VQE continued

Recall from the previous lecture that we introduced the Variational Quantum Eigensolver. It is based on the variational principal which states that for any Hermitian H

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq \lambda_0$$ where λ_0 is the smallest eigenvalue of H.

Note: this holds for mixed states e.g. $\mathrm{Tr}(\rho(\vec{\theta})H) \geq \lambda_0$
AND $\mathrm{Var}[H]_\psi = \langle\psi|H^2|\psi\rangle - \langle\psi|H|\psi\rangle^2 \geq 0$
see MacClean et al 2015

[VQE]
This leads to the following algorithm:

1. Prepare $|\psi(\vec{\theta}_i)\rangle$ on a quantum computer where $\vec{\theta}$ are some adjustable programming parameters on the QPU
2. Measure $\langle H\rangle(\vec{\theta}_i) = \langle\psi(\vec{\theta}_i)|H|\psi(\vec{\theta}_i)\rangle$
3. Use a classical non-linear optimizer (such as Nelder-Mead) to determine $\vec{\theta}_{i+1}$ that decreases $\langle H\rangle(\vec{\theta})$
4. Iterate until convergence of $\langle H\rangle(\vec{\theta})$. Then $\langle H\rangle \approx \lambda_0$ and $|\psi(\vec{\theta}_i)\rangle \approx \vec{x}_0$

eigenstate of H s.t. $H\vec{x}_0 = \lambda_0\vec{x}_0$

VQE for Quantum Chemistry (Peruzzo et al 2013)

VQE was introduced in the context of a quantum chemistry simulation known as the electronic structure problem. In this problem one is given a description of a molecule (represented by its Hamiltonian) and then we are tasked to find the molecule's ground state and ground state energy.

Molecules + Electronic structure

A molecule is a quantum system w/ state $|\psi\rangle$. The time evolution is given by a unitary operator* $U(t) = e^{-iHt/\hbar}$

H is the Hamiltonian of the system and it describes the dynamics of the molecule.

* assuming the molecule is just sitting there w/ no time-dependance

H is a fixed Hermitian operator whose details are given by the dynamics of the physical system. In general

$$H = \underset{\substack{\nearrow \\ \text{kinetic} \\ \text{energy}}}{T} + \underset{\substack{\nwarrow\ \text{potential} \\ \text{energy}}}{V}$$

Becaus $H = H^{+}$ we can decompose H into a basis formed by its eigenvalues and eigenvectors

$$H = \sum_{E} E|E\rangle\langle E|$$

These are refferd to as the energy eigenstates and energies of the system. The smallest energy is called the ground state energy and is associated with the ground state eigenvector.

<u>Evolution</u> in quantum mechanics is described by the Schrödinger Equation

$$i\hbar \frac{d}{dt}|\psi\rangle = \underset{\uparrow\ \text{Hamiltonian}}{H}|\psi\rangle$$

Thus for any energy eigenstate

$$\frac{d|E_j\rangle}{dt} = -\frac{iH}{\hbar}|E_j\rangle = -\frac{iE_j}{\hbar}|E_j\rangle \Rightarrow |E\rangle \mapsto e^{-iE_jt/\hbar}|E\rangle$$

evolution is just multiplication by some overall phase factor.

In fact general evolution for a time-independent H is given by

$$|\psi\rangle \mapsto e^{-iHt/\hbar}|\psi\rangle$$

This is easy to see by expanding $|\psi\rangle$ into the eigenbasis of H.

When our system is a molecule the ground state tells us the most stable structure of the molecule which is useful for determining chemical properties like reaction rates, Defn Given a set of nuclear charges N_i and a number of electrons the Hamiltonian describing their interactions is*:

* in atomic units

$$H = \underbrace{-\sum_i \frac{\nabla^2_{R_i}}{2M_i}}_{\substack{\text{nuclear}\\\text{kinetic}}} \underbrace{-\sum_i \frac{\nabla^2_{r_i}}{2}}_{\substack{\text{electronic}\\\text{kinetic}}} \underbrace{-\sum_{ij} \frac{N_i}{|R_i - r_j|}}_{\substack{\text{attraction}\\\text{to nucleus}}} + \underbrace{\sum_{i,j>i} \frac{N_i N_j}{|R_i - R_j|}}_{\substack{\text{nuclear}\\\text{repulsion}}} + \underbrace{\sum_{i,j>i} \frac{1}{|r_i - r_j|}}_{\substack{\text{electron}\\\text{repulsion}}}$$

R_i = nuclear positions

r_i = electronic positions

M_i = nuclear masses

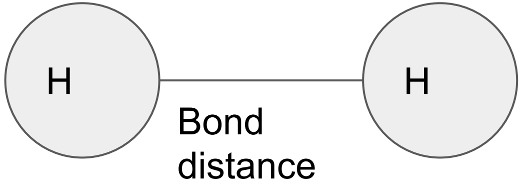
Typically chemists then make the Born-Oppenheimer approximation by assuming the nuclei are classical point charges w/ fixed positions R_i.

This is called first quantized form.

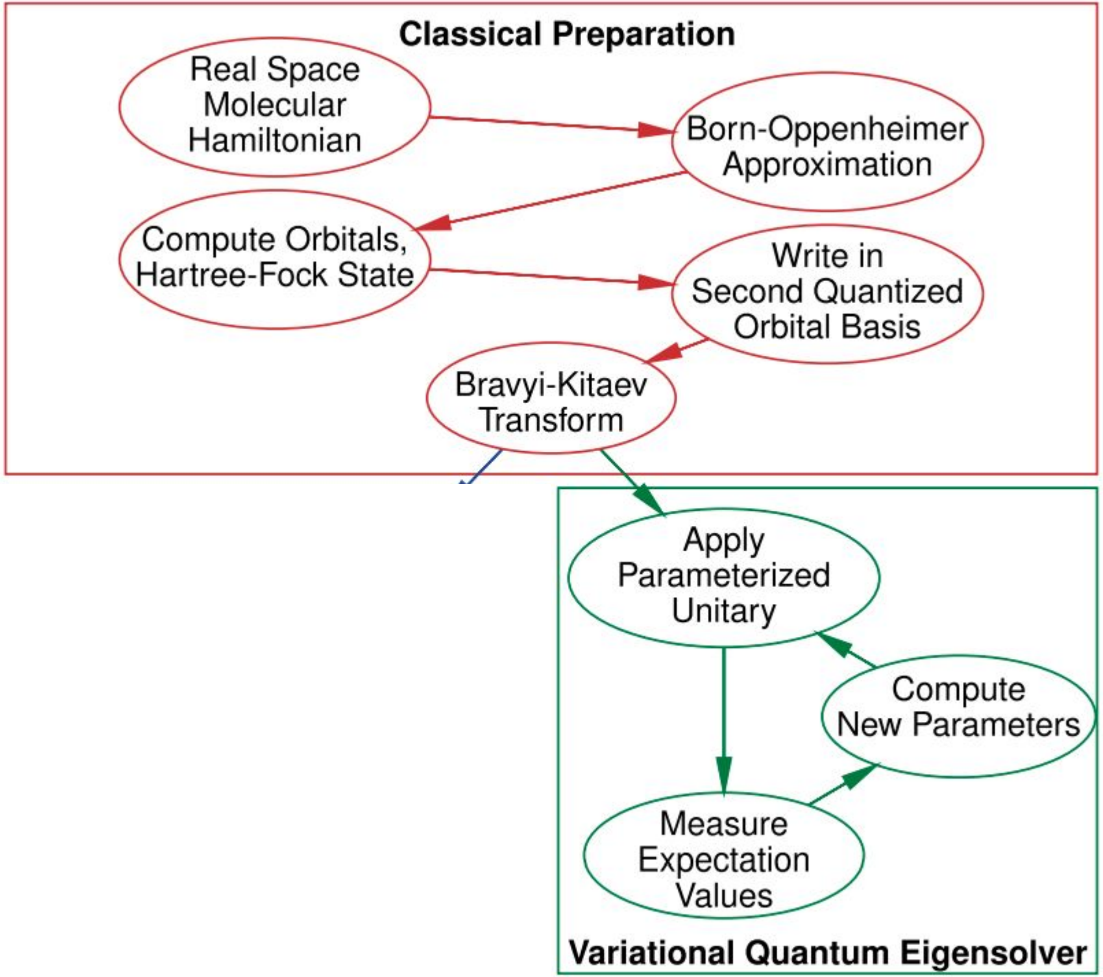
VQE H2 Example

How to find the ground state of H_2

O’Malley, P. J., et al (2016). Scalable quantum simulation of molecular energies. *Physical Review X*, *6*(3), 031007.



Steps for VQE


Classical Preparation
Real Space Molecular Hamiltonian
Born-Oppenheimer Approximation
Compute Orbitals, Hartree-Fock State
Write in Second Quantized Orbital Basis
Bravyi-Kitaev Transform
Apply Parameterized Unitary
Compute New Parameters
Measure Expectation Values
Variational Quantum Eigensolver

Step 1: Map into a Pauli representation of H

$$H = \sum_{i,j<i}^{N_n} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i=1}^{N_e} \frac{-\nabla^2_{r_i}}{2} - \sum_{ij}^{N_n,N_e} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j<i}^{N_e} \frac{1}{|r_i - r_j|}.$$

↓

$$\begin{aligned} H = {} & f_0 \mathbb{1} + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 \\ & + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 X_0 Z_1 X_2 + f_6 Y_0 Z_1 Y_2 \\ & + f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 \\ & + f_6 X_0 Z_1 X_2 Z_3 + f_6 Y_0 Z_1 Y_2 Z_3 + f_7 Z_0 Z_1 Z_2 Z_3 \end{aligned}$$

How many qubits are needed to simulate this?

Step 1: Map into a Pauli representation of H

$$H = \sum_{i,j<i}^{N_n} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i=1}^{N_e} \frac{-\nabla^2_{r_i}}{2} - \sum_{ij}^{N_n,N_e} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j<i}^{N_e} \frac{1}{|r_i - r_j|}.$$

$$\Big\downarrow$$

$$\begin{aligned} H = {} & f_0 \mathbb{1} + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 \\ & + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 X_0 Z_1 X_2 + f_6 Y_0 Z_1 Y_2 \\ & + f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 \\ & + f_6 X_0 Z_1 X_2 Z_3 + f_6 Y_0 Z_1 Y_2 Z_3 + f_7 Z_0 Z_1 Z_2 Z_3 \end{aligned}$$

Step 1: Map into a Pauli representation of H

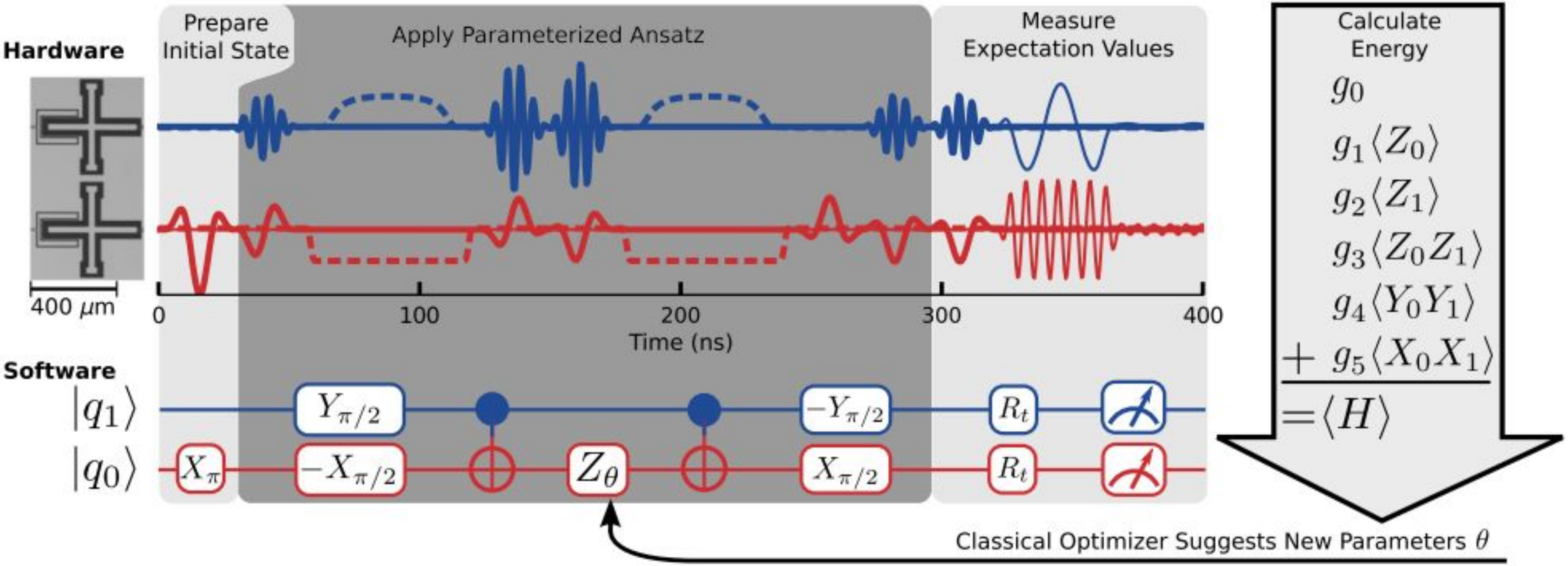
$$H = \sum_{i,j<i}^{N_n} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i=1}^{N_e} \frac{-\nabla_{r_i}^2}{2} - \sum_{ij}^{N_n, N_e} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j<i}^{N_e} \frac{1}{|r_i - r_j|}.$$

$$\Big\downarrow$$

$$\begin{aligned} H = {} & f_0 \mathbb{1} + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 \\ & + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 X_0 Z_1 X_2 + f_6 Y_0 Z_1 Y_2 \\ & + f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 \\ & + f_6 X_0 Z_1 X_2 Z_3 + f_6 Y_0 Z_1 Y_2 Z_3 + f_7 Z_0 Z_1 Z_2 Z_3 \end{aligned}$$

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

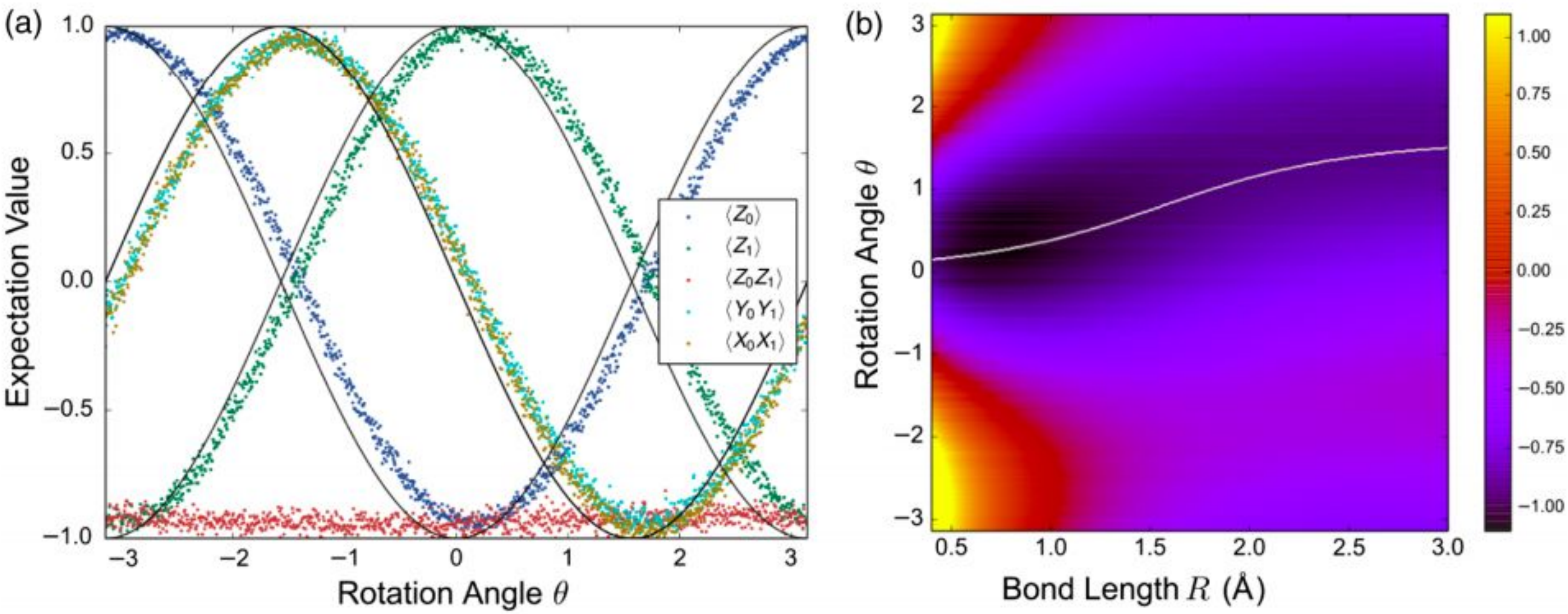
Step 2: Pick ansatz



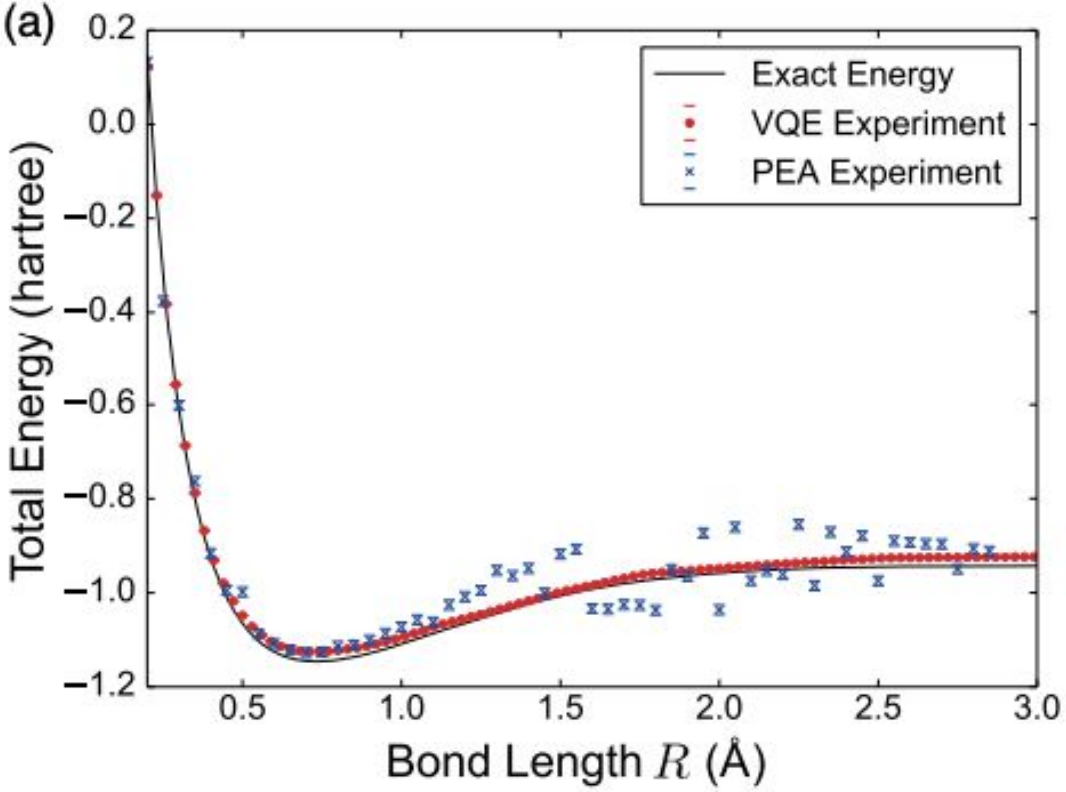
Remind Will to draw the circuit on the board

Step 3: Optimize Over Expectations

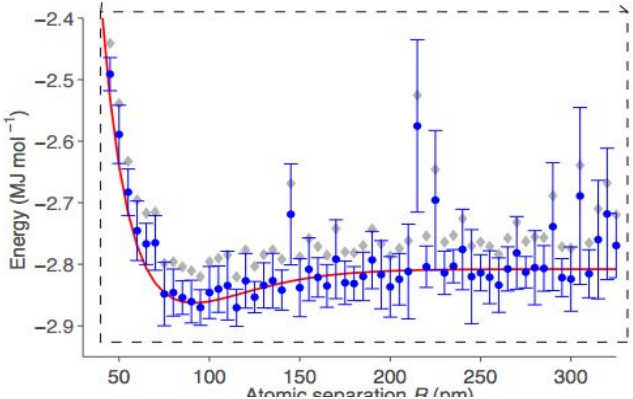
Step 3: ~~Optimize~~ Brute Force Over Expectations



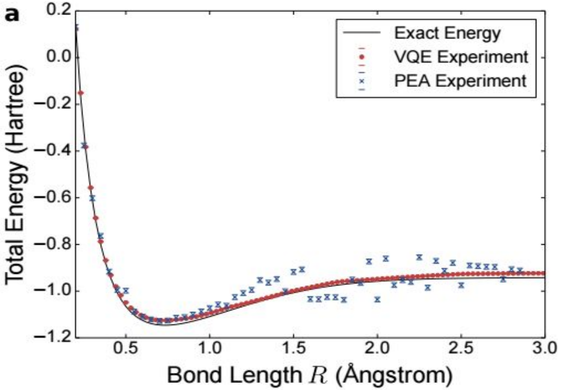
Step 3: Plot Optimum



VQE Simulations on Quantum Hardware

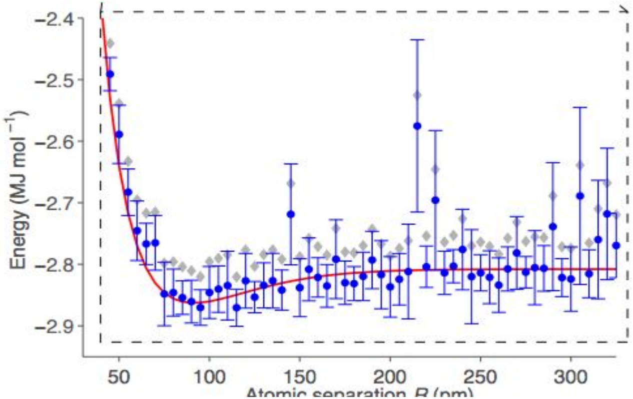


Peruzzo et al. 1304.3061

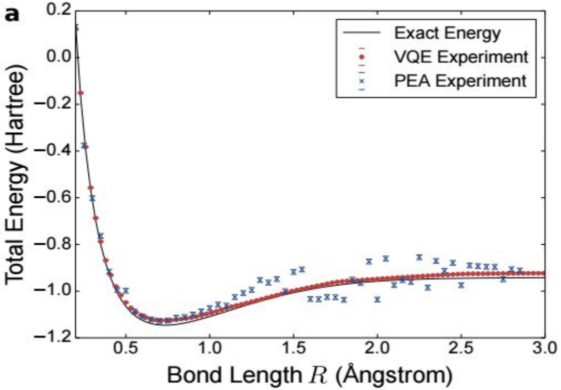


O'Malley et al. 1512.06860

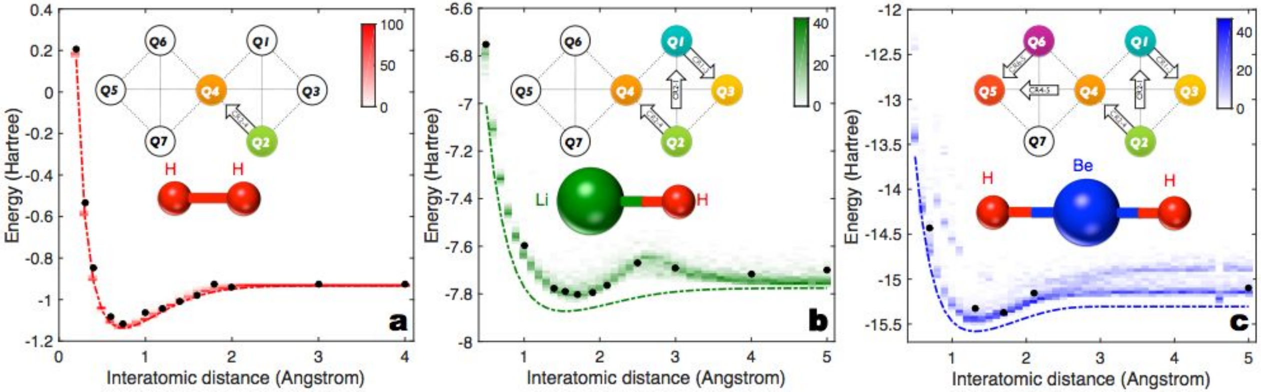
VQE Simulations on Quantum Hardware



Peruzzo et al. 1304.3061



O’Malley et al. 1512.06860



Kandala et al. 1704.05018

The Variational Quantum Eigensolver

Used for the electronic structure problem in quantum chemistry

1. MOLECULAR DESCRIPTION

e.g. Electronic Structure Hamiltonian

$$H = \sum_{i,j<i}^{N_n} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i=1}^{N_e} \frac{-\nabla^2_{r_i}}{2} - \sum_{ij}^{N_n,N_e} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j<i}^{N_e} \frac{1}{|r_i - r_j|}.$$

2. MAP TO QUBIT REPRESENTATION

e.g. Bravyi-Kitaev or Jordan-Wigner Transform

e.g. DI-HYDROGEN

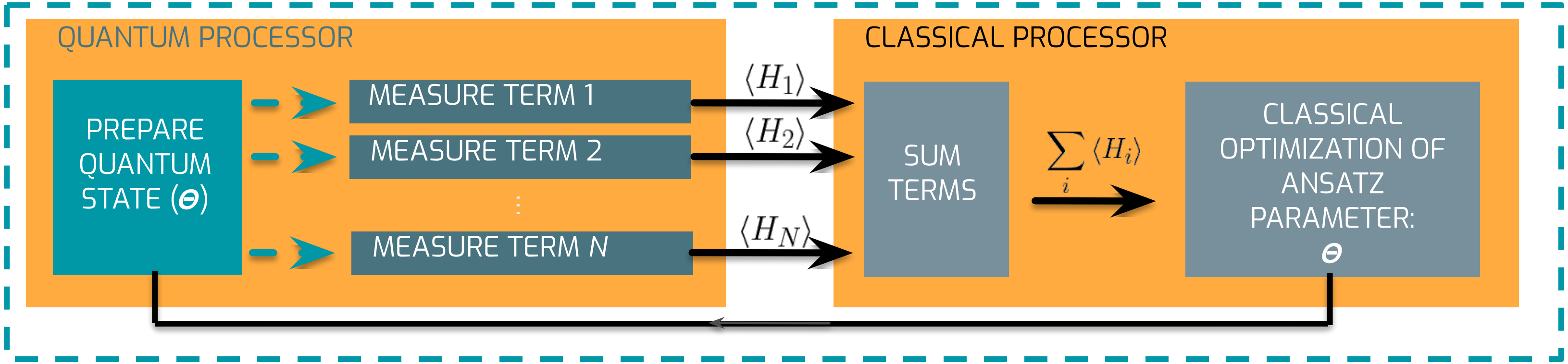
$$\begin{aligned} H = {} & f_0 \mathbb{1} + f_1 Z_0 + f_2 Z_1 + f_3 Z_2 + f_1 Z_0 Z_1 \\ & + f_4 Z_0 Z_2 + f_5 Z_1 Z_3 + f_6 X_0 Z_1 X_2 + f_6 Y_0 Z_1 Y_2 \\ & + f_7 Z_0 Z_1 Z_2 + f_4 Z_0 Z_2 Z_3 + f_3 Z_1 Z_2 Z_3 \\ & + f_6 X_0 Z_1 X_2 Z_3 + f_6 Y_0 Z_1 Y_2 Z_3 + f_7 Z_0 Z_1 Z_2 Z_3 \end{aligned}$$

3. PARAMETERIZED ANSATZ

e.g. Unitary Coupled Cluster
Variational Adiabatic Ansatz

$$\frac{\langle \varphi(\vec{\theta}) | \, H \, | \varphi(\vec{\theta}) \rangle}{\langle \varphi(\vec{\theta}) | \varphi(\vec{\theta}) \rangle} \geq E_0$$

4. RUN Q.V.E. QUANTUM-CLASSICAL HYBRID ALGORITHM



QUANTUM PROCESSOR

PREPARE QUANTUM STATE (*ϴ*)

MEASURE TERM 1

MEASURE TERM 2

⋮

MEASURE TERM *N*

$\langle H_1 \rangle$

$\langle H_2 \rangle$

$\langle H_N \rangle$

CLASSICAL PROCESSOR

SUM TERMS

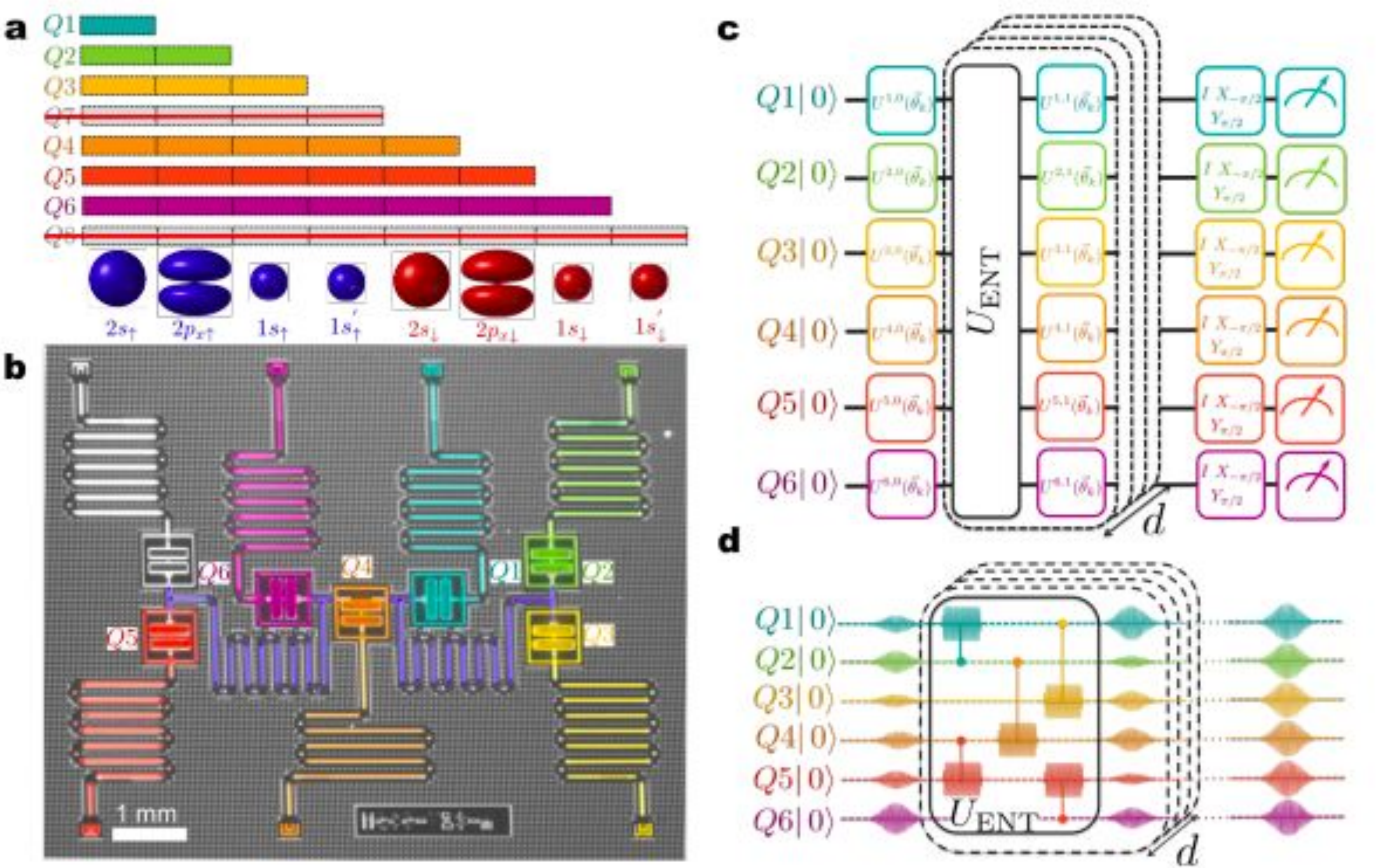
$\sum_i \langle H_i \rangle$

CLASSICAL OPTIMIZATION OF ANSATZ PARAMETER: *ϴ*

O'Malley, P. J. J., et al. (2015). Scalable Quantum Simulation of Molecular Energies. *arXiv:1512.06860.*
Wecker, D., et al. (2015). Progress towards practical quantum variational algorithms. *Physical Review A*, *92*(4), 042303.

McClean, J. R. et al. (2015). The theory of variational hybrid quantum-classical algorithms. *arXiv:1509.04279.*
Peruzzo, A., et al. (2014). A variational eigenvalue solver on a photonic quantum processor. *Nature communications*, *5*.

Example: Hardware Ansatz



Kandala, A., Mezzacapo, A., Temme, K., Takita, M., Brink, M., Chow, J. M., & Gambetta, J. M. (2017). Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets. *Nature*, *549*(7671), 242.

Mapping into Pauli representation

In second quantized form we project the electronic Hamiltonian into a spin-orbital basis. Thus instead of talking about realspace positions we talk about occupations of discrete orbitals.

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

where
a_i is the annihilation operator
$a_j^\dagger$ is the creation operator

This means roughly that $h_{pq} a_p^\dagger a_q$ is the "hopping" term for a single electron to go from orbital q to orbital p. and

$h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$ is the ~~[illegible]~~ hopping term for a pair of electrons to go together from orbitals r & s to orbitals p & q

This is sufficient as all interactions in this system are pairwise (Coulomb) interactions. There are no natively n-body interactions for ~~[illegible]~~ $n > 2$.

Electrons are Fermions and so their a_i and $a_i^\dagger$ form a Fermionic algebra w/ the following commutation relations:

$$\{a_p^\dagger, a_r\} = a_p^\dagger a_r + a_r a_p^\dagger = \delta_{p,r} \Rightarrow a a^\dagger = 1 - a^\dagger a$$

$$\{a_p^\dagger, a_r^\dagger\} = \{a_p, a_r\} = 0 \Rightarrow a_p a_p = a_p^\dagger a_p^\dagger = 0$$

Ideally we would hope to use our qubits to represent the occupations of the orbitals. (Rember that the Pauli exclusion principle states that each orbital can have at most two electrons) This would require $2N_e$ qubits for N_e electrons.

e.g.

Spin + and spin −

$$|0110\ldots\rangle$$

1 electron in orbital 0th

1 electron in orbital 1st

Pauli exclusion short proof

$\hat{n} = a_p^\dagger a_p$ gives the # of electrons in p and $a a^\dagger = 1 - n$ (easy to show)

$\hat{n}(1 - \hat{n}) = a^\dagger a a a^\dagger = 0$

Thus $n = 0$ or $n = 1$

We can then represent the creation and annihilation operators as

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

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

Where we have a Pauli operator representation

$$Q^+ = |1\rangle\langle 0| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \frac{1}{2}(X - iY)$$

$$Q^- = |0\rangle\langle 1| = \frac{1}{2}(X + iY)$$

However these don't immediately obey the Fermionic anticommutation relations.

Let's check this using the pyQuil pauli algebra package.

What's going on here is that Fermions have native properties that qubits don't. Namely that if you swap two fermions then you are supposed to acquire a phase. (For more details see Seeley, Richard, Love 2012)

To capture this we can define the Jordan-Wigner Transform

$$a_p^\dagger = \left(\prod_{m<p} Z_m\right) Q_p^+$$

$$a_p = \left(\prod_{m<p} Z_m\right) Q_p^-$$

JW-overhead

$O(n)$ Pauli operators per fermionic operator.

Alternative Bravyi-Kitaev transform

$\Theta(\log n)$ Pauli overhead per Fermionic operator

see (Seeley, Richard, Love 2012) for details

Once we have a Pauli operator representation we must ~~[illegible]~~ choosing an ansatz [see McClean, ~~[illegible]~~ et al 2015 for details]

Ex Variationally Prepared States

Let $|\Psi(\vec{\theta})\rangle = e^{-iV(\vec{\theta})}|0\rangle$ where

$V(\vec{\theta})$ is an adiabatic evolution into H e.g.

$$V(\vec{\theta}) = A(\theta)H_0 + B(\theta)H$$

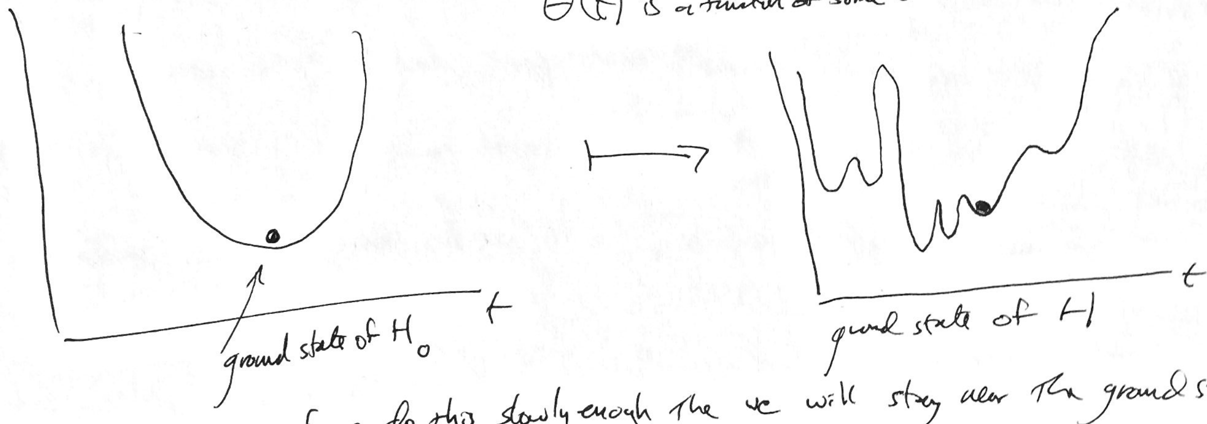
Our final target H as a Pauli decomposition

some initial simple H_0 like $H_0 = \sum_i X_i$

and $\theta \in [0,1]$ w/ $A(0) = B(1) = 1$

$A(1) = B(0) = 0$

$\theta(t)$ is a function of some t



Adiabatic theorem says if we do this slowly enough the we will stay near the ground state.

So we let VQE pick our annealing schedule mapping $e^{-iV(\vec{\theta})}$ into our parameterized gate set.

→ We could start in a state that is the best classically computable state

→ We can use this to produce states that are hard to make classically since adiabatic evolution is equal to general QC

(Aharonov et al 2007)

▷ We can also be inspired to choose states that are hard classically but we believe will be good models:

e.g. Unitary coupled cluster a unitary version of coupled cluster that is the gold standard classical method.

~~The idea is to explore~~ to some order k (where in practice k=2 works well)

$$|\psi_{cc}^{(k)}(\vec{\theta})\rangle = e^{T^{(k)}(\vec{\theta})}|\Phi_R\rangle$$

⌞ initial guess or "reference state"

↓ has $\mathcal{O}((3N)^k)$ real params and so is quadratic in params.

This can be turned into gates efficiently using, for example, Suzuki-Trotter.

▷ We can also choose an a-theoretical method and use a hardware ansatz (See slides and [Kandala et al 2017])

Solving for the optimal state

Non-convex optimization. More to come in future lectures.

In the meantime scipy.minimize has Nelder-Mead for small examples.