QuantumGuards 2020

Calculating thermodynamic observables of LiH using Qiskit simulations

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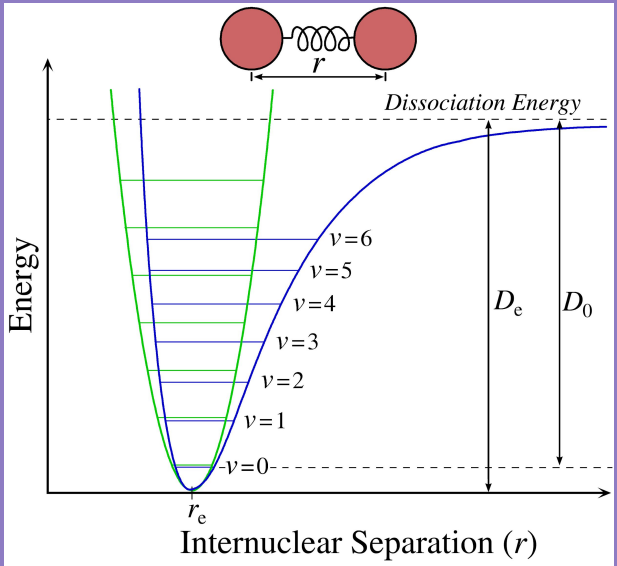
What are Thermodynamic Observables?

- Enthalpy: comprises of the system's internal energy (energy to create the system) plus the amount of work needed to establish its volume and pressure in the environment.
- Entropy: a measure of a system's thermal energy per unit temperature unavailable for doing work (measure of molecular disorder)
- Gibbs free energy: quantifies the maximum amount of reversible work that can be performed at a constant temperature and pressure.

Calculation Process:

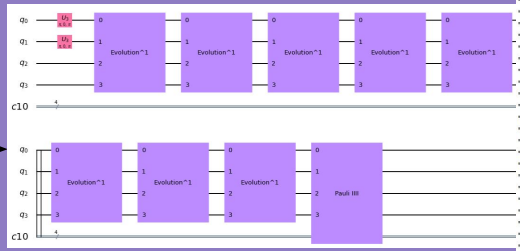


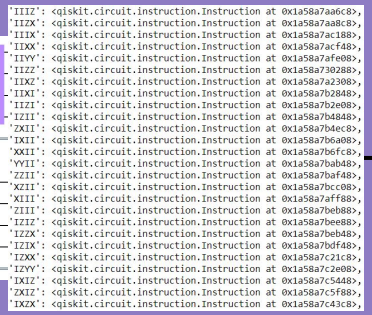
1. Calculate the Born-Oppenheimer potential energy surface (BOPES)
    a. Requires solving Schrodinger equation for a fixed position of nuclear coordinates
2. Determine vibrational modes,
3. Calculate the components of the partition function.
4. Calculate thermodynamic observables as a function of temperature and pressure.

*Use quantum computing to help with Schrodinger equation! Entanglement and superposition of qubits naturally represent and operate on quantum states.

Calculation In Qiskit

1.Qiskit Chemistry Drivers:
-Specify molecule, basis set and method
- Basis set: STO-3G corresponding to 1s, 2s, 2p orbitals
-Method: RHF (restricted Hartree Fock)





2. After running the driver, FermionicOperator convert the one body, two-body integral calculations into a qubit operator.
-WeightedPauliOperator gives us an instruction set for qubit circuit.

3. Prepare initial state using HartreeFock and set up the variational form using Qiskit Chem UCCSD form.

Using Qiskit VQE algorithm, we input the variatonal form, the qubit operator and the optimizer.

4. Plot the simulated results and fit to a Morse potential to obtain the equilibrium potential energy well depth, width and equilibrium bond length

5. Calculate thermodynamic observables in terms of these fitted parameters

Variational Quantum Eigensolver

- Hybrid quantum-classical algorithm
- Applies Variational Method of quantum mechanics which minimizes the expectation value of the Hamiltonian for some trial wavefunction
- Can also be used to determine the excited states.
- Reduces the long coherence times required by the quantum phase estimation algorithm

Variational Method

Suppose we have the Hamiltonian/qubit operator and a trial wavefunction (ansantz)

$$H = H^\dagger$$

$$H = \sum_{i=1}^{N} \lambda_i |\psi_i\rangle\langle\psi_i|$$

Taking expectation value with ansantz:

$$\langle H \rangle_\psi \equiv \langle \psi | H | \psi \rangle = \sum_{i=1}^{N} \lambda_i |\langle \psi_i | \psi \rangle|^2$$

It follows that: $\lambda_{min} \leq \langle H \rangle_\psi$ since $|\langle \psi_i | \psi \rangle|^2 \geq 0$

Result: We get an upper bound on the ground state energy!

VQE

$$|\psi_0\rangle = U_0 |0\rangle .$$

Initial Guess

$$f(\theta) = \langle U(\theta)\psi_0 | H | U(\theta)\psi_0 \rangle .$$

Cost Function

Variational Form

For some initial state, circuit is parameterized (via unitary operators) and expectation will be minimized.

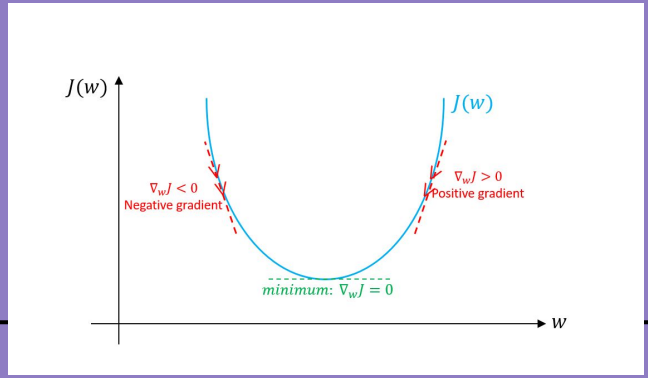
Parameter Optimization

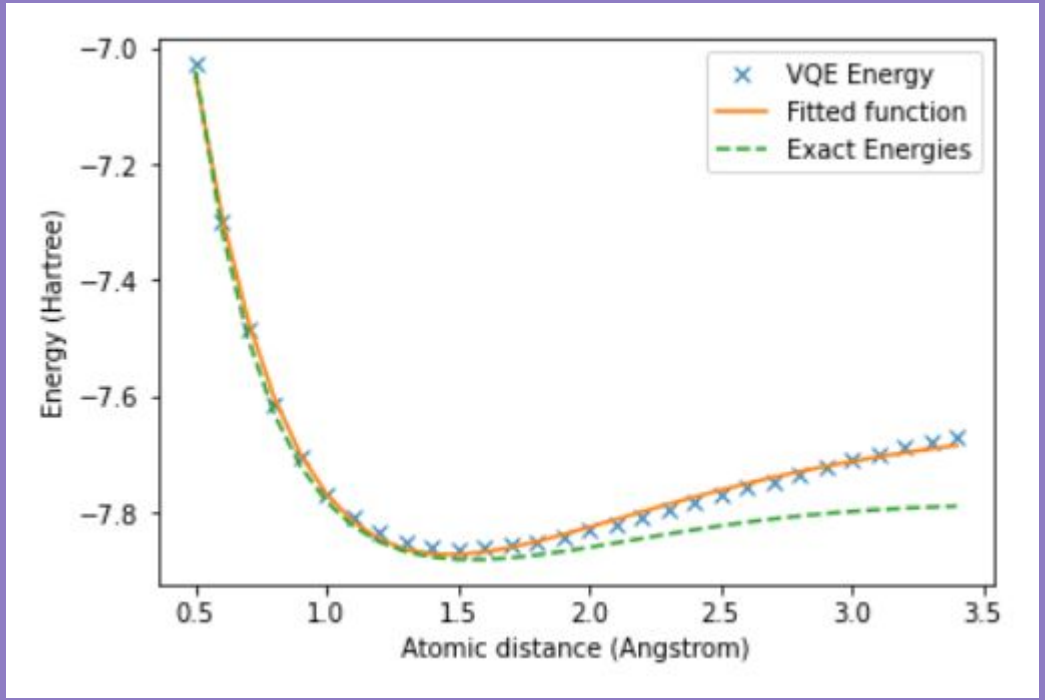
After selecting an efficient parameterized variational form, the parameters are optimized to minimize the expectation value of the Hamiltonian.

Popular optimizer is gradient descent where each parameter is updated in the direction of largest energy change (|gradient|).

- Has a tendency to get stuck at poor local minima and can be expensive in terms of circuit evaluations.

$$w_{n+1} = w_n - \gamma \nabla_w J(w_n)$$

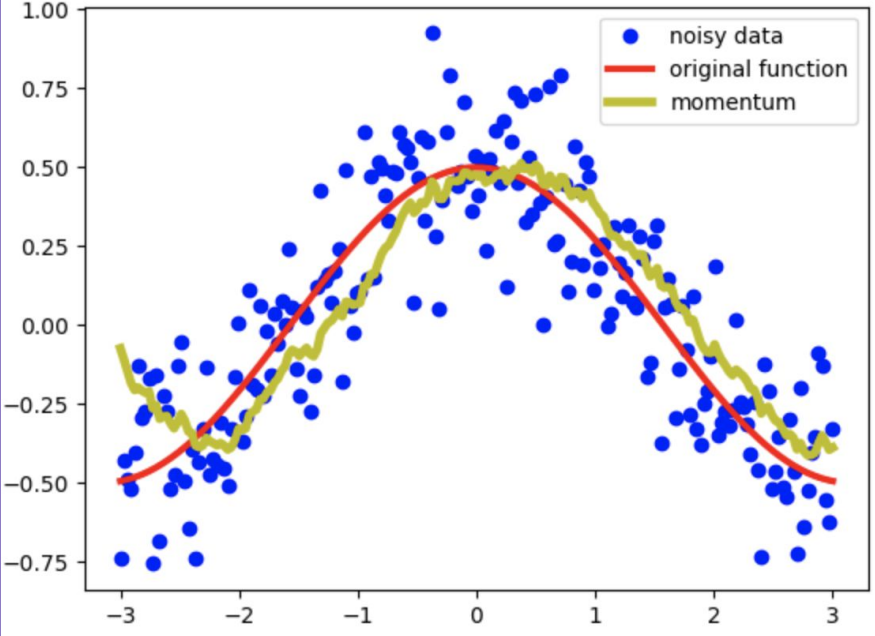




Here we started with the initial Hartree Fock state and did not update parameters as we apply VQE.

The simulation results follow the Morse model closely but for larger interatomic distances the model and our results deviate from the the exact energies.

GRABER - Optimization



momentum — data from exponentially weighed averages.

- This is a method used to classically optimize the VQE algorithm.
- It improves the precision and efficiency of the VQE algorithm, essentially smoothing the data
- Based on stochastic gradient descent method with momentum

Momentum

-Tunable parameter adjusts dependence on previous gradient

-Already implemented in built-in AQGD optimizer

-Since AQGD already used momentum, smart termination and parameter-shift rule, we modified AQGD module into GRABER

$$m^k = (1-\mu)g^k + \mu m^{k-1},$$
$$\theta^{k+1} = \theta^k - \gamma^k m^k$$

Bootstrapping

GRABER utilizes advanced starting point information (“bootstrapping”).

We implemented initial point updates for VQE by using the optimal_params property when running the optimizer on a specific molecule and bond length.

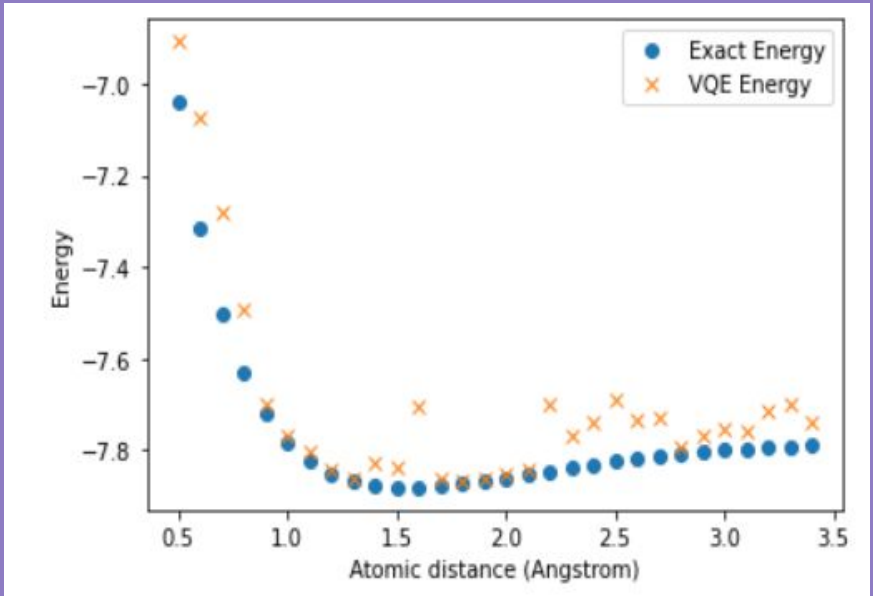
Epochs

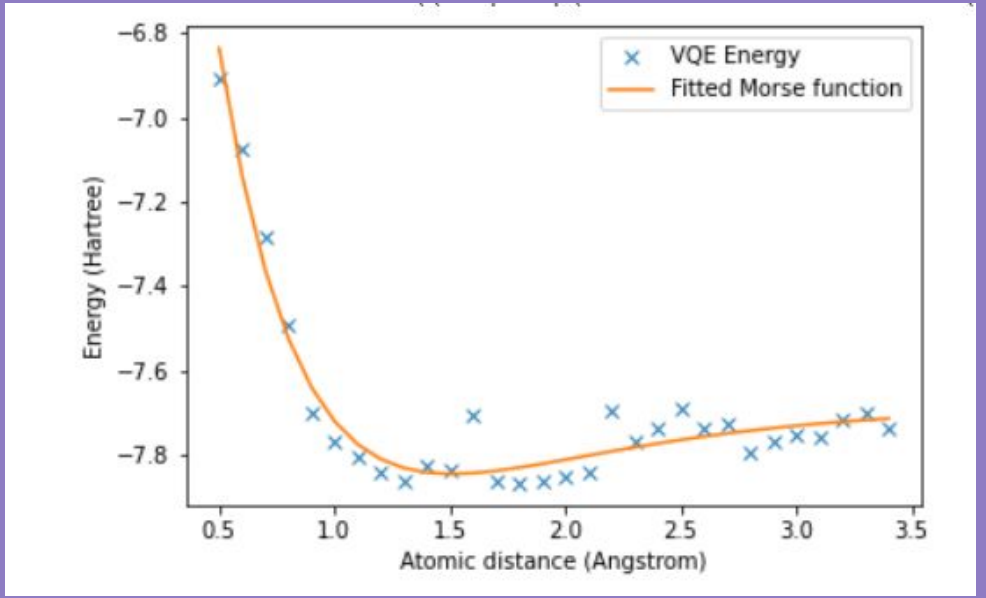
Custom step length schedule with 2 parameters: offset(N) and initialEta (initial step size)

Adaptive Termination:

Method monitors convergence to a stationary point when the change in the average objective function is some window is less than the tolerance.

Results (Offset = 10, InitialEta = 3)





Stochastic Gradient Descent (SGD)

-Cost function (in this case expectation value of Hamiltonian) is sum over input dataset: ith data → Qi

-SGD computes gradient from random selection of Qi, saving time and computational resources

-We ran out of time before implementing this

Normal Gradient Descent

$$w := w - \eta \nabla Q(w) = w - \frac{\eta}{n} \sum_{i=1}^{n} \nabla Q_i(w),$$

Stochastic Gradient Descent

$$w^{new} := w^{old} - \eta \nabla Q_i(w^{new}).$$

SGD (cont)

-Hamiltonian is computed as weighted sum of trial wavefunction overlap with the eigenvalues ((weights = probabilities)

-each Qi = (ith eigenvalue)* (probability of ith eigenstate)

-eigenvalues are known when using weighted pauli matrices, so only probabilities must be calculated (with inner product)

-We ran out of time before successfully implementing SGD

Resampling

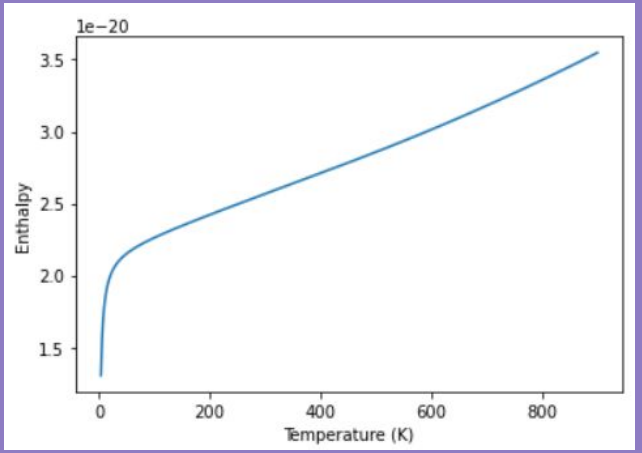
-Adaptively adjusts its estimate of the final energy/objective via resampling
-Individual circuit shots are used to estimate the variance
- The number of repeated samples is adjusted as:

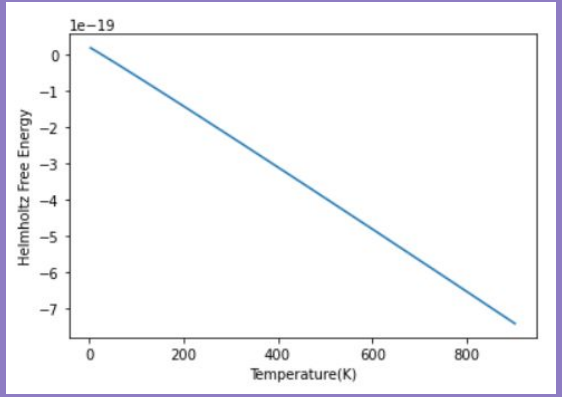
$$N = \lceil \sigma^2 / \epsilon^2 \rceil$$

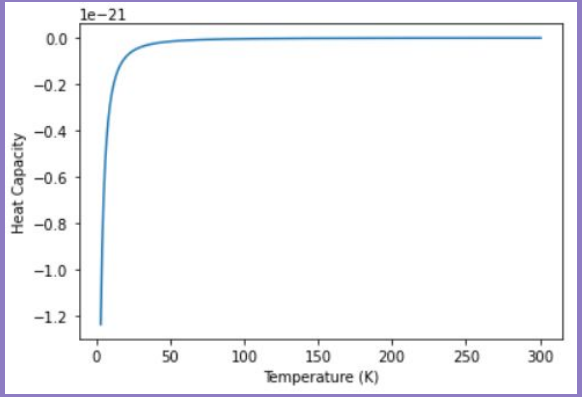
- Assuming a normal distribution, this N guarantees that we have a probability of > 68% of the energy estimate being within a tolerance (0.001, in this case)

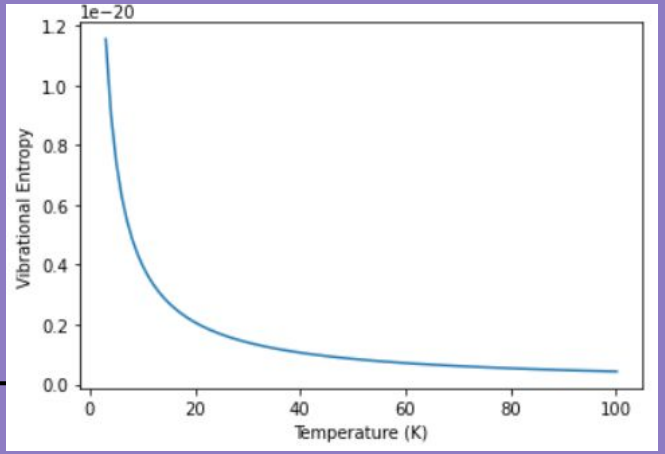
Thermodynamic Results

Potential Well Depth: 0.245 Hartree
Width of well: 1.1 Angstrom
Equilibrium Bond length: 1.5 Angstrom (compared to 1.6 Angstrom)

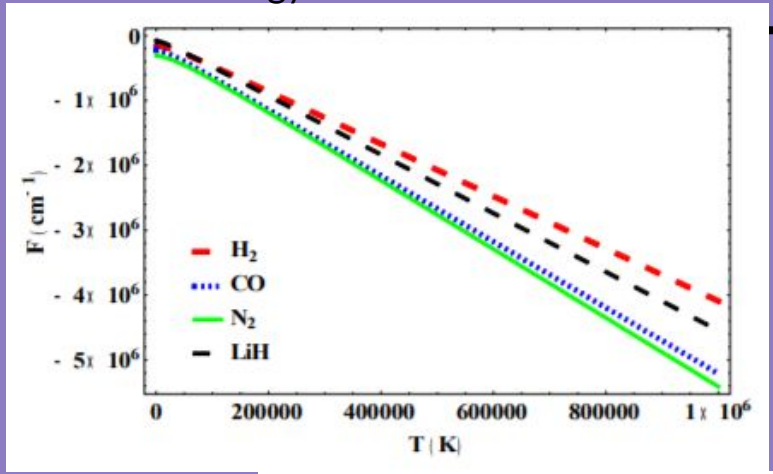


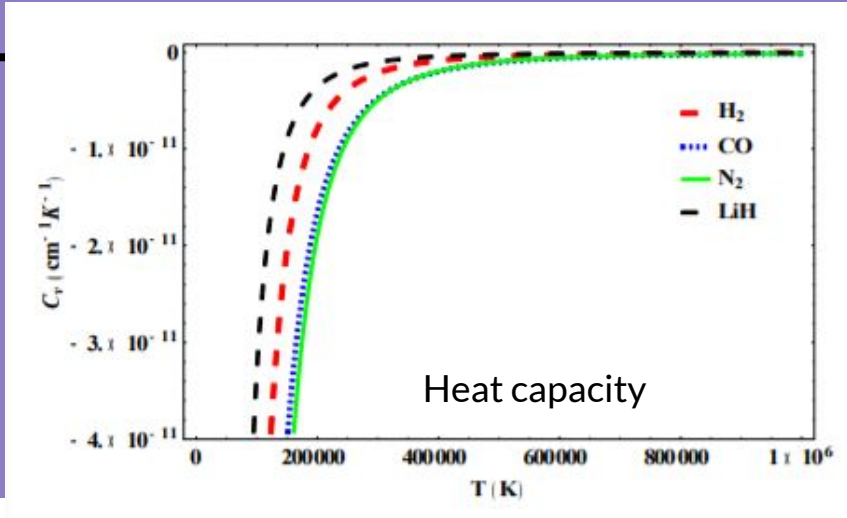


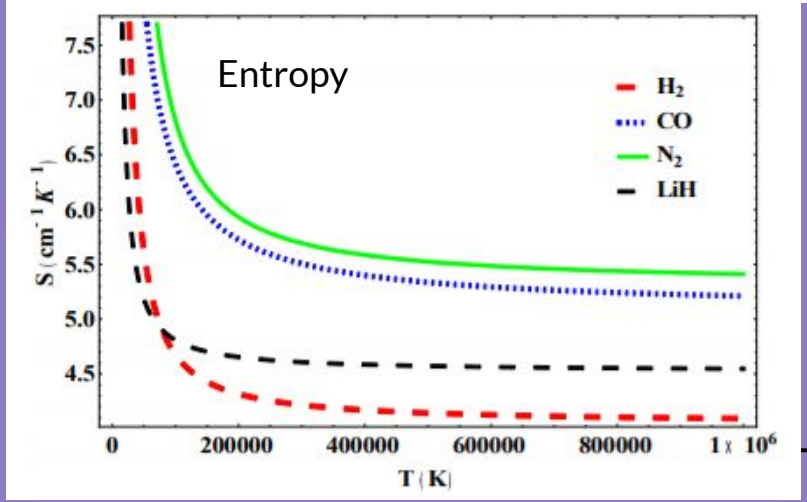




Free Energy


F (cm⁻¹)
0
- 1 x 10⁶
- 2 x 10⁶
- 3 x 10⁶
- 4 x 10⁶
- 5 x 10⁶
H₂
CO
N₂
LiH
0
200000
400000
600000
800000
1 x 10⁶
T (K)


Heat capacity
C_v (cm⁻¹ K⁻¹)
0
- 1. x 10⁻¹¹
- 2. x 10⁻¹¹
- 3. x 10⁻¹¹
- 4. x 10⁻¹¹
H₂
CO
N₂
LiH
0
200000
400000
600000
800000
1 x 10⁶
T (K)


Entropy
S (cm⁻¹ K⁻¹)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
H₂
CO
N₂
LiH
0
200000
400000
600000
800000
1 x 10⁶
T (K)

Next Steps

-Implement SGD with the rest of graber functionality to increase speed

-Implement Resampling to account for randomness in results

-Test on different molecules

- Test on IBMQ backends

Sources

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- https://www.openpr.com/news/1835143/lithium-hydride-market-expected-to-witness-a-sustainable-growth
- https://chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/13%3A_Molecular_Spectroscopy/13.05%3A_Vibrational_Overtones
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- https://www.researchgate.net/publication/338593811_Thermodynamic_Properties_of_Improved_Deformed_Exponential-type_Potential_IDEP_for_some_Diatomic_Molecules