Quantum computation for chemistry and materials

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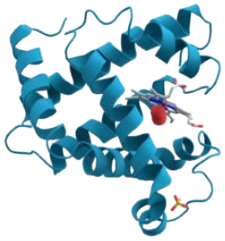
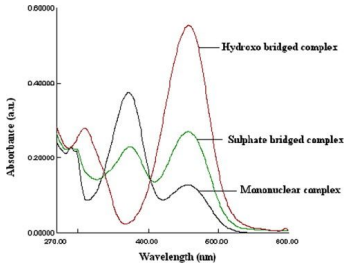
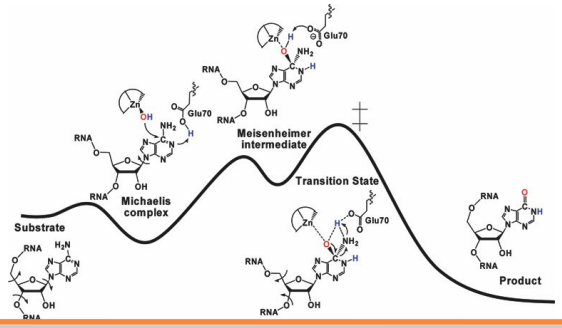
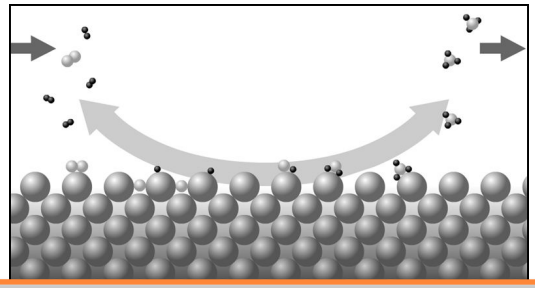
Simulating Chemistry



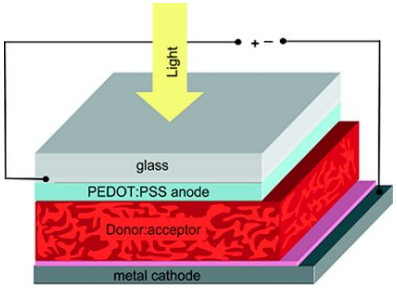
Understanding

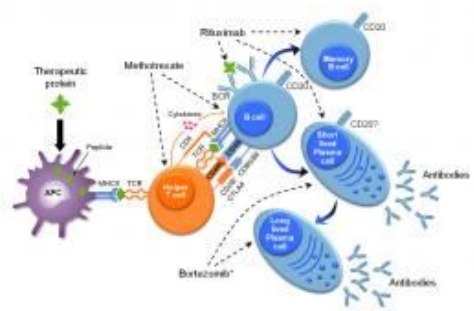






Control

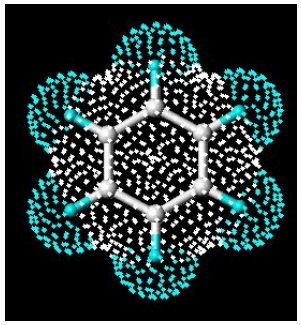




The Electronic Structure Problem

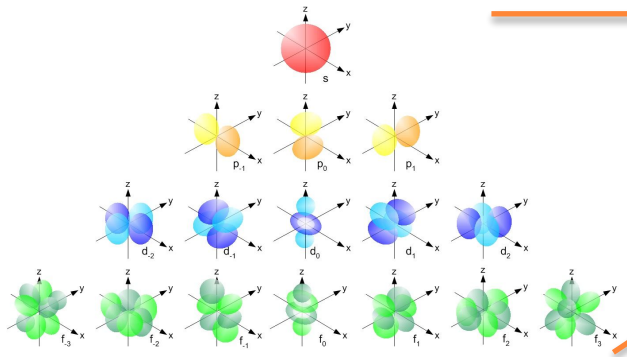
"The underlying physical laws necessary for the mathematical theory of a large part of physics and **the whole of chemistry** are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

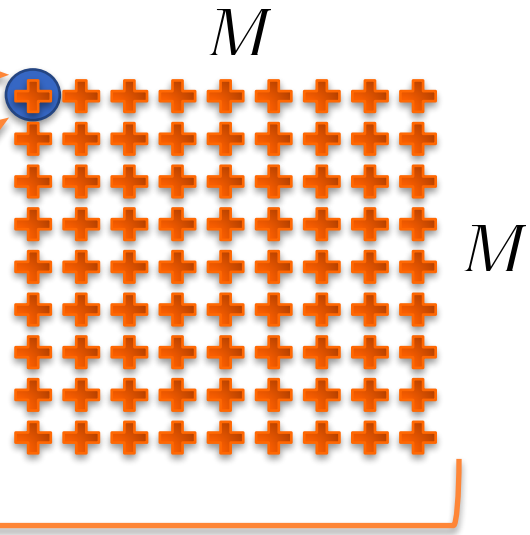
-Paul Dirac



$$\mathcal{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

The exponential problem

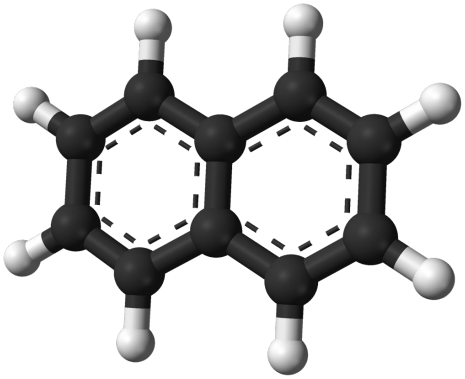




$$D = M^N$$

$$M = 100$$

$$N = 80$$



$$D = 100^{80} = 10^{160}$$

Electrons:

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

One mole

$$10^{23}$$

Particles in universe

$$10^{80}$$

Grand solutions from a grand device

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

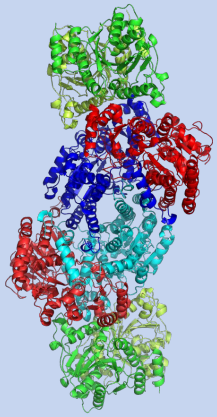
Humans: Haber Process

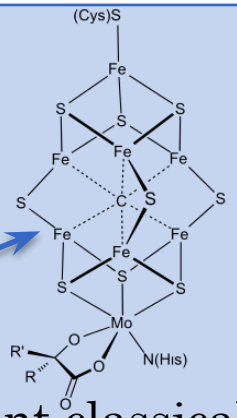
400°C & 200 atm

1-2% of ALL energy on earth, used on Haber process

Nature: Nitrogenase

25° C & 1 atm





"FeMoco"

Beyond all current classical methods

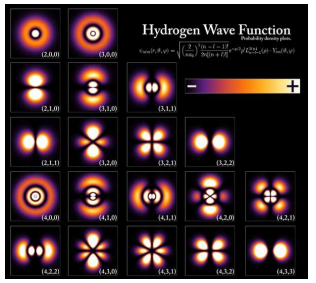
Both electronic structure and substrate attachment almost totally unknown

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

Classical Pre-Calculations

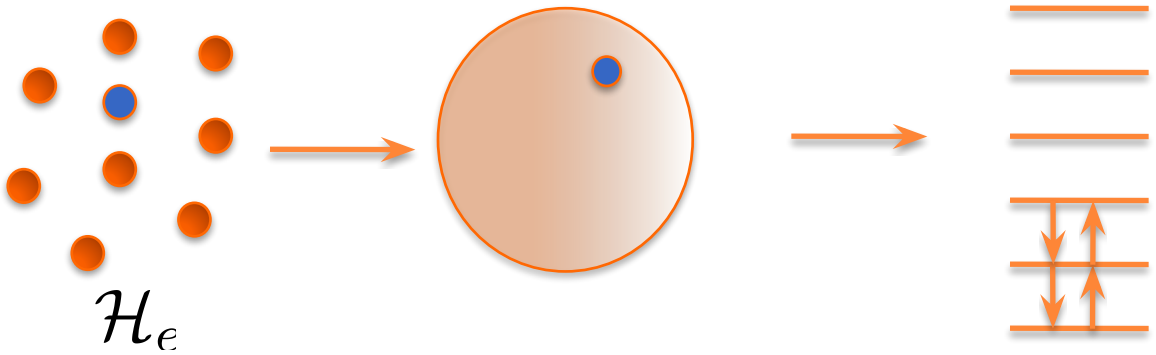
Problem Input: "Second-Quantized Electronic Hamiltonian"

$$\mathcal{H}_e(R) = h_{pq}(R)\hat{a}_p^\dagger \hat{a}_q + h_{pqrs}(R)\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$



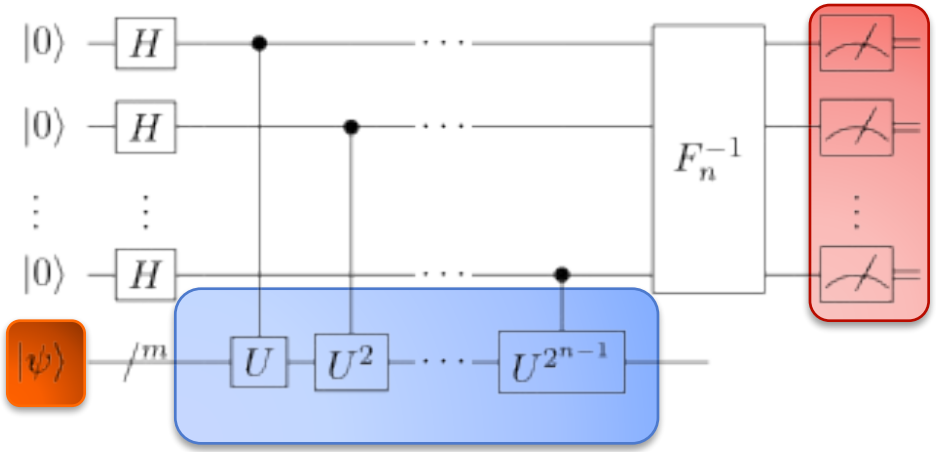
Atom Centered Basis

Hartree-Fock (Mean-Field)

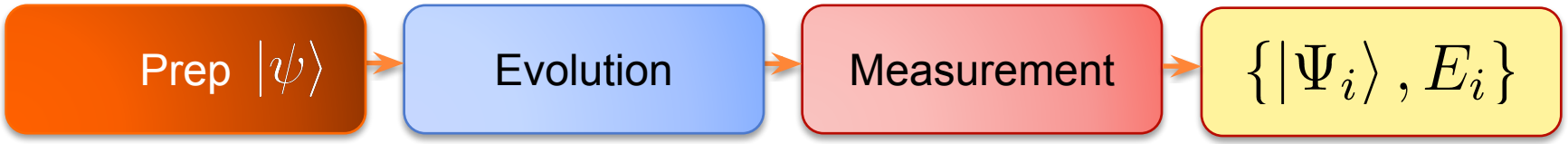


Molecular Orbitals

Quantum Advantage in Chemistry



$$U = e^{-iH\delta t}$$



Classical: Exponential cost

Quantum: Modest polynomial cost

Challenge: Algorithm can require > millions of coherent gates

Aspuru-Guzik, Dutoi, Love, Head-Gordon, *Science* 309, 1704–1707 (2005).

A Co-design Perspective

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

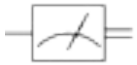
Problem: General or optimal solution can require millions of gates.

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

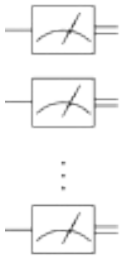
Peruzzo†, **McClean†**, Shadbolt, Yung, Zhou, Love, Aspuru-Guzik, O'Brien. *Nature Communications*, 5 (4213):1– 7, 2014.
† Equal Contribution by authors

Easy Task For A Quantum Computer

$\langle \sigma_i^z \rangle$



$\langle \sigma_1^z \sigma_2^z \ldots . \sigma_n^z \rangle$



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

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

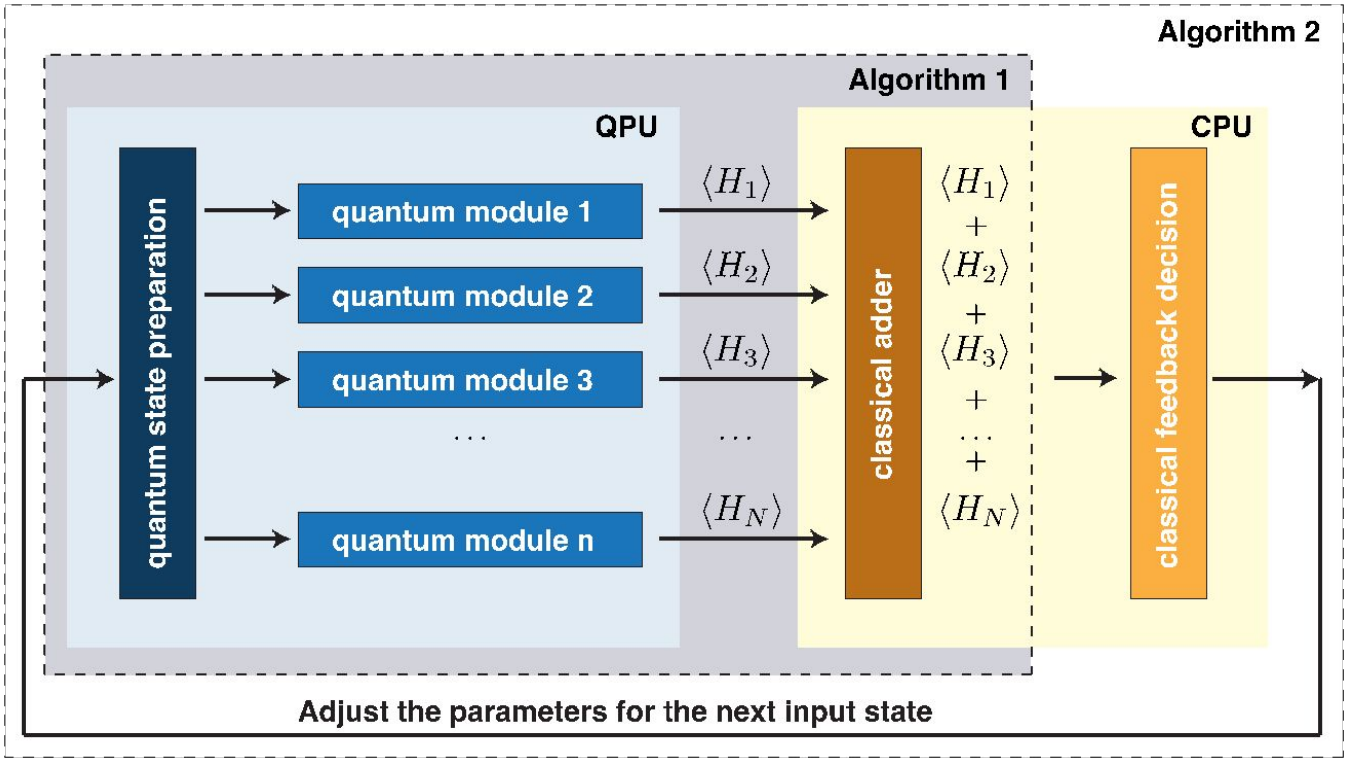
Easy for a Quantum Computer: Easy for a Classical Computer:

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

Suggests Hybrid Scheme:

- Parameterize Quantum State with Classical Experimental Parameters
- Compute Averages using Quantum Computer
- Update State Using Classical Minimization Algorithm

Variational Quantum Eigensolver

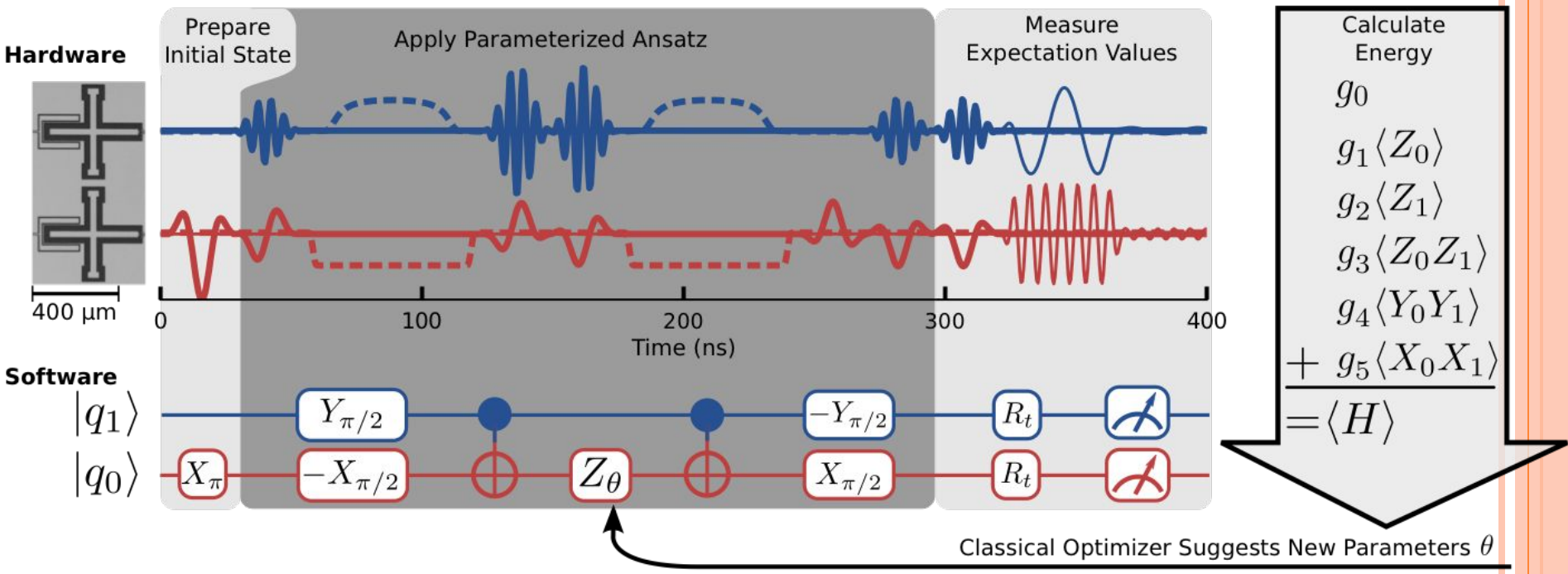


$$\min_{\vec{\theta}} \langle \Psi(\vec{\theta}) | H | \Psi(\vec{\theta}) \rangle$$

Peruzzo†, **McClean†**, Shadbolt, Yung, Zhou, Love, Aspuru-Guzik, O'Brien.
Nature Communications, **5** (4213):1–7, 2014.
† Equal Contribution by authors

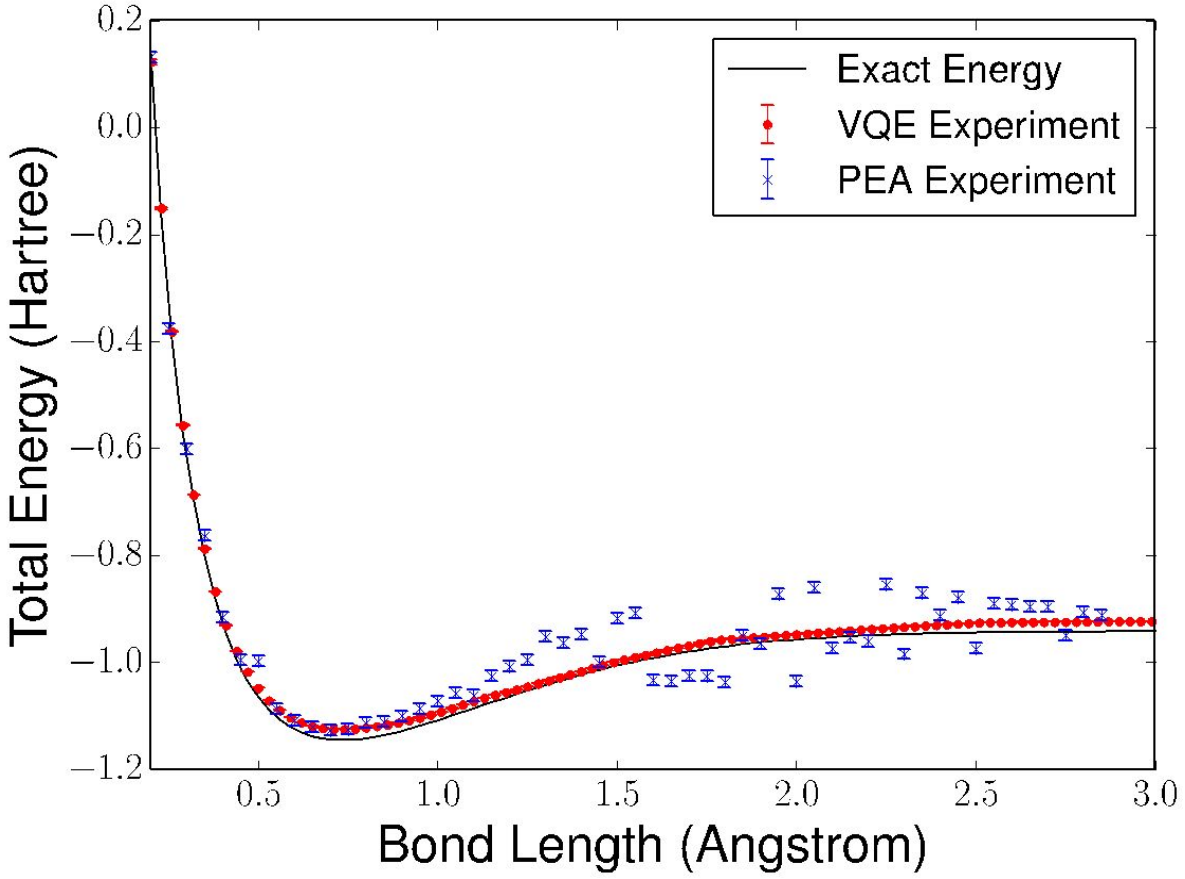
McClean, Romero, Babbush, Aspuru-Guzik
New Journal of Physics **18** 023023 (2016)

Scalable Simulation of Molecular Energies in Superconducting Qubits



P.J.J. O'Malley, R. Babbush,…, J.R. McClean et al.
"Scalable Simulation of Molecular Energies"
Physical Review X 6 (3), 031007 (2016)

Variational Error Suppression



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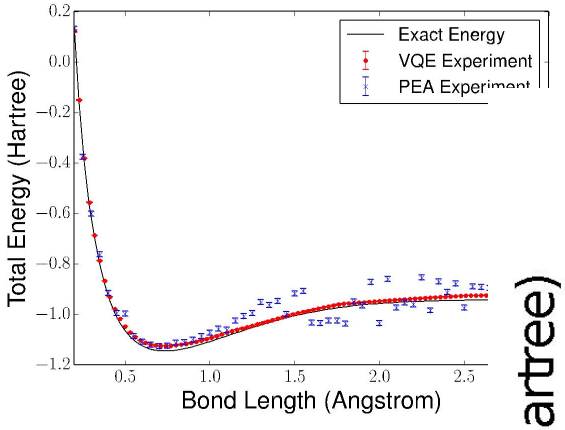
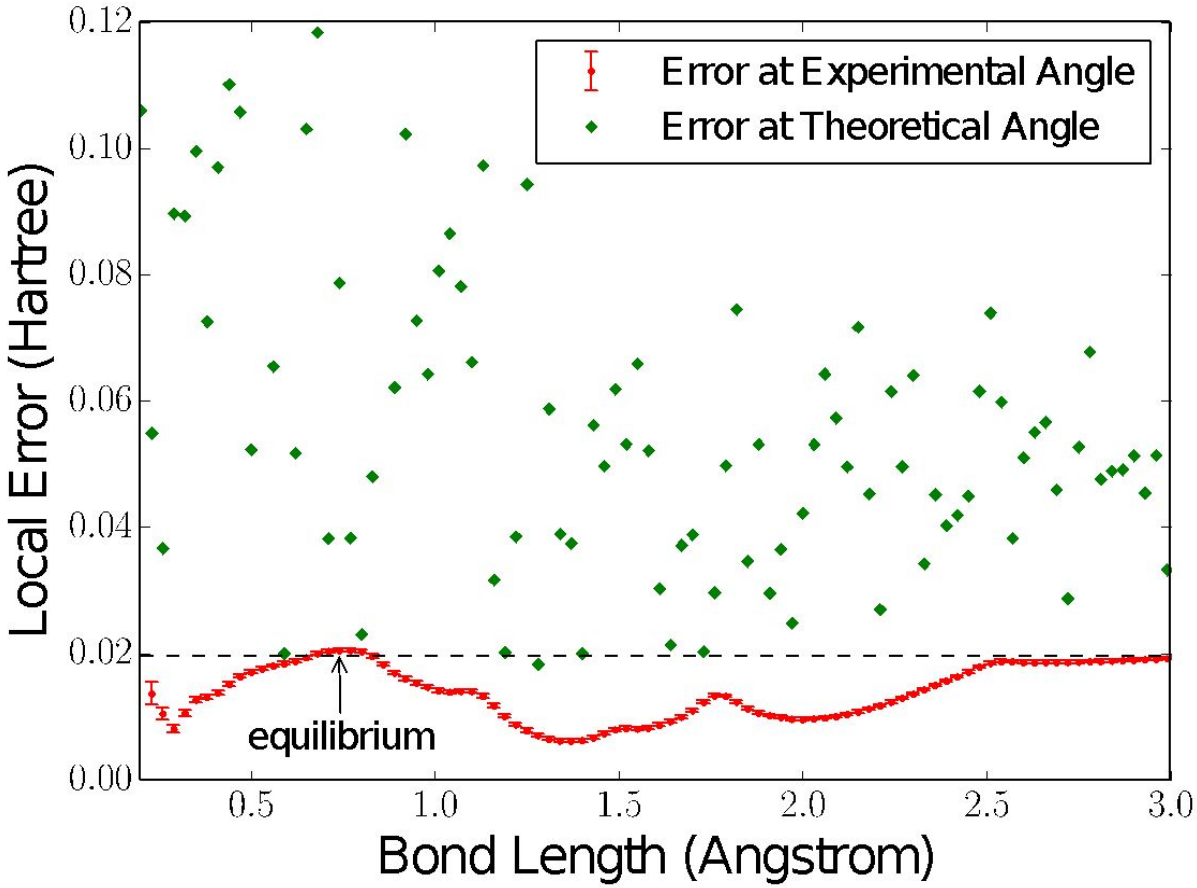
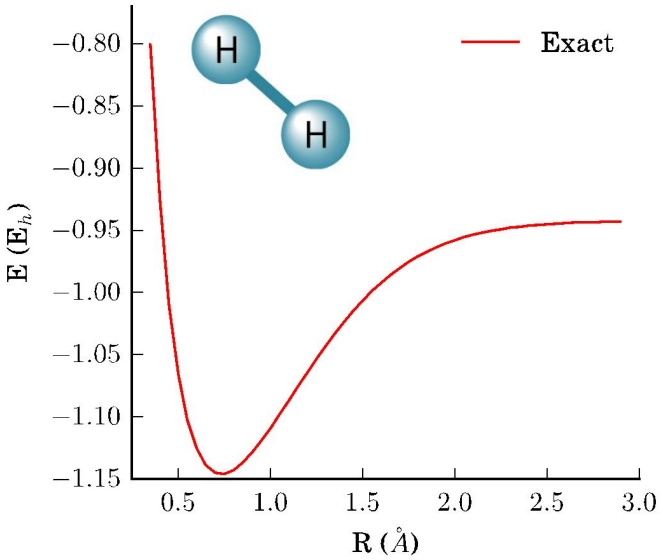




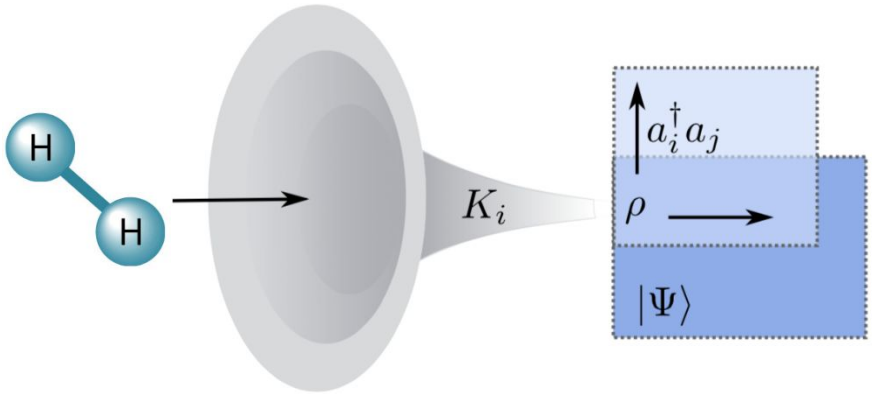
Quantum Subspace Expansion (QSE)

Quantum State on Quantum Device



Expand to a Quantum Subspace

Extra Quantum Measurements



Classical Generalized Eigenvalue Problem

$$HC = SCE$$

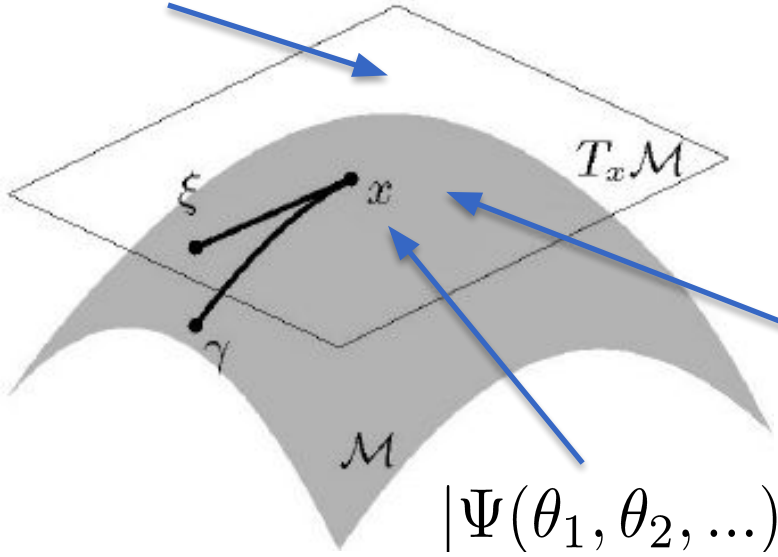
Excited State Energy and Properties

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

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



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

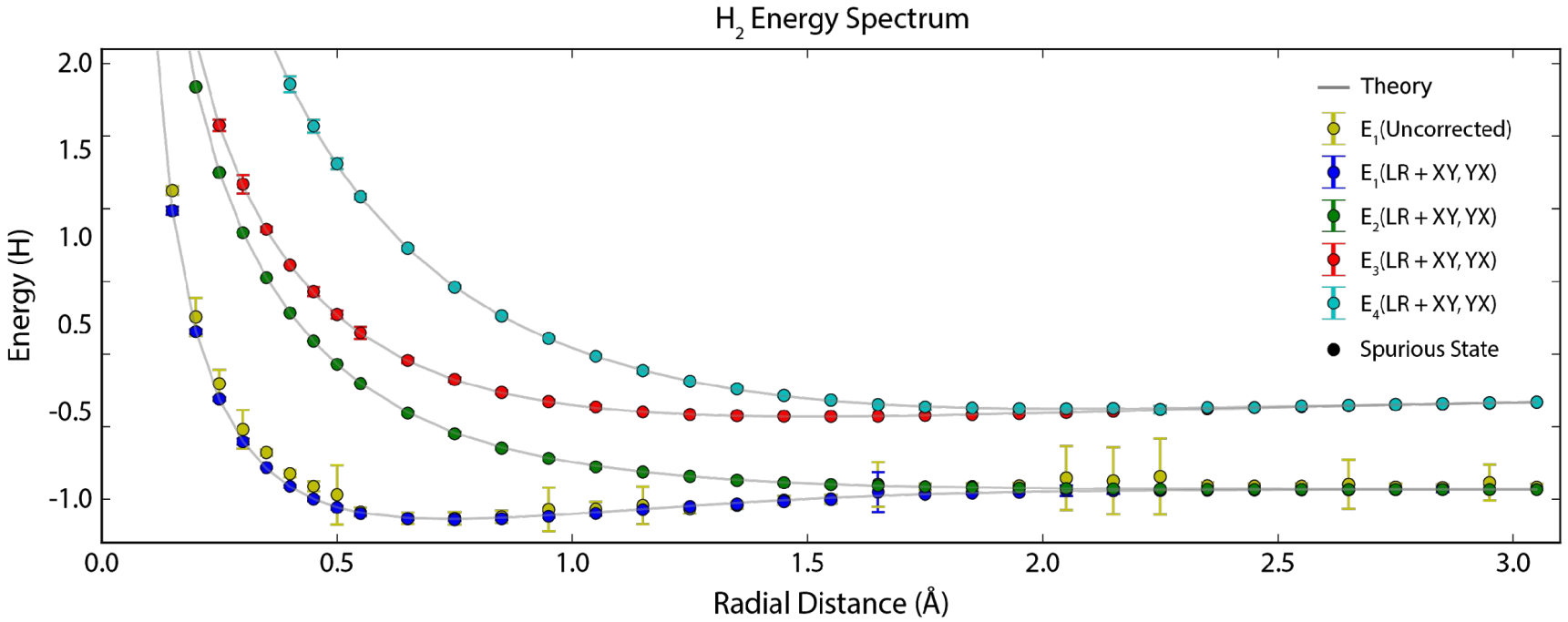
Probe: $\langle\Psi(\theta_1,\theta_2,...)|O_j^\dagger$

Local Metric S

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

$$HC = SCE$$

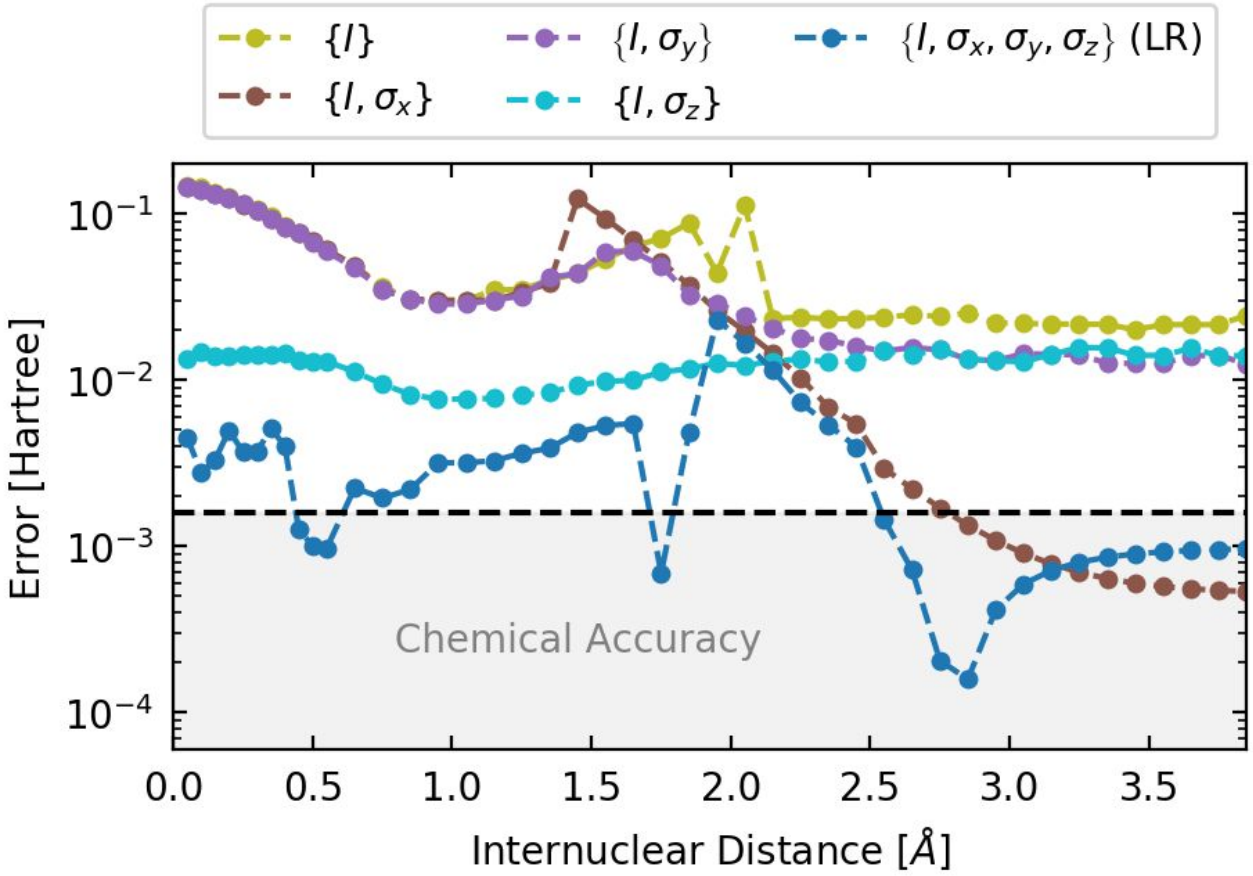
Experimental H_2 Spectrum



- 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
Phys. Rev. X **8**, 011021 (2018)

Experimental H_2 Spectrum



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Colless, Ramasesh, Dahlen, Blok, Kimchi-Schwartz, **McClean**, Carter, de Jong, Siddiqi
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Simple 1 Qubit Example

$$H = \begin{pmatrix} -0.24 & 1.92 \\ 1.92 & -0.99 \end{pmatrix} \rho_{pure} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \rho_{mix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$H_{ij} = \mathrm{Tr}\left[\rho O_i^\dagger H O_j\right] \qquad S_{ij} = \mathrm{Tr}\left[\rho O_i^\dagger O_j\right]$$

Set 0

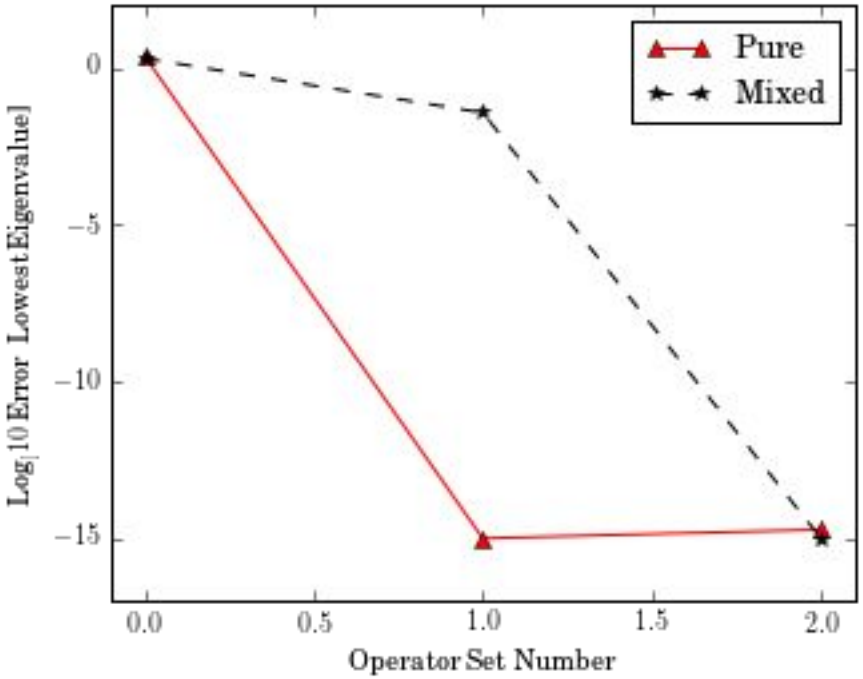
$$O_i \in \{I\}$$

Set 1

$$O_i \in \{I, X\}$$

Set 2

$$O_i \in \{I, X, Y, Z\}$$



Operators to mitigate incoherent errors

Pure States:

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

$$\xrightarrow{HC = SCE}$$

$$\sum_i c_i O_i|\Psi\rangle$$

Mixed States:

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

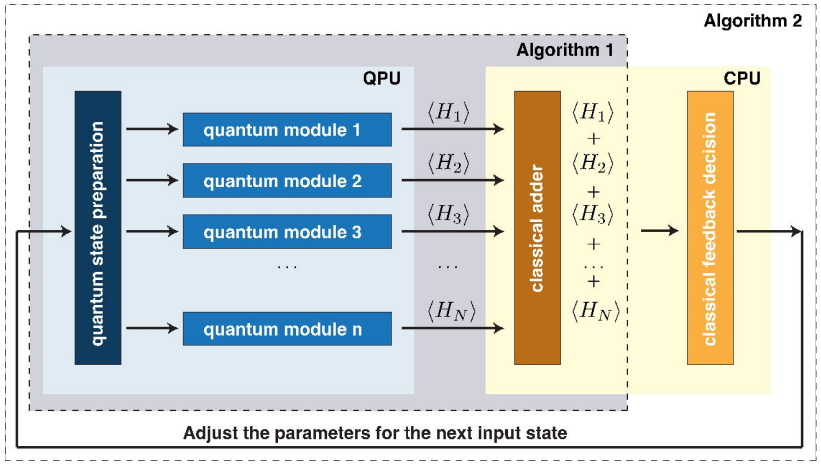
$$\tilde{O} = \sum_i c_i O_i$$

Fully mitigates errors iff

$$\tilde{O}\rho\tilde{O}^\dagger = \rho_0$$

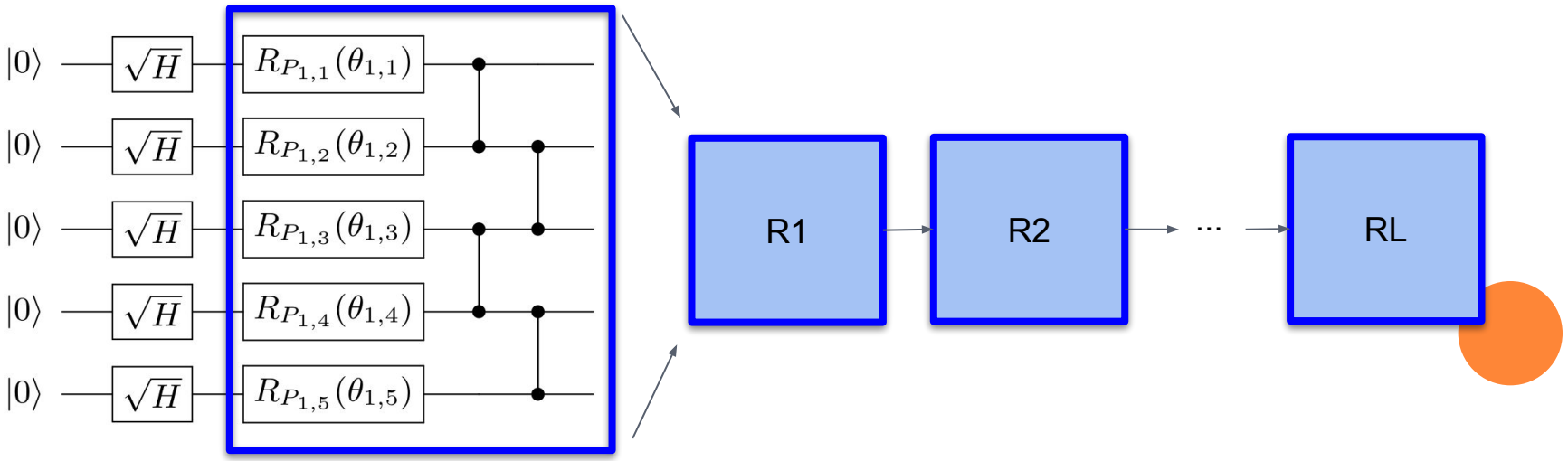
$$\tilde{O} = \sum_i \alpha_i|\Psi_0\rangle\langle\Psi_i| + \sum_{ij} \beta_{ij}|\Psi_i\rangle\langle\Psi_j^\perp|$$

Network / Ansatz Parameterization

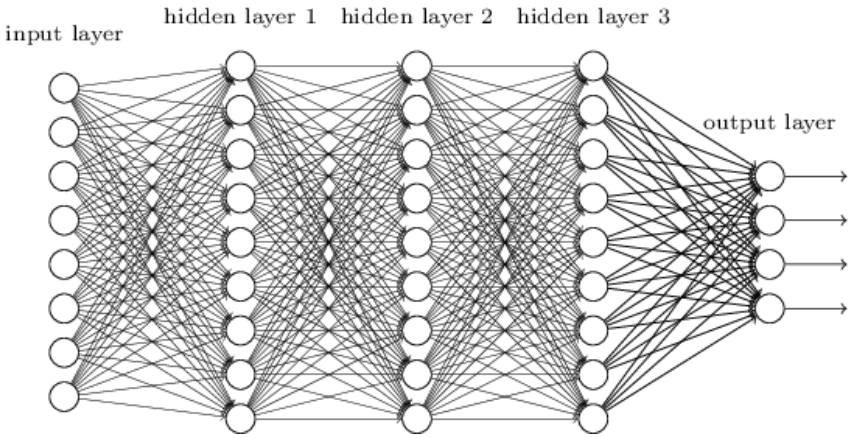


$$\min_{\vec{\theta}} \langle \Psi(\vec{\theta}) | H | \Psi(\vec{\theta}) \rangle$$

Chemistry
Nuclear Physics
Optimization (QAOA)
Machine learning
Algorithm learning
...



Classical Deep Networks



$$\delta^l = \Sigma'(z^l)(w^{l+1})^T \Sigma'(z^{l+1})(w^{l+2})^T \dots \Sigma'(z^L)\nabla_a C$$

Diagonal matrix
< 1/4

Loss/Objective

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

Partial Remedies:

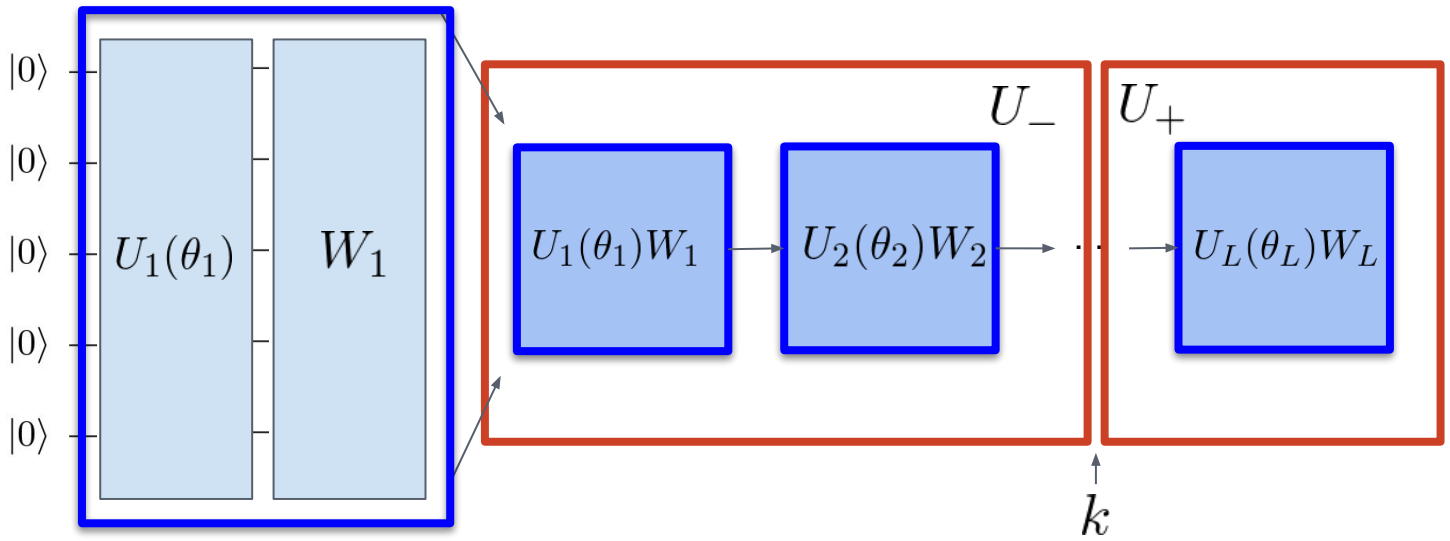
1. Longer training
2. ReLU activation functions
3. Batch normalization
4. Initialization strategies
5. Skip networks (ResNets)
6. Unitary feed forward networks

Estimation Complexity	
Classical	Quantum
$O(\log(1/\epsilon))$	$O(1/\epsilon^{\alpha})$

"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", Ilya Sutskever, James Martens, George Dahl and Geoffrey Hinton (2013).

Random Parameterized Quantum Circuits (RPQC)



$$U_l(\theta_l) = \exp\left(-i\theta_l P_l\right)$$

$$P_k = V$$

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

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

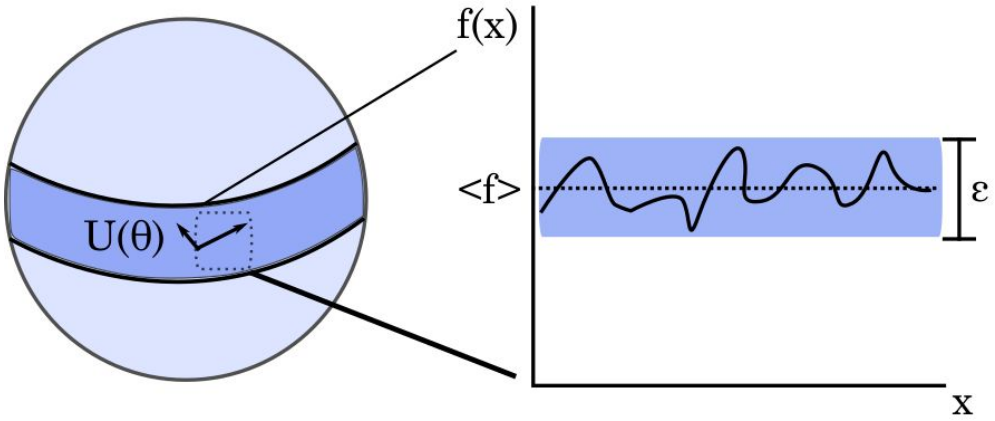
RPQC Definition:

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:

$$S_\epsilon = \{x \in S^{(2n-1)} | d(x_j, 0) \leq \epsilon/2\} \qquad \mu\left(S^{(2n-1)}\right) = 1$$

f "smooth" (Lipschitz continuous w/ constant) η

Then:

$$\mu\left(S_\epsilon\right) = 1 - \exp\left(-cn\epsilon^2\right)$$

$$\Pr\left\{|f(x) - \langle f \rangle| \geq \epsilon\right\} \leq \exp\left(\frac{-n\epsilon^2}{9\pi^3\eta^2}\right)$$

Outline of Analytic Results

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

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

Average: Either U_- or U_+ are 1-designs

$$\langle \partial_k E \rangle = 0$$

Variance:

$$\mathrm{Var}\left[\partial_k E\right] = \langle (\partial_k E)^2 \rangle =$$

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

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

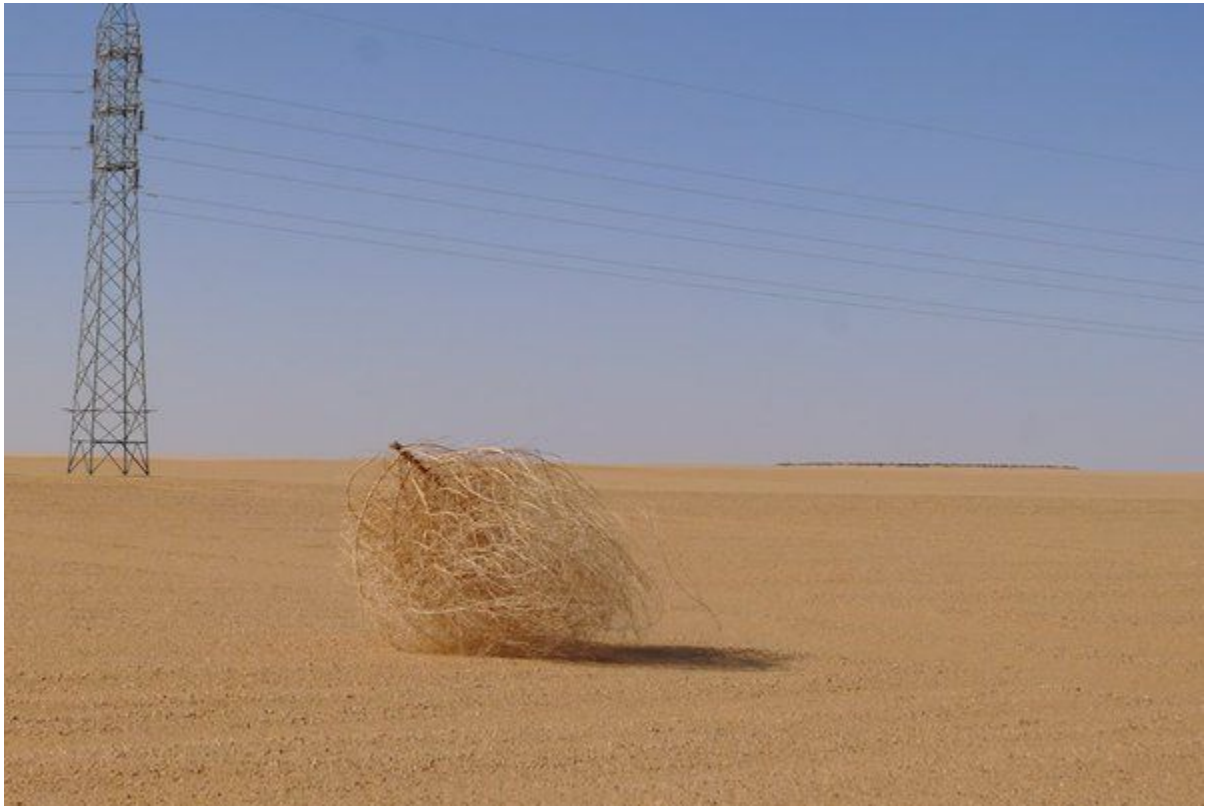
Case 2: U_+ is a 2-design but not U_-

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

Case 3: Both are 2-designs

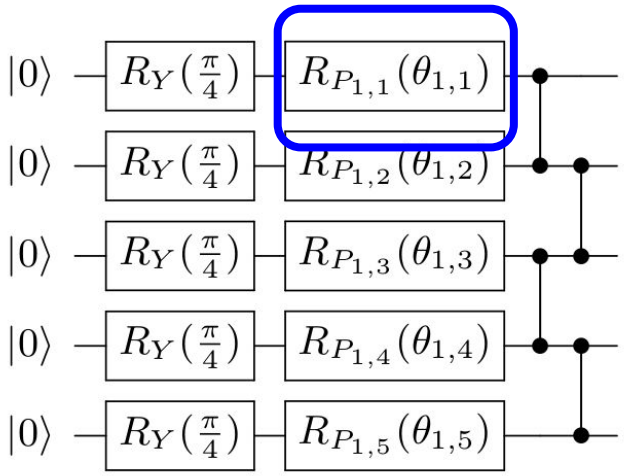
$$2\mathrm{Tr}\left(H^2\right) \mathrm{Tr}\left(\rho^2\right) \left(\frac{\mathrm{Tr}\left(V^2\right)}{2^{3n}} - \frac{\mathrm{Tr}\left(V\right)^2}{2^{4n}} \right)$$

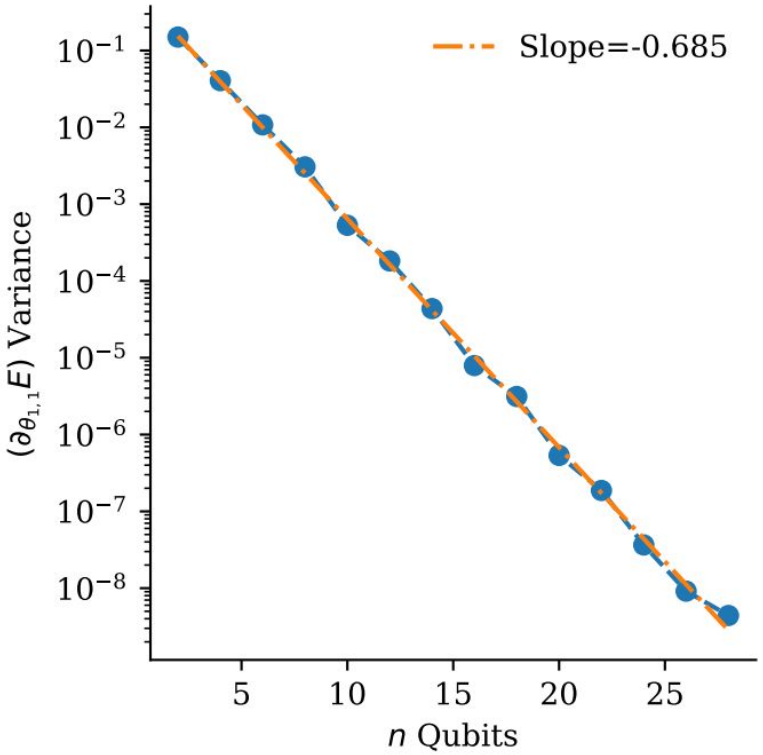
A rare picture of the gradient landscape



Gradients vanishing in practice

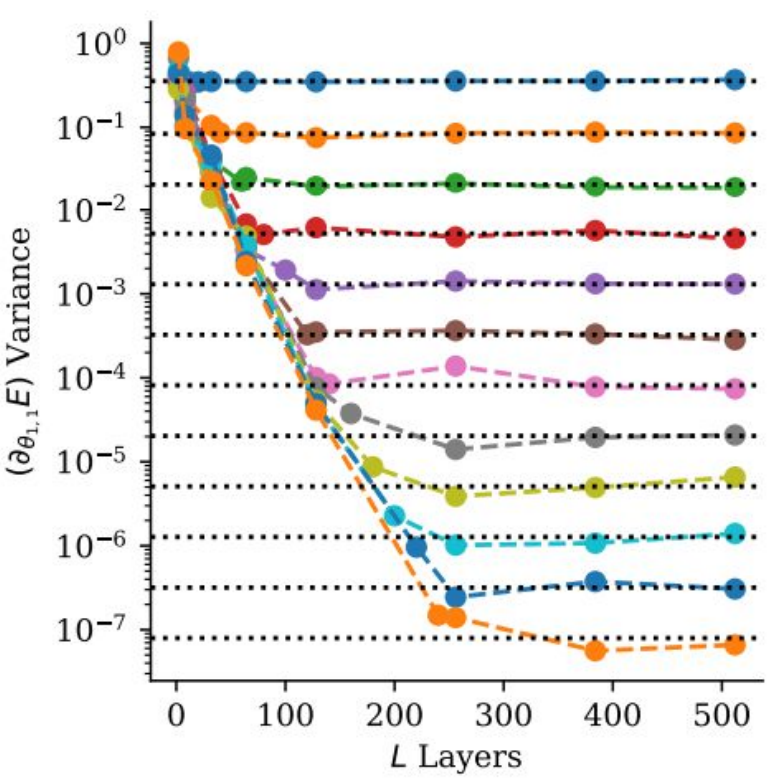
$$H = -Z_1 Z_2$$





$$R_{P_{i,j}}(\theta_{i,j}) = \exp(-i\theta_{i,j} P_{i,j})$$
$$P_{i,j} \in \{X, Y, Z\}$$

Convergence with depth

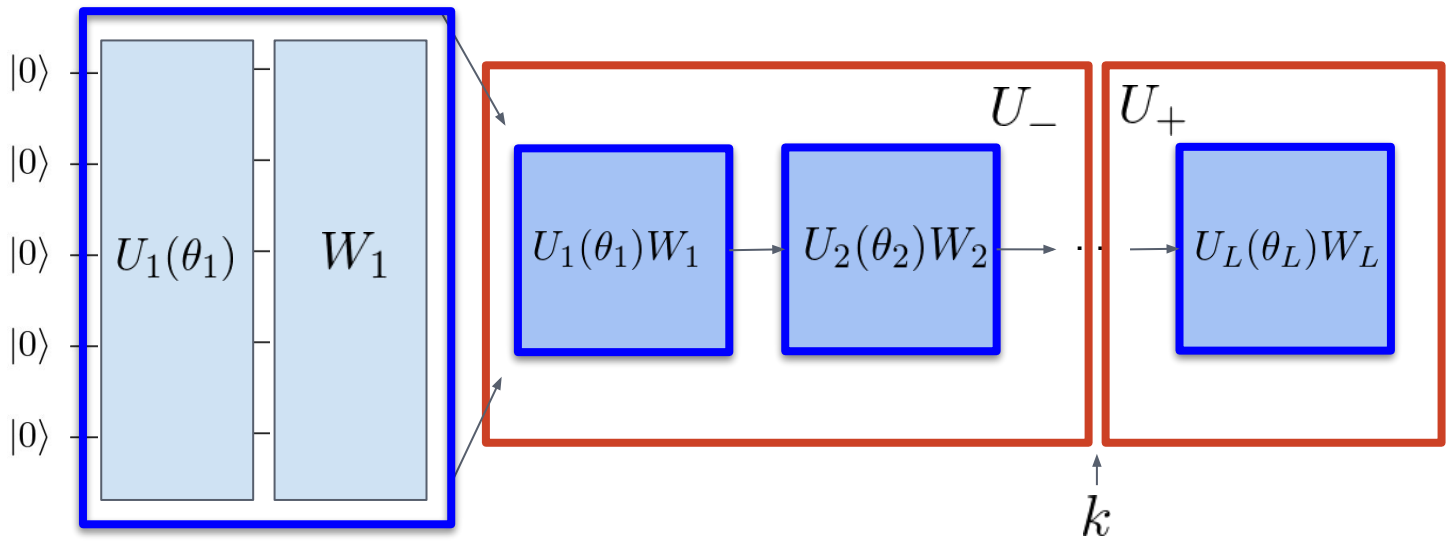


2 Qubits

4 Qubits

22 Qubits

Black holes in your circuits?

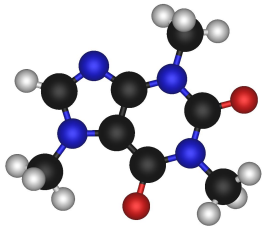


McClean, Boixo, Smelyanskiy, Babbush, Neven
"Barren Plateaus in Quantum Neural Network Training Landscapes"
Nature Communications Vol **9**, 4812 (2018)

Domain Knowledge Matters

Year	Reference	Representation	Algorithm	Time Step Depth	Coherent Repetitions	Total Depth
2005	Aspuru-Guzik et al. [1]	JW Gaussians	Trotter	$\mathcal{O}(\text{poly}(N))$	$\mathcal{O}(\text{poly}(N))$	$\mathcal{O}(\text{poly}(N))$
2010	Whitfield et al. [2]	JW Gaussians	Trotter	$\mathcal{O}(N^5)$	$\mathcal{O}(\text{poly}(N))$	$\mathcal{O}(\text{poly}(N))$
2012	Seeley et al. [3]	BK Gaussians	Trotter	$\widetilde{\mathcal{O}}(N^4)$	$\mathcal{O}(\text{poly}(N))$	$\mathcal{O}(\text{poly}(N))$
2013	Perruzzo et al. [4]	JW Gaussians	UCC	Variational	Variational	$\mathcal{O}(\text{poly}(N))$
2013	Toloui et al. [5]	CI Gaussians	Trotter	$\mathcal{O}(\eta^2 N^2)$	$\mathcal{O}(\text{poly}(N))$	$\mathcal{O}(\text{poly}(N))$
2013	Wecker et al. [6]	JW Gaussians	Trotter	$\mathcal{O}(N^5)$	$\mathcal{O}(N^6)$	$\mathcal{O}(N^{11})$
2014	Hastings et al. [7]	JW Gaussians	Trotter	$\mathcal{O}(N^4)$	$\mathcal{O}(N^4)$	$\mathcal{O}(N^8)$
2014	Poulin et al. [8]	JW Gaussians	Trotter	$\mathcal{O}(N^4)$	$\sim N^2$	$\sim N^6$
2014	McClean et al. [9]	JW Gaussians	Trotter	$\sim N^2$	$\mathcal{O}(N^4)$	$\sim N^6$
2014	Babbush et al. [10]	JW Gaussians	Trotter	$\mathcal{O}(N^4)$	$\sim N$	$\sim N^5$
2015	Babbush et al. [11]	JW Gaussians	Taylor	$\widetilde{\mathcal{O}}(N)$	$\widetilde{\mathcal{O}}(N^4)$	$\widetilde{\mathcal{O}}(N^5)$
2015	Babbush et al. [12]	CI Gaussians	Taylor	$\widetilde{\mathcal{O}}(N)$	$\widetilde{\mathcal{O}}(\eta^2 N^2)$	$\widetilde{\mathcal{O}}(\eta^2 N^3)$
2015	Wecker et al. [13]	JW Gaussians	UCC	Variational	Variational	$\mathcal{O}(N^4)$
2016	McClean et al. [14]	BK Gaussians	UCC	Variational	Variational	$\mathcal{O}(\eta^2 N^2)$
2017	Babbush et al. [15]	JW Plane Waves	Trotter	$\mathcal{O}(N)$	$\mathcal{O}(\eta^{1.83} N^{0.67})$	$\mathcal{O}(\eta^{1.83} N^{1.67})$
2017	Babbush et al. [15]	JW Plane Waves	Taylor	$\widetilde{\mathcal{O}}(1)$	$\widetilde{\mathcal{O}}(N^{2.67})$	$\widetilde{\mathcal{O}}(N^{2.67})$
2017	Babbush et al. [15]	JW Plane Waves	TASP	Variational	Variational	$\mathcal{O}(N)$

Typical chemistry problem workflow



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

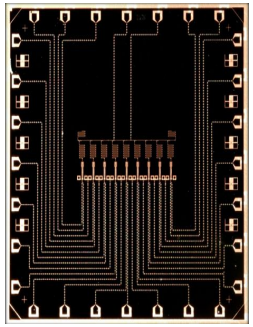
$$H = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l$$

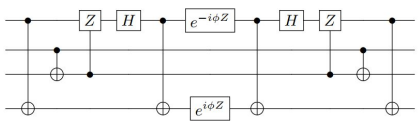
Integral Generation
- Depends on basis set, often uses external software

Starter Calculation (e.g. Hartree-Fock)
- Integral basis change
- Initial state preparation

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

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



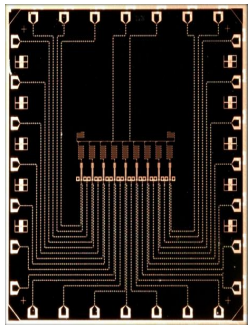


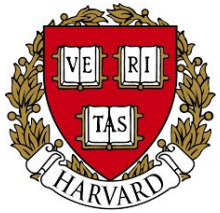
Select Problem & Algorithm
- Energies, properties etc.
- Quantum Phase Estimation
- Variational Quantum Eigensolver (& Ansatz)

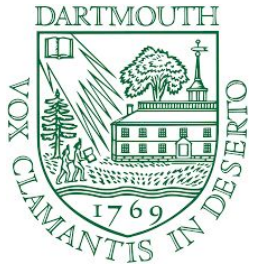
Map to hardware

OpenFermion (www.OpenFermion.org)

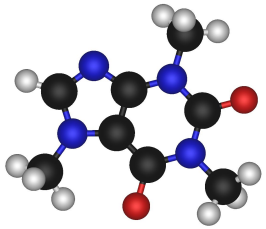
An open source quantum simulation package for quantum computers







Typical chemistry problem workflow



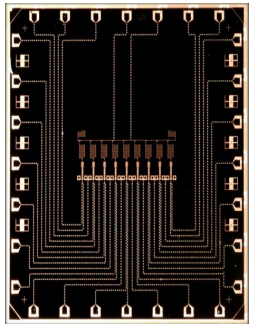
```
geometry = [['H', [0, 0, 0]],
            ['H', [0, 0, 0.74]]]
basis = 'sto-3g'
multiplicity = 1
charge = 0
h2_molecule = MolecularData(geometry, basis,
    multiplicity, charge)
```

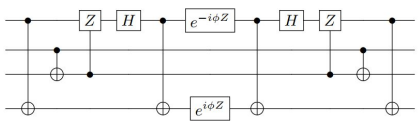
$$H = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l$$

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

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

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

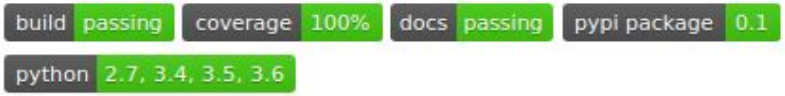





```
...
evolution_operator = (
    uccsd_singlet_evolution(test_amplitudes,
                            n_qubits,
                            n_electrons))
evolution_operator | wavefunction
...
```

Development Philosophy

OpenFermion



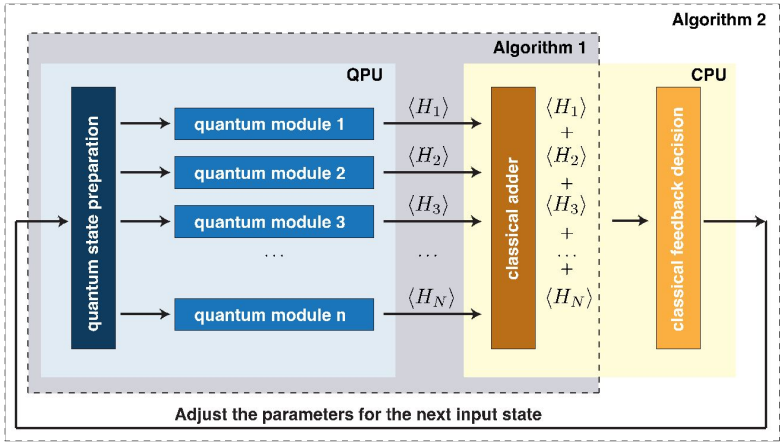
OpenFermion is an open source effort for compiling and analyzing quantum algorithms to simulate fermionic systems, including quantum chemistry. Among other functionalities, the current version features data structures and tools for obtaining and manipulating representations of fermionic and qubit Hamiltonians.

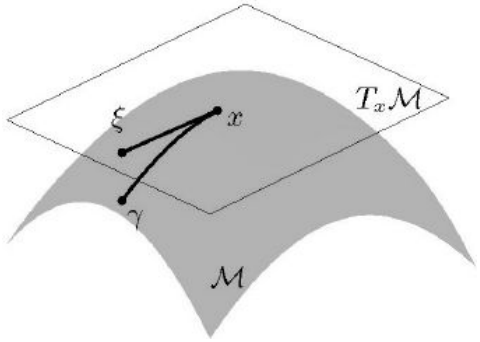
Apache 2.0 open-source license

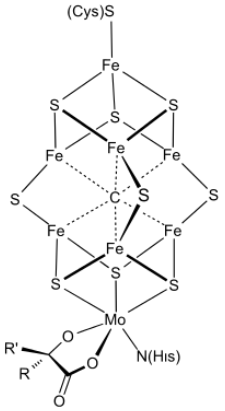
Contribution (Pull Request) → **Automatic Testing**
Extensive tests (>99% coverage)
Enforce no decrease in coverage → **Code Review**
Feedback on design choices
Google style & PEP8 enforced

All contributors added to website and release papers

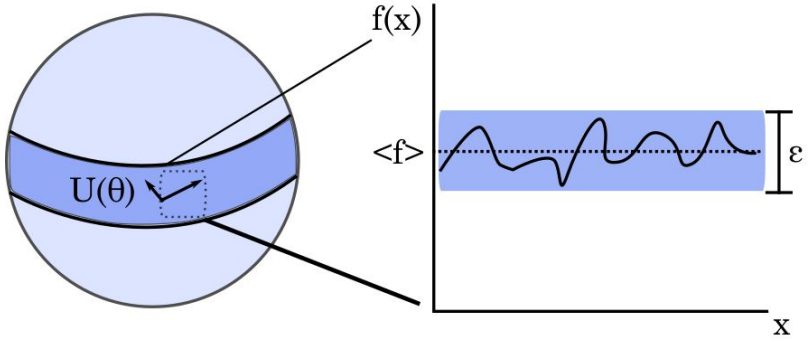
Summary

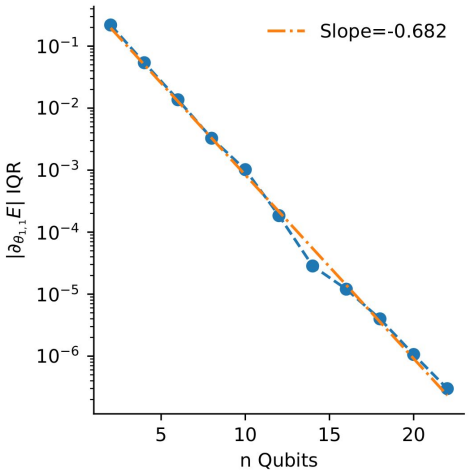






Learn from history, watch out for vanishing gradients!





Acknowledgements

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