Quantum Computing Electronic Structure

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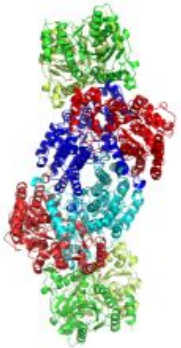
Why Electronic Structure?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- $400\ °C$
- $200\ atm$

~2% of World's total energy supply



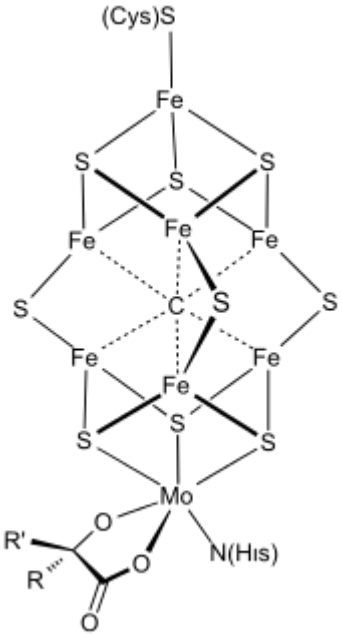
Nitrogenase

- $25\ °C$
- $1\ atm$

Why Electronic Structure?

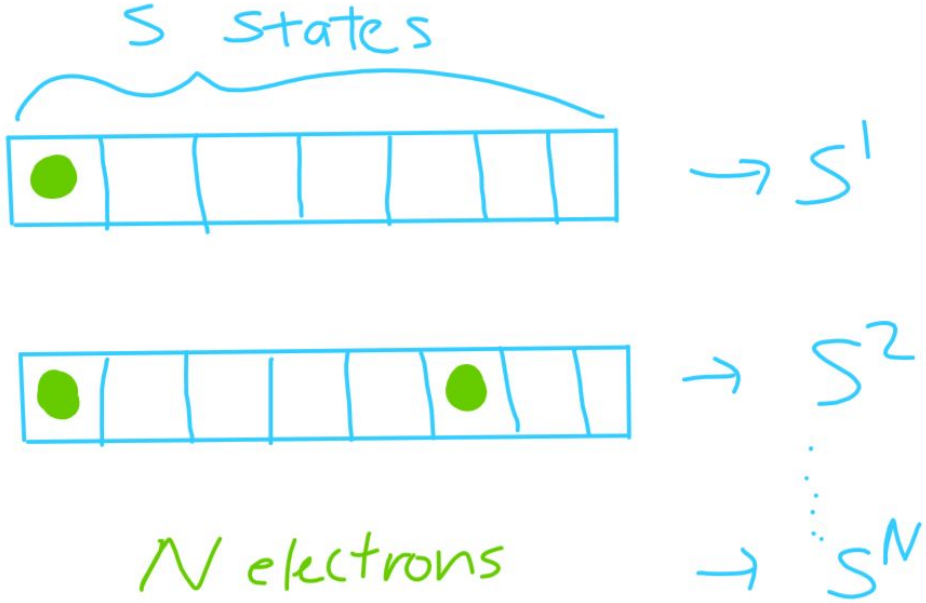
- **Catalytic mechanism** i.e. “how it accelerates the reaction” is not well understood.
- Crux: Composed of transition metal compounds that are **strongly correlated.**
- Classically: Intractable
- Quantum Computing: 150-200 *logical* qubits

FeMo-co:
Iron, Molybdenum, Carbon, Hydrogen , Oxygen



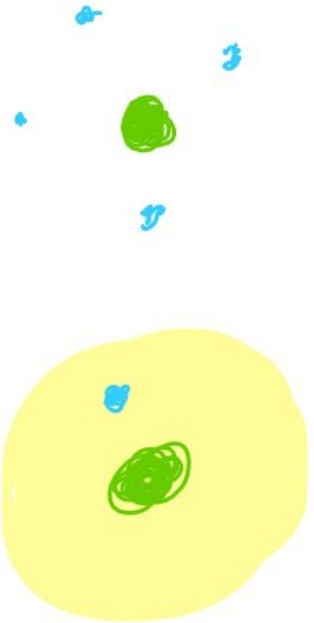
Why is it so hard?

- Exponential Problem
- Correlated motion
- Quantum properties like interference



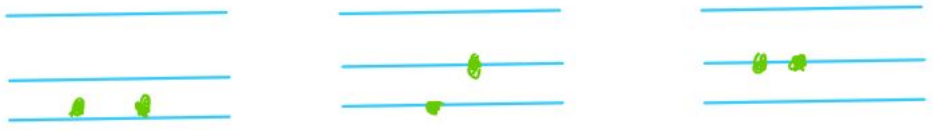
What are Chemists doing? Hartree Fock

- Treat effects of other electrons “on average”
- Uses Variational procedure to assign orbitals to electrons.
- Recovers 99% of total energy



What are Chemists doing? Configuration Interaction

- Recognizes contribution of excited states to **correlation energy**
- If given a complete basis set, provides **exact solution**



$$\Psi_{\mathrm{CI}} = a_0\Phi_{\mathrm{HF}} + \sum_{\mathrm{S}} a_s\Phi_s + \sum_{\mathrm{D}} a_d\Phi_d + \cdots = \sum_{i=1} a_i\Phi_i$$

What are Chemists Doing? Truncated CI and CC

Configuration **I**nteraction **S**ingles and **D**oubles

$$\Psi_{CISD} = (1 + T_1 + T_2)\Phi_0 = \Phi_0 + T_1\Phi_0 + T_2\Phi_0$$

$$\Psi_{CCSD} = e^{T_1+T_2}\Phi_0 = \Phi_0 + T_1\Phi_0 + (T_1^2 + T_2)\Phi_0 + (T_1T_2 + T_1^3)\Phi_0 + \ldots$$

Coupled **C**luster **S**ingles and **D**oubles

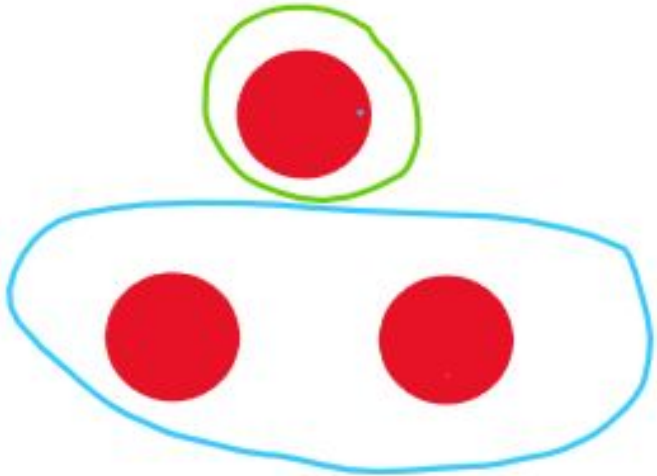
Single Excitations

Double Excitations

Triple Excitations

What are Chemists doing? Coupled Cluster

- Approximating excited states using smaller excitation operators
- Need to calculate the **cluster amplitudes** i.e. “weights of the excitations”
- Truncated CC methods break down if system is strongly correlated.



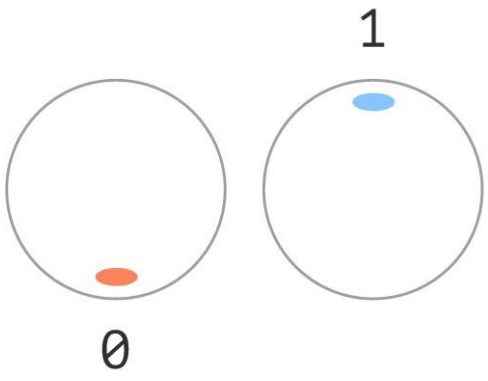
$$T_1 = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} t_a^i a_a^\dagger a_i$$

What we desire?

- Most classical methods either require **too many resources** or account for **too little correlation**.
- Goal: a **feasible** way of getting the to **exact** energy.
- Quantum Computers can help!

What is Quantum Computing?

Bit



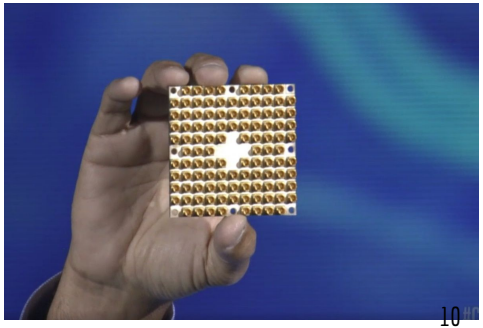
Qubit

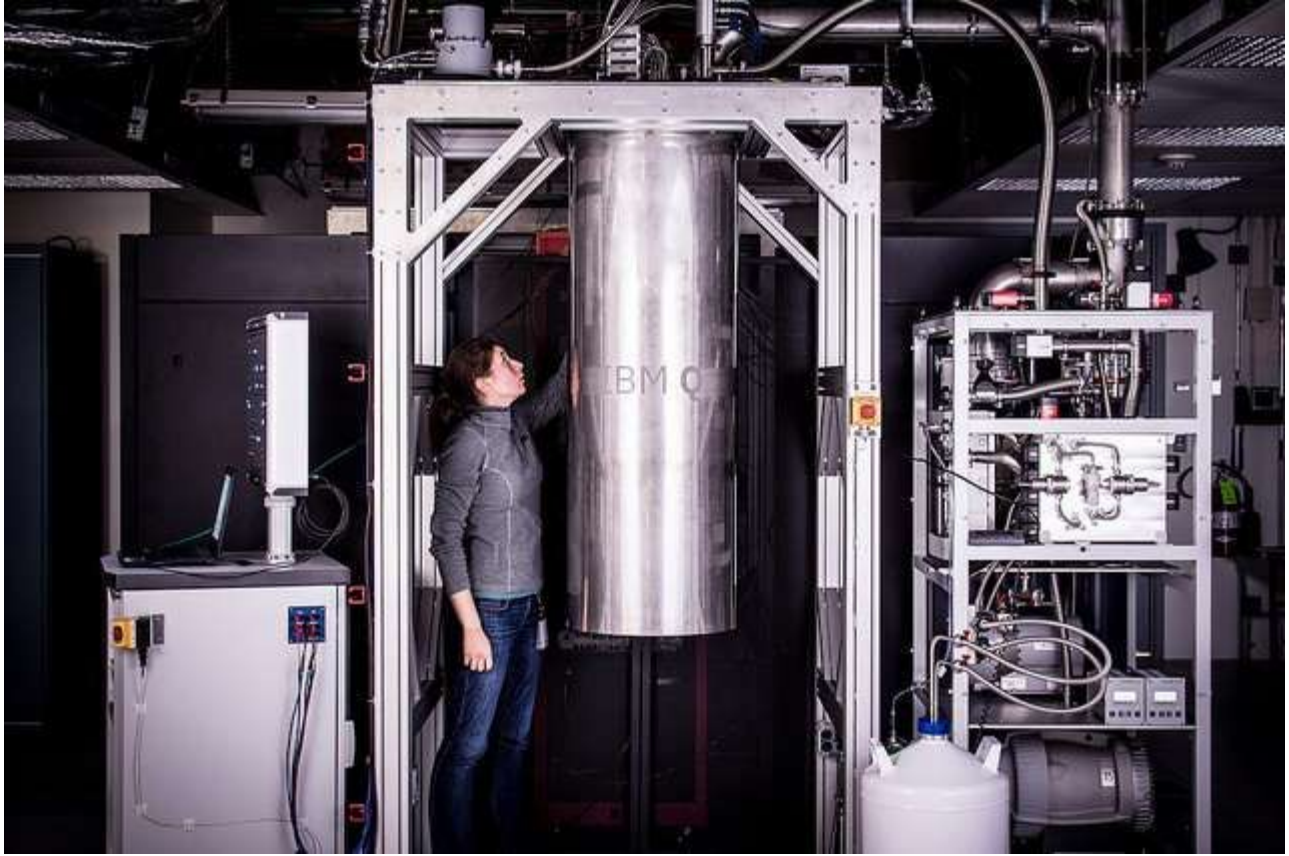
$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

$$|\alpha|^2 + |\beta|^2 = 1$$

Fuchs, Franz Georg, and Franz Georg FuchsEpost. “Diving Deep into Quantum Computing.” *#SINTEFblog*, 1 Apr. 2019, blog.sintef.com/digital-en/diving-deep-into-quantum-computing/.

Intel’s 49 qubit superconducting “quantum chip”





Dilution refrigerator that houses IBM’s quantum computer

https://phys.org/news/2017-05-ibm-powerful-universal-quantum-processors.html

Why Quantum Computing?

Myth : Quantum computer is a **faster** version of classical computer

Fact: Only efficient for **certain types** of problems and gate speed is almost 100 times slower than that of classical logic gates

Myth: Quantum Computing is **powerful** because it tries all the possible solutions in parallel.

Fact: Amplitudes leading to wrong answer “interfere destructively” with each other and the amplitudes leading to the right answer “interfere constructively”

Why Quantum Computing?

- A **n-qubit** quantum computer stores 2^n complex coefficients
- A **300 qubit** quantum computer stores as many coefficients as there are **protons in the universe**.
- However, we can only access n bits of information at the end.

$$|\psi_1\rangle = \alpha\,|0\rangle + \beta\,|1\rangle$$

$$|\psi_2\rangle = \alpha\,|00\rangle + \beta\,|01\rangle + \gamma\,|10\rangle + \delta\,|11\rangle$$

$$\vdots$$

$$|\psi_n\rangle = \sum_{i=1}^{2^n} \alpha_i \left|a_i^1 a_i^2 \cdots a_i^n\right\rangle$$

Second Quantization First Quantization Mess

Name- Tagging Electrons:

Electron 1 occupies Spin Orbital i.

Electron 2 occupies Spin Orbital j.

Exchange Symmetry Trap

What if I swap the 2 electrons?

$$\frac{1}{\sqrt{2}} \det \begin{pmatrix} \chi_i(\mathbf{x_1}) & \chi_j(\mathbf{x_1}) \\ \chi_i(\mathbf{x_2}) & \chi_j(\mathbf{x_2}) \end{pmatrix} = \frac{1}{\sqrt{2}} \left(\chi_i(\mathbf{x_1})\chi_j(\mathbf{x_2}) - \chi_j(\mathbf{x_1})\chi_i(\mathbf{x_2}) \right)$$

Second Quantization Better Bookkeeping

Avoid Name Tagging

“ Spin Orbital i and Spin Orbital j both have 1 electron.”

$$|11\rangle$$

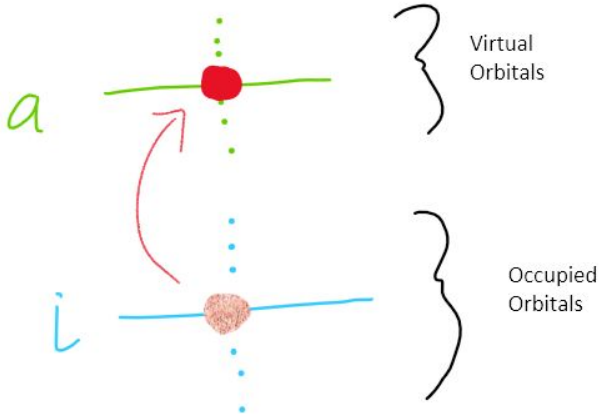
Exchange Symmetry Trap

What if I swap the 2 electrons?

Second Quantization

Fermionic Operators

- With elegant notation, come elegant operators.



Creation Operator

$$a^\dagger |0\rangle = |1\rangle$$

$$a |1\rangle = |0\rangle$$

Annihilation Operator

$$T_1 = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} t_a^i a_a^\dagger a_i$$

Second Quantization Anticommutation Relations

Exchange symmetry is satisfied by the following anticommutation relations:

$$a_i a_j + a_j a_i = 0$$

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$$

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$$

Second Quantization Quantum Encoding Methods

- Makes mapping from the fermionic **Fock Space** to **Hilbert space** of qubits **efficient**.
- Second Quantized methods include **Jordan Wigner**, **Parity basis** and **Bravyi Kitaev** encodings.
- Methods differ on number of qubit operations to realise fermionic operator

Jordan Wigner

$$\begin{bmatrix} o_0 \\ o_1 \\ o_2 \\ o_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 1 \\ 1 \end{bmatrix}$$

Parity Basis

$$\begin{bmatrix} o_0 \mod 2 \\ o_0 + o_1 \mod 2 \\ o_0 + o_1 + o_2 \mod 2 \\ o_0 + o_1 + 0_2 + o_3 \mod 2 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 0 \\ 1 \end{bmatrix}$$

Quantum Encoding Mapping Operators

- Under Jordan Wigner encoding, qubits represent spin orbitals.
- To add and remove electrons from them, we act on qubits with combinations of pauli gates.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

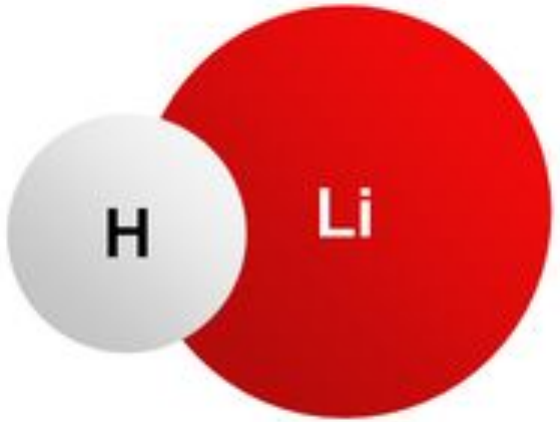
Pauli Matrices

$$a^\dagger = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \frac{\sigma^x - i\sigma^y}{2}$$

$$a = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \frac{\sigma^x + i\sigma^y}{2}$$

Variational Quantum Eigensolver Simulation

- Using simulators (ideal quantum computers) to calculate energy of LiH molecule as we pull the lithium and hydrogen atom apart.
- In this simulation, we are working with
  - 4 qubits
  - 12 spin orbitals (1s, 2s, 2p)
  - 4 electrons



https://en.wikipedia.org/wiki/Lithium_hydride

Variation Quantum Eigensolver (1)

Find the eigenvalue E

$$H\psi = E\psi$$

Find Parameters $\vec{t} = \{t_i\}$ such that we minimize

$$\langle \psi(\vec{t}) | H | \psi(\vec{t}) \rangle$$

1. **Prepare** a state with a given a set of parameters
2. **Act** on the state with the Hamiltonian.
3. **Measure** the expectation value.
4. **Find** *better* parameters for the next iteration.

State Preparation Reference State

- Reference state is generally chosen as the **hartree fock state** because of its high overlap with the ground state.

State Preparation UCCSD

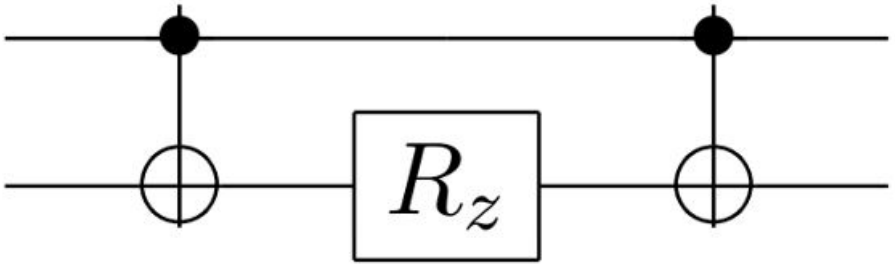
- Since quantum gates are reversible and hence unitary operators, we need the coupled cluster operator be unitary.

$$U(\vec{t}) = e^{T-T^\dagger} = e^{\sum_j t_j(\tau_j - \tau_j^\dagger)}$$

$$\Psi = e^{T-T^\dagger}\Phi_0$$

State Preparation Why UCCSD?

$$e^{i(\sigma_z \otimes \sigma_z)} \longrightarrow$$



Measurement

Decompose *the* ***H*** *into local Hamiltonians* H_i.

Convert *those local Hamiltonians* H_i *into Qubit Hamiltonians* O_i

Measure *the expectation value of each* O_i *and add them up to get the energy*

$$E = \sum_i h_i \langle O_i \rangle$$

Measurement Example

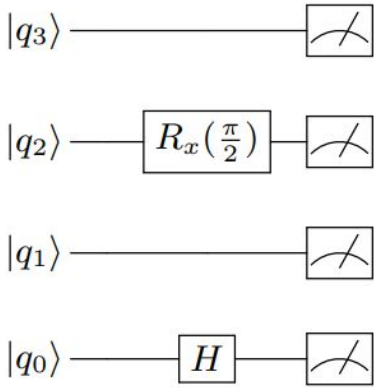


Figure 2. Circuit illustrating the measurement of the term $\sigma_3^z\sigma_2^y\sigma_1^z\sigma_0^x$ in the Z basis. We must apply H or $R_x(-\frac{\pi}{2})$ gates (or equivalent) to change basis when measuring Pauli-Y and Pauli-X operations.

Example: Deconstructing Hamiltonian into tensor products of identity and pauli matrices

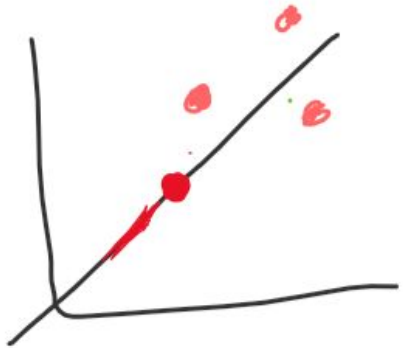
$$H = -0.2IIII - 0.1IIII\sigma_z - 0.0031II\sigma_z\sigma_x + \ldots$$

Optimization

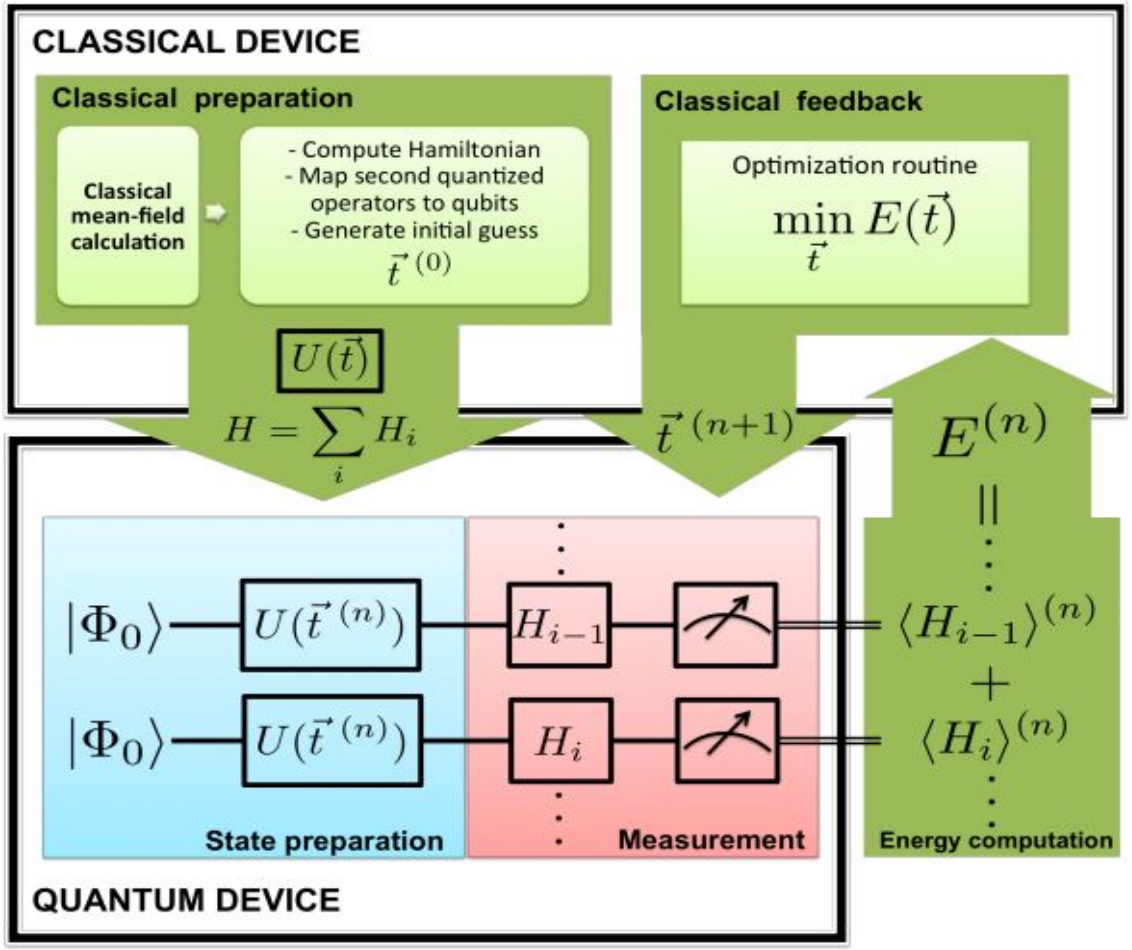
a) “Robustness” against noise

b) Number of Function Evaluations

Direct Search Algorithms



Gradient Descent Algorithms

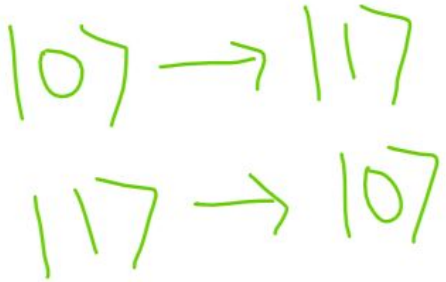


Romero, et al. "Strategies for Quantum Computing Molecular Energies Using the Unitary Coupled Cluster Ansatz." *ArXiv.org*, 10 Feb. 2018, arxiv.org/abs/1701.02691.

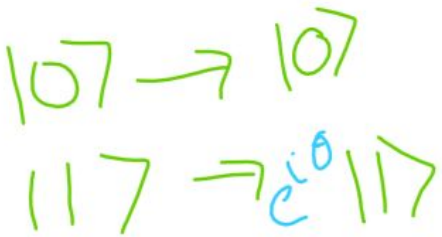
Quantum Error

- **Environment** can change the state of qubits, resulting in errors to our computations.
- These errors are usually a combination of phase flip and bit flip.
- Example: Thermal Relaxation error

Bit Flip



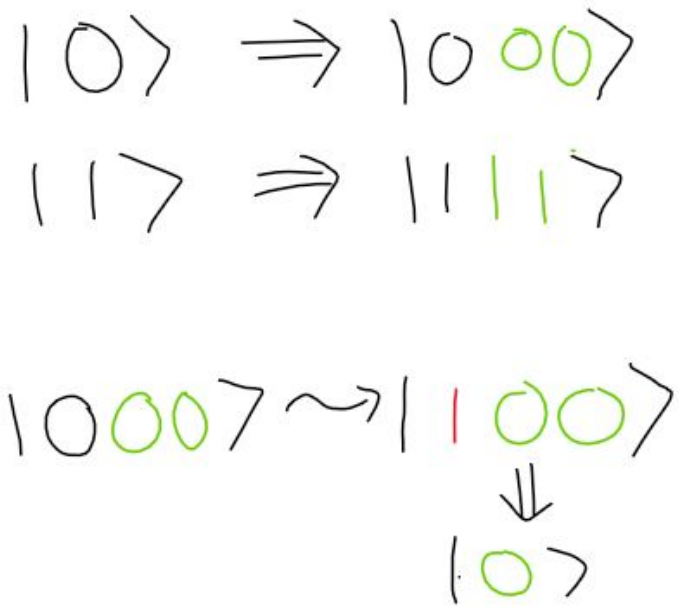
Phase Flip



Quantum Error Correction

- Fixing quantum errors using additional *ancilla* qubits
- May need up to 1000 helper qubits to correct for 1 qubit
- Near term quantum computers (NISQ devices) will only contain ~ 50-100 qubits.

Example:

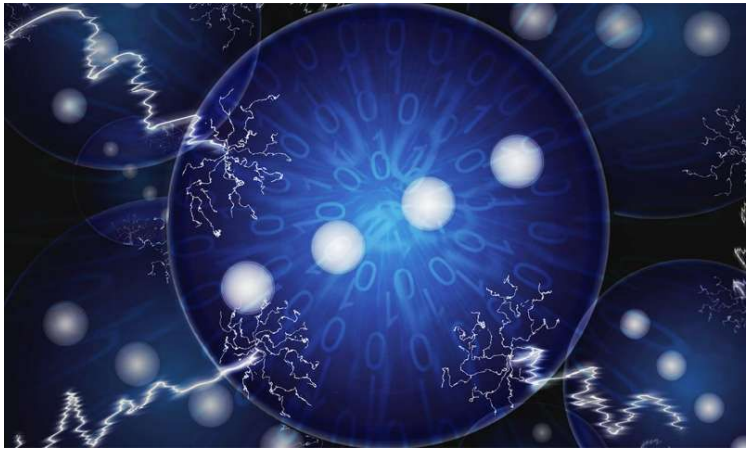


Quantum Error Mitigation

- For low depth (small) circuits, techniques like
  - Extrapolation
  - Probabilistic Error Cancellation
  - Quantum Subspace Expansion

  require a multiplicative overhead in number of measurements to mitigate errors.

- Hence, error mitigation does not require as many resources as error correction



https://phys.org/news/2017-11-ion-qubits-early-glimpse-quantum.html

Future for Chemistry Simulations

- Collaboration between chemists, physicists and computer scientists to improve upon
  - **State Preparation** like UCCSD ansatz
  - **Error Mitigation** techniques to reduce noise burden
  - **Systems and observables** more resistant to noise than others. (Eg: Dipole moment and charge density)

“It’s like the first day we see a plane flying, and we want to go to the moon.” - Marco De Vivo, theoretical chemist at Genoa, on quantum computing and drug discoveries

References

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arXiv:1701.02691v2 **[quant-ph]**

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