

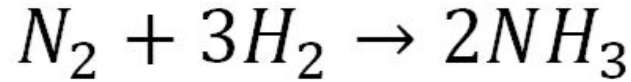


# Quantum Computing Electronic Structure

Eesh Gupta



# Why Electronic Structure?



- 400 °C
- 200 atm

↖  
~2% of World's  
total energy  
supply



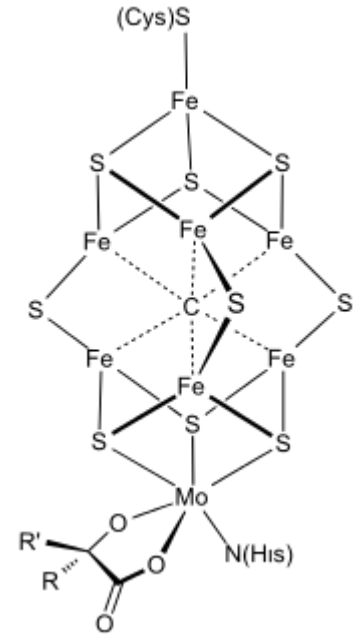
Nitrogenase

- 25 °C
- 1 atm

# Why Electronic Structure?

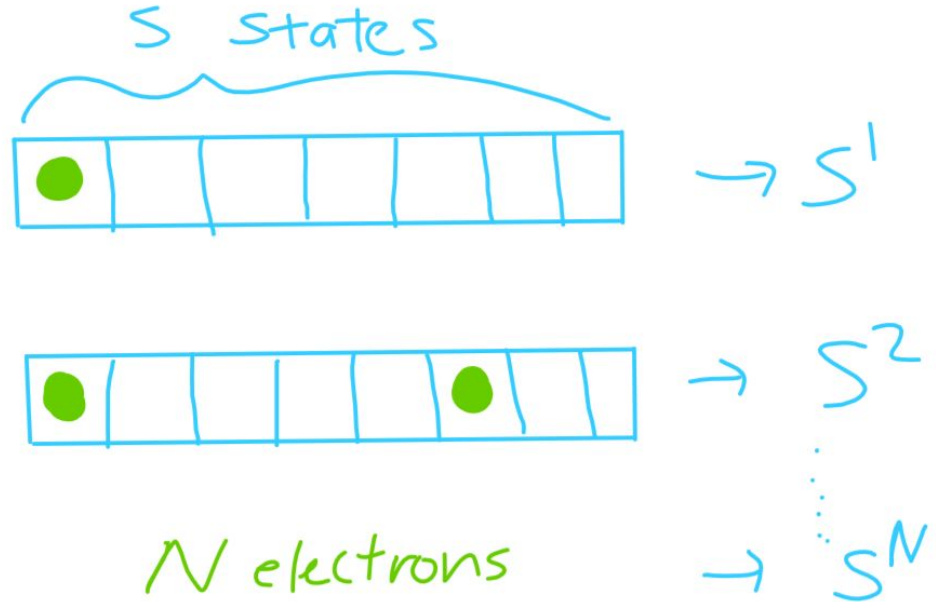
- **Catalytic mechanism** i.e.  
“how it accelerates the reaction” is not well understood.
- Crux: Composed of transition metal compounds that are **strongly correlated**.
- Classically: Intractable
- Quantum Computing: 150-200 *logical* qubits

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



# Why is it so hard?

- Exponential Problem
- Correlated motion
- Quantum properties like interference



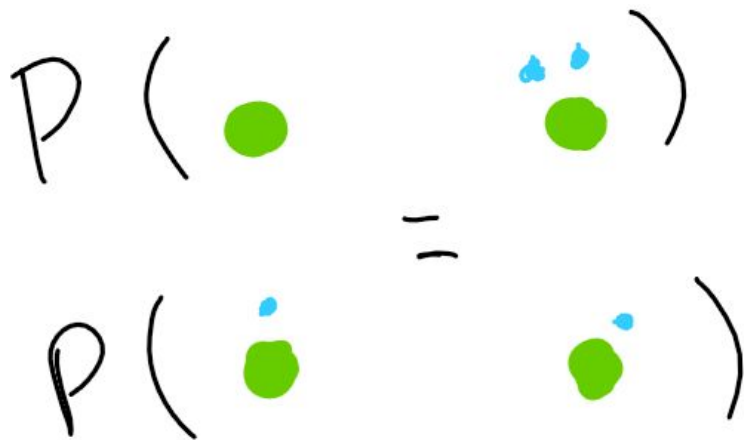
# What are Chemists doing? Hartree Fock

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

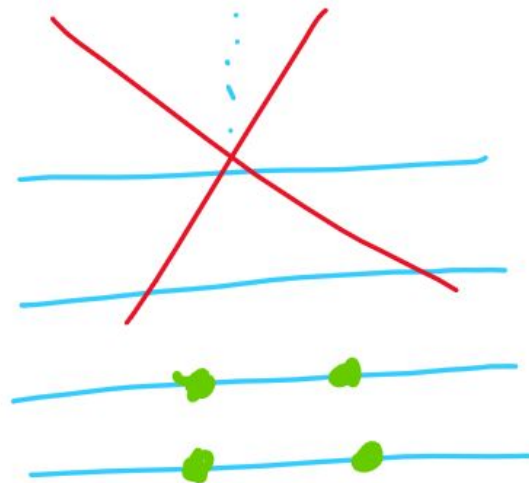


# What are Chemists doing?

Failures of Hartree Fock



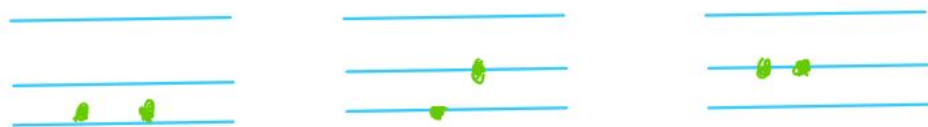
Limited Correlation



Pigeonholing n electrons into n orbitals

# What are Chemists doing? Configuration Interaction

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



$$\Psi_{\text{CI}} = a_0 \Phi_{\text{HF}} + \sum_{\text{S}} a_{\text{s}} \Phi_{\text{s}} + \sum_{\text{D}} a_{\text{d}} \Phi_{\text{d}} + \cdots = \sum_{i=1} a_i \Phi_i$$

$\downarrow$   $\downarrow$

$T_1 \Phi_{\text{HF}}$   $T_2 \Phi_{\text{HF}}$

# What are Chemists Doing? Truncated CI and CC

Configuration  
Interaction  
Singles and  
Doubles



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

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

Coupled  
Cluster  
Singles  
and Doubles



Single  
Excitations



Double  
Excitations



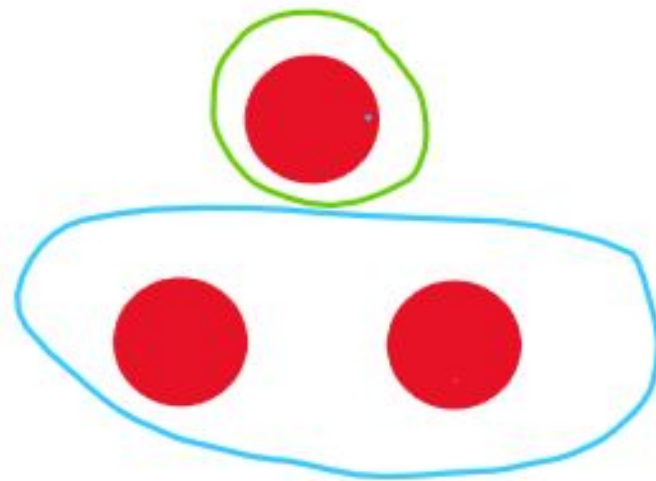
Triple  
Excitations



# 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.



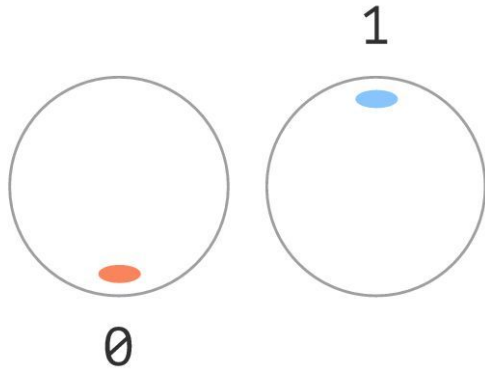
$$T_1 = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} t_a^i a_a^\dagger a_i$$

# What we desire?

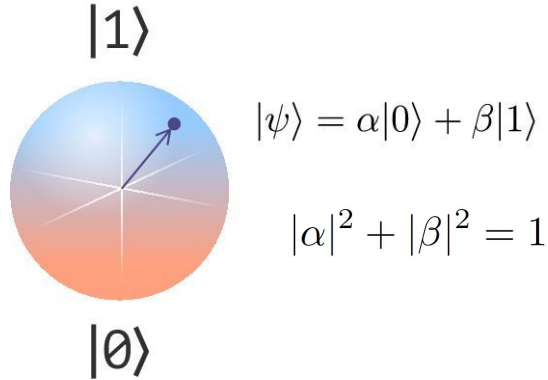
- Most classical methods either require **too many resources** or account for **too little correlation**.
- Goal: a **feasible** way of getting the to **exact** energy.
- Quantum Computers can help!

# What is Quantum Computing?

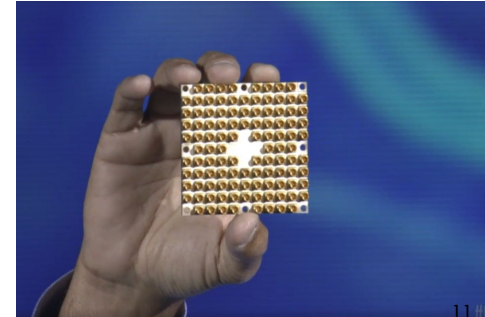
Bit



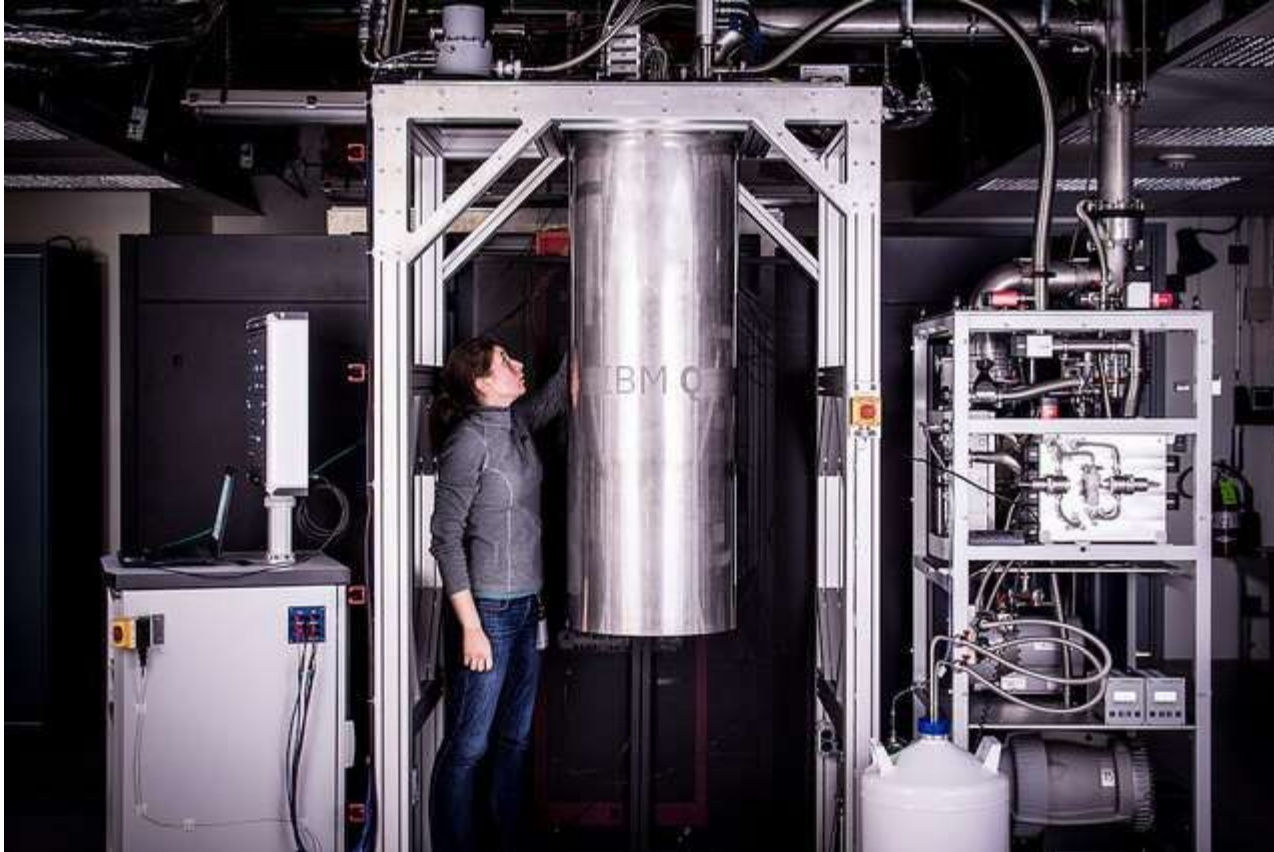
Qubit



Intel's 49 qubit  
superconducting  
"quantum chip"



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/](https://blog.sintef.com/digital-en/diving-deep-into-quantum-computing/).



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.

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

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

$$\vdots$$

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

# 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?



$$\frac{1}{\sqrt{2}} \det \begin{pmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{pmatrix} = \frac{1}{\sqrt{2}} (\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2))$$

# 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

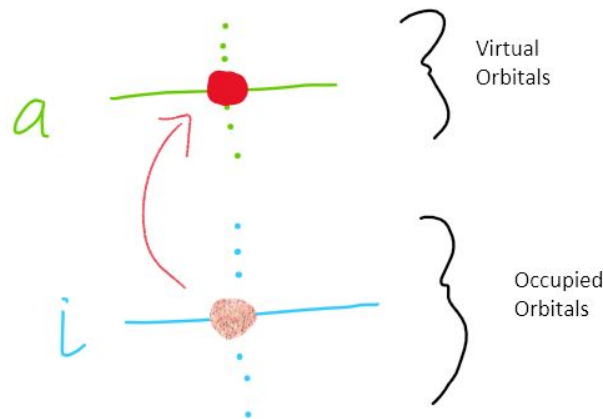
- With elegant notation, come elegant operators.

Creation  
Operator

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

Anihilation  
Operator

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



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

# 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

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

# 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.

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

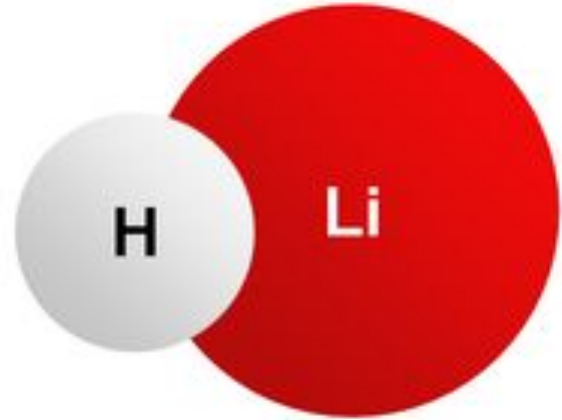
$$a = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \frac{\sigma^x + i\sigma^y}{2}$$

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

Pauli  
Matrices

# 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](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.

QC  
CC

# 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.

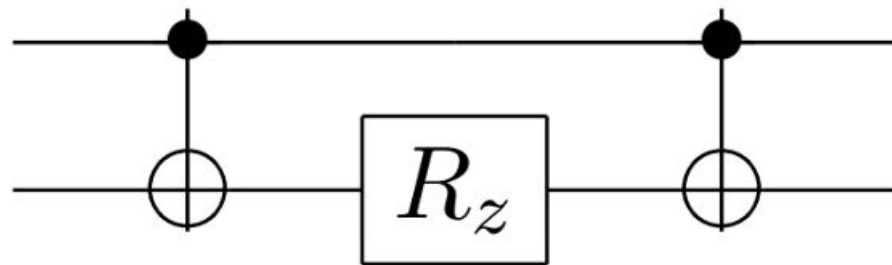
$$U(\vec{t}) = e^{T-T^\dagger} = e^{\sum_j t_j (\tau_j - \tau_j^\dagger)}$$

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



# 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

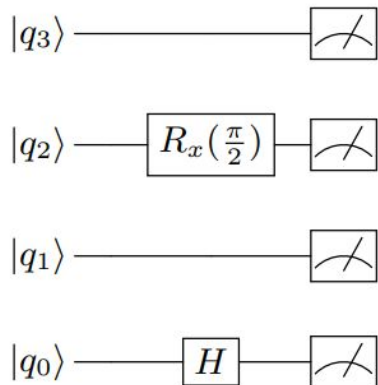


Figure 2. Circuit illustrating the measurement of the term  $\sigma_3^z \sigma_2^y \sigma_1^z \sigma_0^x$  in the Z basis. We must apply  $H$  or  $R_x(-\frac{\pi}{2})$  gates (or equivalent) to change basis when measuring Pauli-Y and Pauli-X operations.

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

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

# Optimization

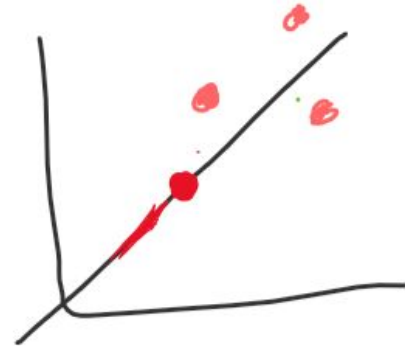
- a) “Robustness” against noise
- b) Number of Function Evaluations

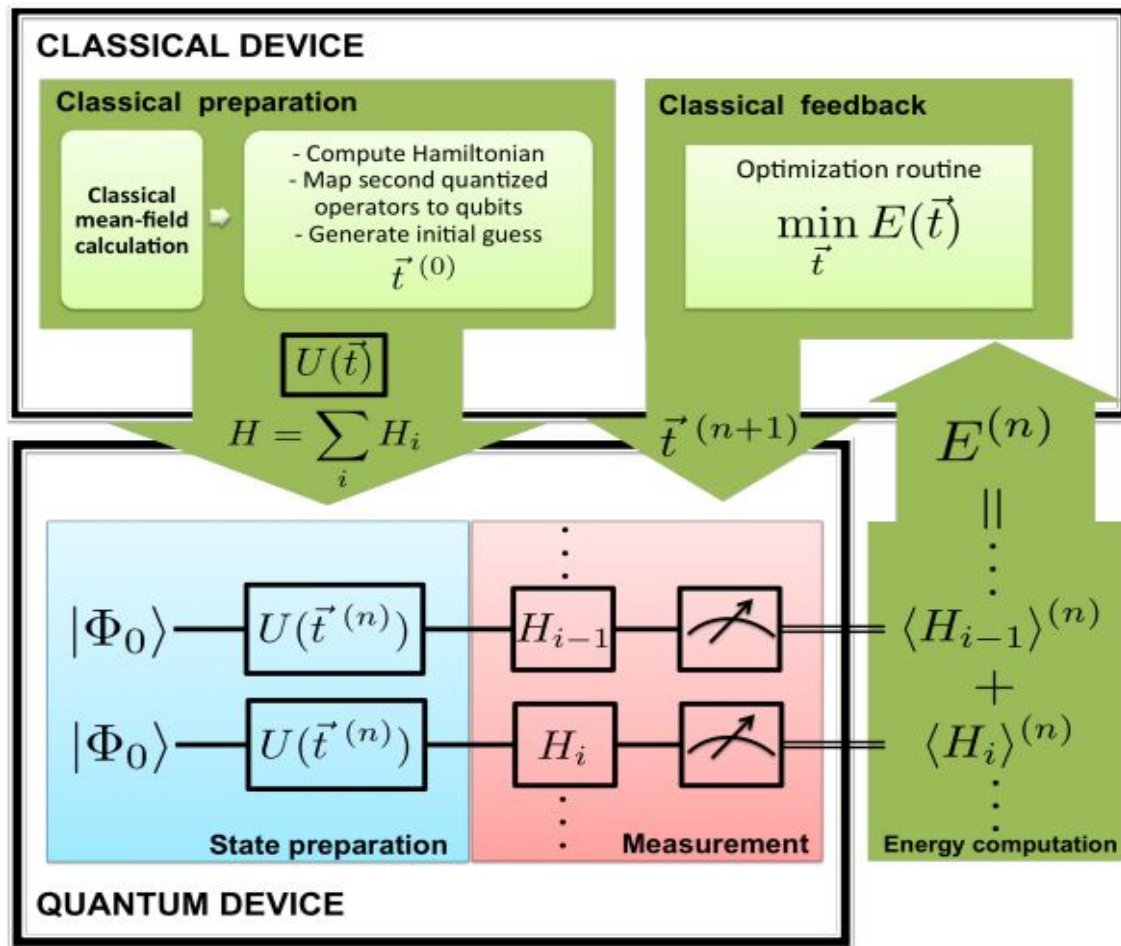


*Direct Search Algorithms*

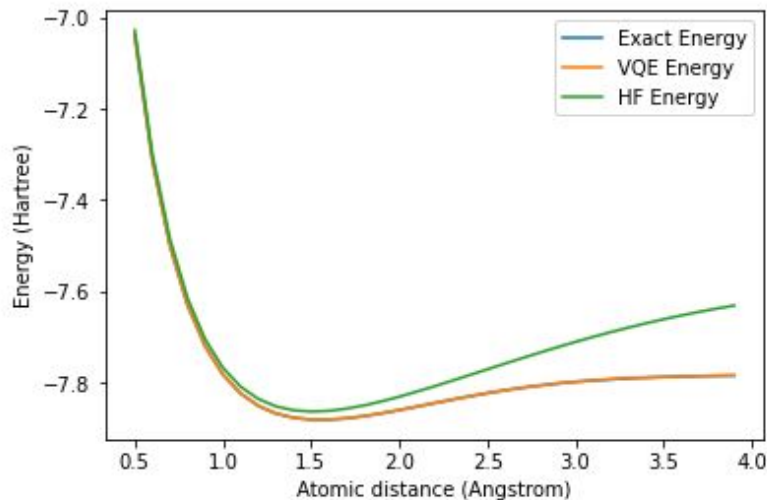


*Gradient Descent Algorithms*

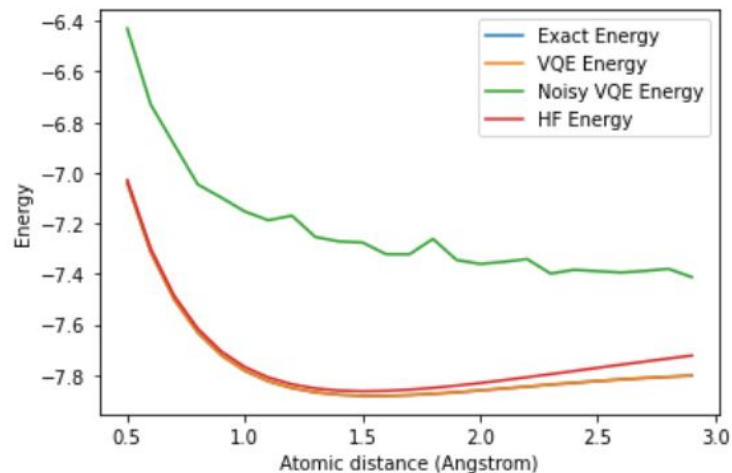




# Dissociation Curves for LiH



**Ideal** Quantum Computer



**Noisy** Quantum Computer  
(Simulation of Noise on Yorktown Machine)

# 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

$$\begin{aligned} |0\rangle &\rightarrow |1\rangle \\ |1\rangle &\rightarrow |0\rangle \end{aligned}$$

Phase Flip

$$\begin{aligned} |0\rangle &\rightarrow |0\rangle \\ |1\rangle &\rightarrow e^{i\theta} |1\rangle \end{aligned}$$

# 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:

$$|0\rangle \Rightarrow |000\rangle$$

$$|1\rangle \Rightarrow |111\rangle$$

$$|000\rangle \rightsquigarrow |100\rangle \downarrow |0\rangle$$

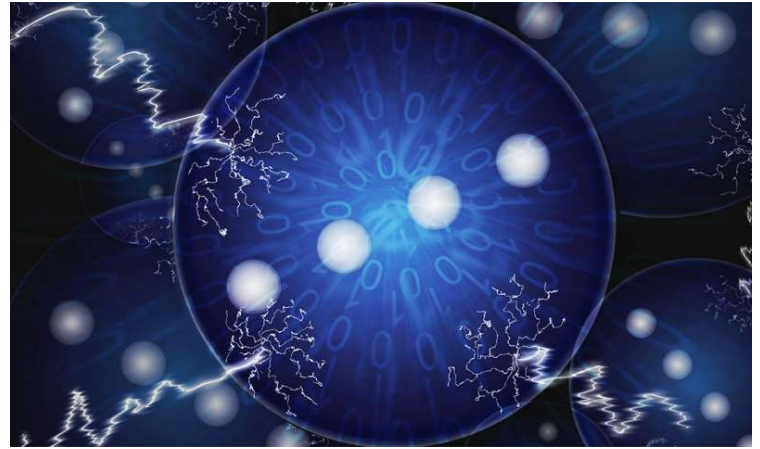


# Quantum Error Mitigation

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

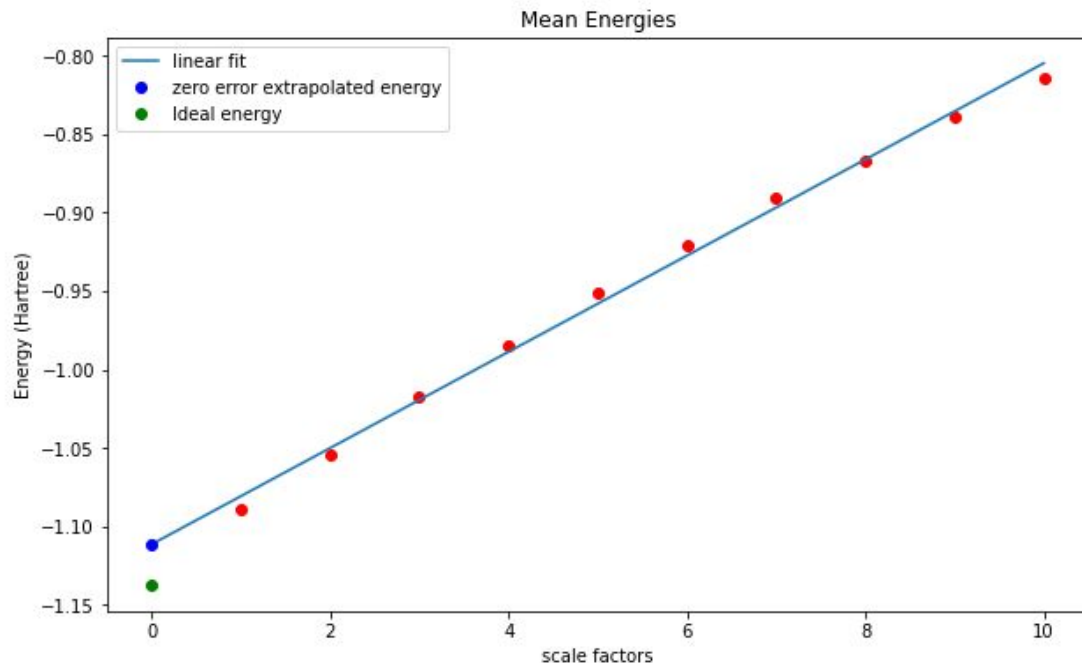
require a multiplicative overhead in number of measurements to mitigate errors.

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



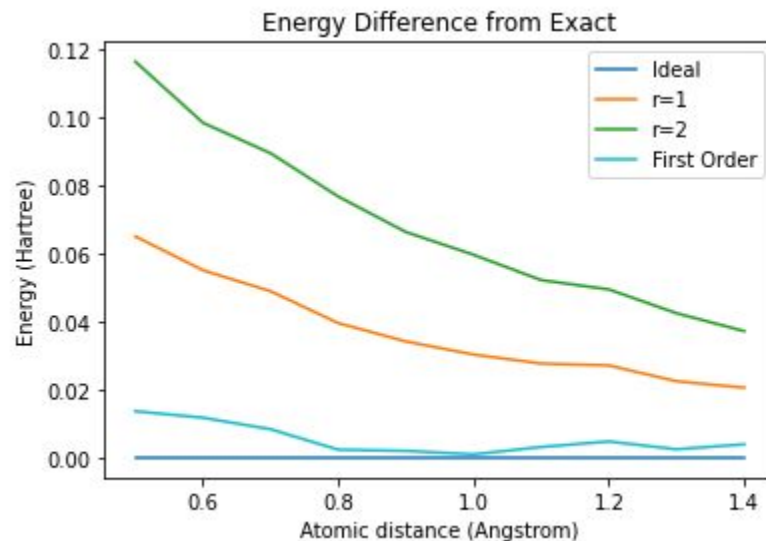
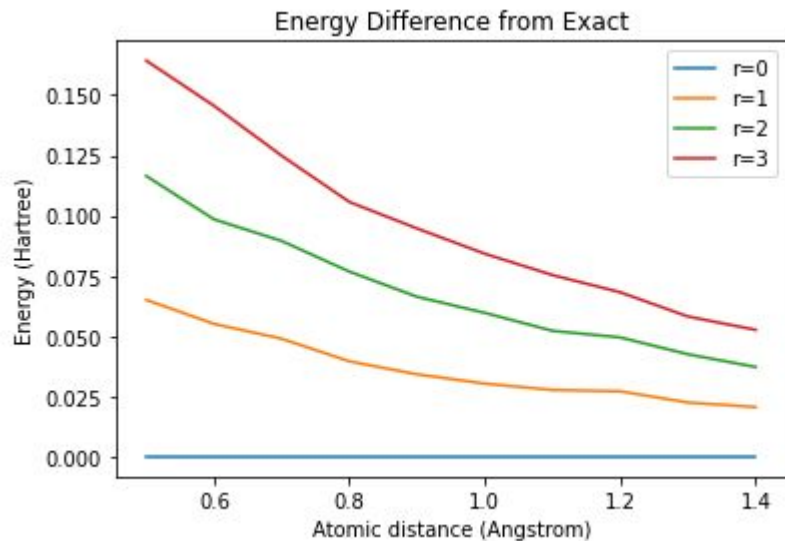
<https://phys.org/news/2017-11-ion-qubits-early-glimpse-quantum.html>

# Extrapolation What?



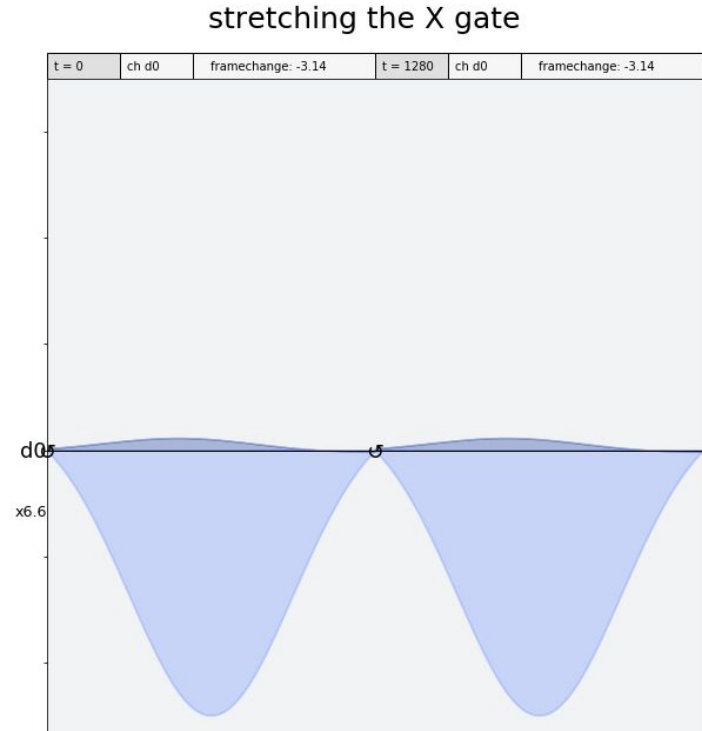
Deliberately make noise worse in order to improve results.

# Extrapolation In Action on H2



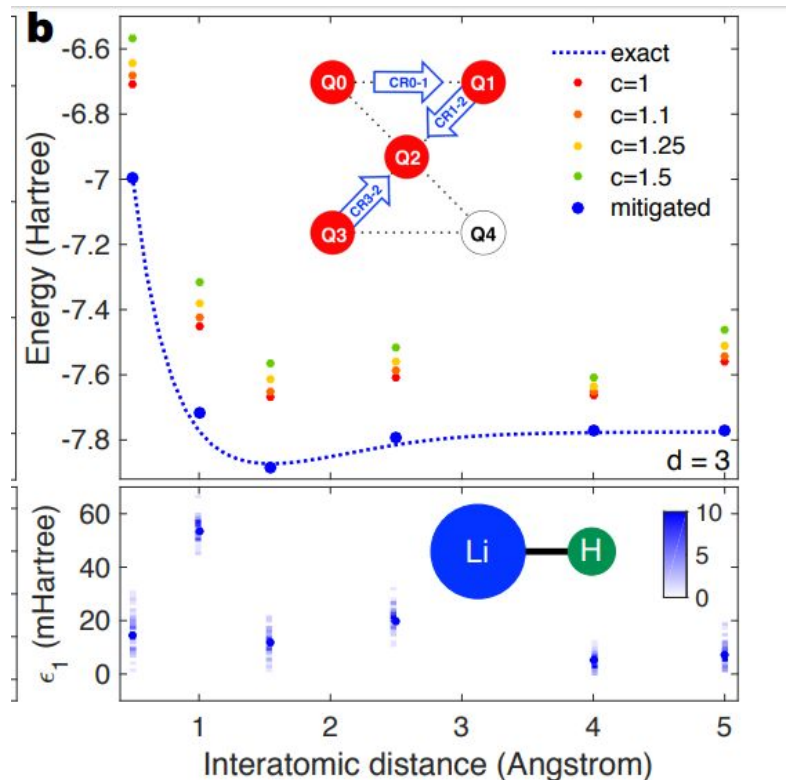
# Extrapolation Noise Amplification

- Every gate operation on the IBMQ devices is executed using **microwave pulses**.
- Stretching these pulses will “**slow down**” the gate operations, giving qubits more time to talk to the environment.
- Hence, stretching pulses amplifies noise.



# Extrapolation

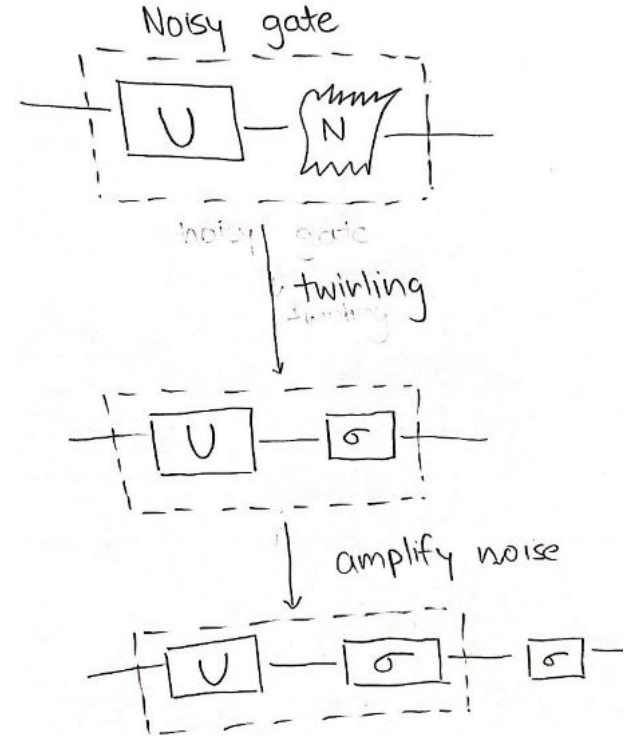
Pulse Stretching and VQE



# Extrapolation

Noise Amplification

- **Reformulate** the **error rate** of gate  $U$  as probability of adding some pauli gate  $P$  after gate  $U$
- Then amplifying the noise rate is really **increasing the probability** of adding pauli gates in the circuit.



# Extrapolation

First Order Example

$$\hat{E}(\lambda) = E^* + a_1\lambda + a_2\lambda^2 + \dots + a_n\lambda^n + \dots$$

$$\hat{E}(2\lambda) = E^* + 2a_1\lambda + 4a_2\lambda^2 + \dots + 2^n a_n\lambda^n + \dots$$

$$\hat{E}^1 = 2\hat{E}(\lambda) - \hat{E}(2\lambda) = E^* + -2a_2\lambda^2 - 6a_3\lambda^3 + \dots$$

Put another way,

$$E^* = \hat{E}^1 + 2a_2\lambda^2 + 6a_3\lambda^3 + \dots$$

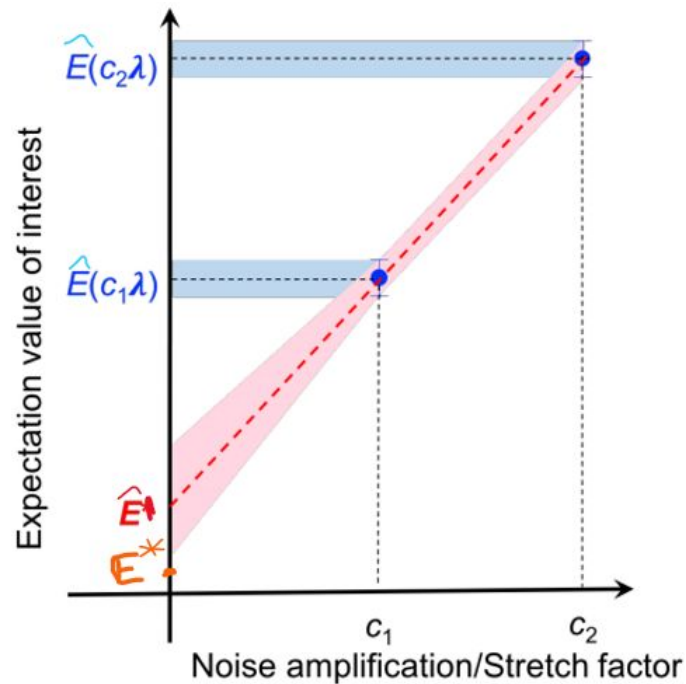
# Extrapolation First Order Example

Before:

$$E^* = \hat{E}(\lambda) + O(\lambda)$$

After:

$$E^* = \hat{E}^1 + O(\lambda^2)$$





# Extrapolation Why

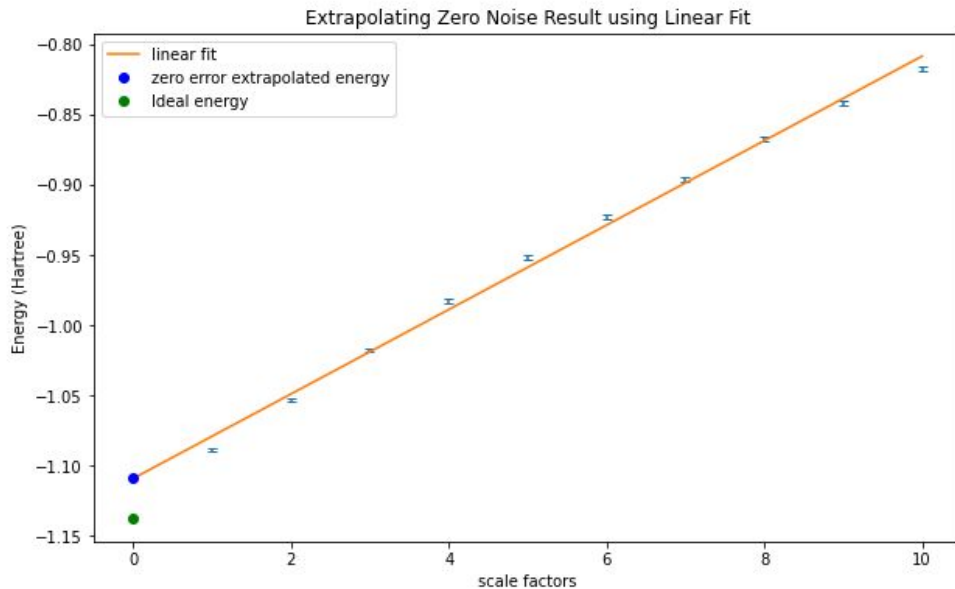
- Extrapolation assumes:
  - Error rate is very small
  - Type of error is consistent with amplified noise

$$E(\lambda) = E^* + a_1\lambda + a_2\lambda^2 + \dots + a_n\lambda^n + \dots$$

# Extrapolation

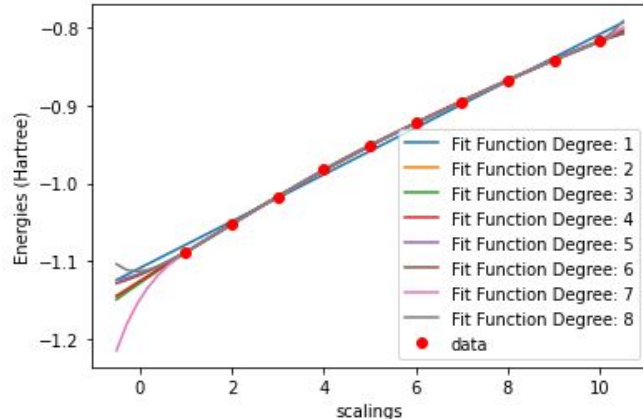
Curve Fitting Problem

1. Assuming we can scale noise as shown, linear fit doesn't look very good. Is there a **better polynomial fit** for the data?
2. Is this the best zero noise approximation? Can we get a **better approximation for the zero error result** using other polynomial fits?



# Extrapolation Better Polynomial Fit?

- Currently using **Chi-Square goodness of fit** test and **F test** to compare different polynomial fits.

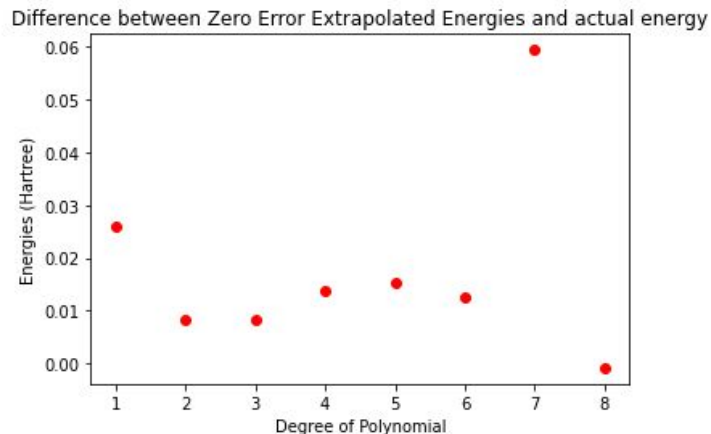
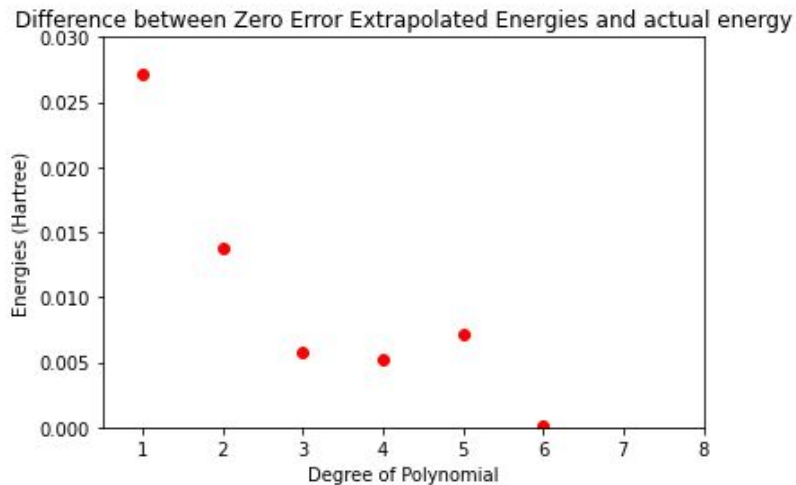


```
F stat for degree 1 vs 2:  
270.16843452608595  
More param is good!  
F stat for degree 2 vs 3:  
0.05396235567804251  
More param is good!  
F stat for degree 3 vs 4:  
3.6399493133582186  
More param is good!  
F stat for degree 4 vs 5:  
0.12556026296551012  
More param is bad!  
F stat for degree 5 vs 6:  
-0.010076728818806788  
More param is good!  
F stat for degree 6 vs 7:  
1.5914264395575415  
More param is bad!  
F stat for degree 7 vs 8:  
0.08030392824436064  
More param is bad!
```

# Extrapolation

Better Zero Noise Result?

- **Statistical fluctuations** make it difficult to check which polynomial fit best approximates zero noise result.
- A possible solution is to find the **error on the zero noise result** for different polynomial fits to fight the fluctuations.



# 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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