# Pauli Strings 100    Grouping / Shaddows

# Shots 1000    Gate error

$2 \times 10^9$ Measurements !!!