Quantum computation for chemistry and materials

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SIMULATING CHEMISTRY

Understanding

Control
**THE ELECTRONIC STRUCTURE PROBLEM**

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the **whole of chemistry** are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

-Paul Dirac

\[ \mathcal{H} |\psi\rangle = E |\psi\rangle \]
THE EXPONENTIAL PROBLEM

$D = M^N$

$M = 100$
$N = 80$

Electrons:

$D = \begin{pmatrix} M \\ N_\alpha \end{pmatrix} \begin{pmatrix} M \\ N_\beta \end{pmatrix}$

One mole:

$10^{23}$

Particles in universe:

$10^{80}$

$M^2$

$D = 100^{80} = 10^{160}$
**Grand Solutions from a Grand Device**

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

**Fertilizer**

**Humans: Haber Process**
- 400°C & 200 atm
- 1-2% of ALL energy on earth, used on Haber process

**Nature: Nitrogenase**
- 25°C & 1 atm
- “FeMoco”
- Beyond all current classical methods
- Both electronic structure and substrate attachment almost totally unknown

Classically – No clear path to accurate solution
Quantum Mechanically – 150-200 logical qubits for solution
CLASSICAL PRE-CALCULATIONS

Problem Input: “Second-Quantized Electronic Hamiltonian”

\[ \mathcal{H}_e(R) = h_{pq}(R)\hat{a}^\dagger_p \hat{a}_q + h_{pqrs}(R)\hat{a}_{p}^{\dagger}\hat{a}_q^{\dagger}\hat{a}_r\hat{a}_s \]

Hartree-Fock (Mean-Field)

Atom Centered Basis

Molecular Orbitals
Quantum Advantage in Chemistry


\[ U = e^{-iH\delta t} \]

**Classical:** Exponential cost

**Quantum:** Modest polynomial cost

**Challenge:** Algorithm can require > millions of coherent gates
A Co-design Perspective

Previously: Given a task, design quantum circuit (or computer) to perform it.

Problem: General or optimal solution can require millions of gates.

Alternative: Given a task and the current architecture, find the best solution possible.

† Equal Contribution by authors
**Easy Task For A Quantum Computer**

\[ \langle \sigma_i^z \rangle \quad \langle \sigma_1^z \sigma_2^z \ldots \sigma_n^z \rangle \]

- Efficient to perform on any prepared quantum state
- In general, it may be very hard to calculate this expectation value for a classical representation, containing an exponential number of configurations

\[ |\Psi\rangle = \sum_{i_1 i_2 \ldots i_N} C^{i_1 i_2 \ldots i_N} |i_1 i_2 \ldots i_N\rangle \]
Back to Basics

Variational Formulation: Minimize $\langle \Psi | H | \Psi \rangle$

Decompose as:

$\mathcal{H} = h^i_\alpha \sigma^i_\alpha + h^{ij}_{\alpha \beta} \sigma^i_\alpha \sigma^j_\beta + h^{ijk}_{\alpha \beta \gamma} \sigma^i_\alpha \sigma^j_\beta \sigma^k_\gamma + ...$

By Linearity:

$\langle \psi | \mathcal{H} | \psi \rangle \equiv \langle \mathcal{H} \rangle = \mathcal{H} = h^i_\alpha \langle \sigma^i_\alpha \rangle + h^{ij}_{\alpha \beta} \langle \sigma^i_\alpha \sigma^j_\beta \rangle + h^{ijk}_{\alpha \beta \gamma} \langle \sigma^i_\alpha \sigma^j_\beta \sigma^k_\gamma \rangle + ...$

Easy for a Quantum Computer: Easy for a Classical Computer:

$\langle \sigma^i_\alpha \sigma^j_\beta \sigma^k_\gamma ... \rangle \rightarrow +, \times \rightarrow \langle H \rangle$

Suggests Hybrid Scheme:

• Parameterize Quantum State with Classical Experimental Parameters
• Compute Averages using Quantum Computer
• Update State Using Classical Minimization Algorithm
Variational Quantum Eigensolver

† Equal Contribution by authors

McClean, Romero, Babbush, Aspuru-Guzik
New Journal of Physics 18 023023 (2016)
SCALABLE SIMULATION OF MOLECULAR ENERGIES IN SUPERCONDUCTING QUBITS

Variational Error Suppression

![Graph showing total energy vs bond length for different experiments.](image)

- Exact Energy
- VQE Experiment
- PEA Experiment
VARIATIONAL ERROR SUPPRESSION
Quantum Subspace Expansion (QSE)

Expand to a Quantum Subspace

Quantum State on Quantum Device

Extra Quantum Measurements

Classical Generalized Eigenvalue Problem

\[ HC = SCE \]

Excited State Energy and Properties

Hybrid Quantum-Classical Hierarchy for Mitigation of Decoherence and Determination of Excited States

McClean, J.R., Schwartz, M.E, Carter, J., de Jong, W.A.
Physical Review A 95 (4), 042308 (2017)
**Quantum Subspace Expansion (QSE)**

General Idea: Learn action of $H$ in a subspace

$$\text{Span}(\{O_i | \Psi(\theta_1, \theta_2, ...)\})$$

Act: $HO_i | \Psi(\theta_1, \theta_2, ...)\rangle$

Probe: $\langle \Psi(\theta_1, \theta_2, ...) | O^\dagger_j \rangle$

Local Metric $S$

$$H_{ij} = \langle \Psi(\theta_1, \theta_2, ...) | O_j^\dagger HO_i | \Psi(\theta_1, \theta_2, ...)\rangle$$

$HC = SCE$
**Experimental H$_2$ Spectrum**

- Linear response (+), measured operators: IZ, ZI, IX, XI, XY, YX
- Spurious state disappears, good reconstruction of excited states

“Computation of Molecular Spectra on a Quantum Processor with an Error-Resilient Algorithm”
Colless, Ramasesh, Dahlen, Blok, Kimchi-Schwartz, McClean, Carter, de Jong, Siddiqi
**Experimental H$_2$ Spectrum**

![Graph showing experimental H$_2$ spectrum with error bars and error lines for different sets of operators.]  

"Computation of Molecular Spectra on a Quantum Processor with an Error-Resilient Algorithm"  
Colless, Ramasesh, Dahlen, Blok, Kimchi-Schwartz, **McClean**, Carter, de Jong, Siddiqi  
**Simple 1 Qubit Example**

\[ H = \begin{pmatrix} -0.24 & 1.92 \\ 1.92 & -0.99 \end{pmatrix} \]

\[ \rho_{\text{pure}} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \]

\[ \rho_{\text{mix}} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

\[ H_{ij} = \text{Tr} \left[ \rho O_i^{\dagger} H O_j \right] \]

\[ S_{ij} = \text{Tr} \left[ \rho O_i^{\dagger} O_j \right] \]

Set 0
\[ O_i \in \{I\} \]

Set 1
\[ O_i \in \{I, X\} \]

Set 2
\[ O_i \in \{I, X, Y, Z\} \]
OPERATORS TO MITIGATE INCOHERENT ERRORS

Pure States:

\[ \tilde{H}_{ij} = \langle \Psi | O_i^\dagger H O_j | \Psi \rangle \]
\[ \tilde{S}_{ij} = \langle \Psi | O_i^\dagger O_j | \Psi \rangle \]

\[ HC = SCE \quad \sum_i c_i O_i | \Psi \rangle \]

Mixed States:

\[ H_{ij} = \text{Tr} \left[ O_i^\dagger H O_j \rho \right] = \langle \langle O_i | H \otimes \rho^* | O_j \rangle \rangle \]
\[ S_{ij} = \text{Tr} \left[ O_i^\dagger O_j \rho \right] = \langle \langle O_i | I \otimes \rho^* | O_j \rangle \rangle \]

\[ \tilde{O} = \sum_i c_i O_i \]

Fully mitigates errors iff

\[ \tilde{O} \rho \tilde{O}^\dagger = \rho_0 \]
\[ \tilde{O} = \sum_i \alpha_i | \Psi_0 \rangle \langle \Psi_i | + \sum_{ij} \beta_{ij} | \Psi_i \rangle \langle \Psi_j^\dagger | \]
**Network / Ansatz Parameterization**

\[
\min_{\vec{\theta}} \langle \Psi(\vec{\theta}) | H | \Psi(\vec{\theta}) \rangle
\]

Chemistry

Nuclear Physics

Optimization (QAOA)

Machine learning

Algorithm learning

...
Prior to 2006, networks with more than ~1-2 hidden layers unsuccessful

Partial Remedies:
1. Longer training
2. ReLU activation functions
3. Batch normalization
4. Initialization strategies
5. Skip networks (ResNets)
6. Unitary feed forward networks

“Understanding the difficulty of training deep feedforward neural networks”,
Xavier Glorot and Yoshua Bengio (2010)

“On the importance of initialization and momentum in deep learning”,
**Random Parameterized Quantum Circuits (RPQC)**

**Claim:** The probability of measuring a gradient component with “significant magnitude” is exponentially small in the number of qubits.

**RPQC Definition:**

$U_\ell(\theta_\ell) = \exp(-i\theta_\ell P_\ell)$

$E(\tilde{\theta}) = \langle 0|U(\tilde{\theta})^\dagger HU(\tilde{\theta})|0\rangle$

$P_k = V$

$\partial_k E \equiv \frac{\partial E(\tilde{\theta})}{\partial \theta_k} = i\langle 0|U_\ell^\dagger \left[V, U_+^\dagger HU_+\right] U_-|0\rangle$

Either $U_-$ and $U_+$ are statistically independent.

Either $U_-$ or $U_+$ is a 2-design (matches Haar measure up to second moment).

**Claim:** The probability of measuring a gradient component with “significant magnitude” is exponentially small in the number of qubits.
**Intuition From Levy’s Lemma**

Define:

\[ S_\epsilon = \{ x \in S^{(2n-1)} | d(x_j, 0) \leq \epsilon / 2 \} \]

\[ \mu \left( S^{(2n-1)} \right) = 1 \]

\( f \) “smooth” (Lipschitz continuous w/ constant) \( \eta \)

Then:

\[ \mu \left( S_\epsilon \right) = 1 - \exp \left( -c n \epsilon^2 \right) \]

\[ \Pr \{ |f(x) - \langle f \rangle| \geq \epsilon \} \leq \exp \left( \frac{-n \epsilon^2}{9 \pi^3 \eta^2} \right) \]
OUTLINE OF ANALYTIC RESULTS

\[ p(U) = \int dU_+ p(U_+) \int dU_- p(U_-) \delta(U_+ U_- - U). \]

\[ \langle \partial_k E \rangle = i \int dU_- p(U_-) \text{Tr} \left\{ \rho_- \int dU_+ p(U_+) \left[ V, U_+^\dagger H U_+ \right] \right\} \]

**Average:** Either \( U_- \) or \( U_+ \) are 1-designs

\[ \langle \partial_k E \rangle = 0 \]

**Variance:**

\[ \text{Var} [\partial_k E] = \langle (\partial_k E)^2 \rangle = \]

Case 1: \( U_- \) is a 2-design but not \( U_+ \)

\[ -\frac{\text{Tr}(\rho^2)}{2^{2n}} \text{Tr} \langle [V, u^\dagger H u]^2 \rangle_{U_+} \]

Case 2: \( U_+ \) is a 2-design but not \( U_- \)

\[ -\frac{\text{Tr}(H^2)}{2^{2n}} \text{Tr} \langle [V, u \rho u^\dagger]^2 \rangle_{U_-}. \]

Case 3: Both are 2-designs

\[ 2 \text{Tr}(H^2) \text{Tr}(\rho^2) \left( \frac{\text{Tr}(V^2)}{2^{3n}} - \frac{\text{Tr}(V)^2}{2^{4n}} \right) \]
A RARE PICTURE OF THE GRADIENT LANDSCAPE
Gradients vanishing in practice

\[ H = -Z_1 Z_2 \]

\[ R_{P_{i,j}}(\theta_{i,j}) = \exp(-i\theta_{i,j} P_{i,j}) \]

\[ P_{i,j} \in \{X, Y, Z\} \]
CONVERGENCE WITH DEPTH

![Graph showing convergence with depth for 2, 4, and 22 qubits. The y-axis represents the variance of $(\theta_i, E)$, and the x-axis represents the number of layers.]
Black holes in your circuits?

McClean, Boixo, Smelyanskiy, Babbush, Neven
“Barren Plateaus in Quantum Neural Network Training Landscapes”
Nature Communications Vol 9, 4812 (2018)
# Domain Knowledge Matters

<table>
<thead>
<tr>
<th>Year</th>
<th>Reference</th>
<th>Representation</th>
<th>Algorithm</th>
<th>Time Step Depth</th>
<th>Coherent Repetitions</th>
<th>Total Depth</th>
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<td>Aspuru-Guzik et al.</td>
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**Typical Chemistry Problem Workflow**

- **Molecule Specification:**
  - XYZ Coordinates
  - Spin & Number of electrons
  - Discretization (Basis set / grid)

- **Integral Generation**
  - Depends on basis set, often uses external software
  - Integral basis change
  - Initial state preparation

- **Starter Calculation** (e.g. Hartree-Fock)
  - Initial state preparation

- **Map to Qubits**
  - Jordan-Wigner
  - Bravyi-Kitaev
  - ...

- **Select Problem & Algorithm**
  - Energies, properties etc.
  - Quantum Phase Estimation
  - Variational Quantum Eigensolver (& Ansatz)

- **Map to hardware**
OPENFERMION (WWW.OPENFERMIION.ORG)

An open source quantum simulation package for quantum computers

[Logos of Berkeley Lab, Rigetti, ETH Zürich, Harvard, Dartmouth, NASA, University of Oxford, University of Michigan]
**Typical Chemistry Problem Workflow**

\[ H = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l \]

\[ H = \sum_{i\alpha} g_i^{\alpha} \sigma_\alpha^i + \sum_{i\alpha j\beta} g_{ij}^{\alpha\beta} \sigma_\alpha^i \sigma_\beta^j + \ldots \]

- `geometry = [['H', [0, 0, 0]], ['H', [0, 0, 0.74]]]
- `basis = 'sto-3g'
- `multiplicity = 1`
- `charge = 0`
- `h2_molecule = MolecularData(geometry, basis, multiplicity, charge)`

- `h2_hamiltonian = (run_psi4(h2_molecule).get_molecular_hamiltonian())`

- `h2_qubit = (jordan_wigner(get_fermion_operator(h2_hamiltonian)))`

- `evolution_operator = (uccsd_singlet_evolution(test_amplitudes, n_qubits, n_electrons))`

- `evolution_operator | wavefunction ...`
Development Philosophy

OpenFermion is an open source effort for compiling and analyzing quantum algorithms to simulate fermionic systems, including quantum chemistry. Among other functionalities, the current version features data structures and tools for obtaining and manipulating representations of fermionic and qubit Hamiltonians.

Apache 2.0 open-source license

Contribution (Pull Request) → Automatic Testing → Code Review

- Extensive tests (>99% coverage)
- Enforce no decrease in coverage
- Feedback on design choices
- Google style & PEP8 enforced

All contributors added to website and release papers
Learn from history, watch out for vanishing gradients!
Acknowledgements