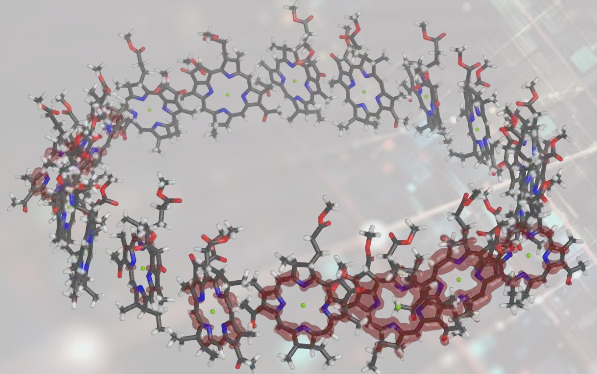
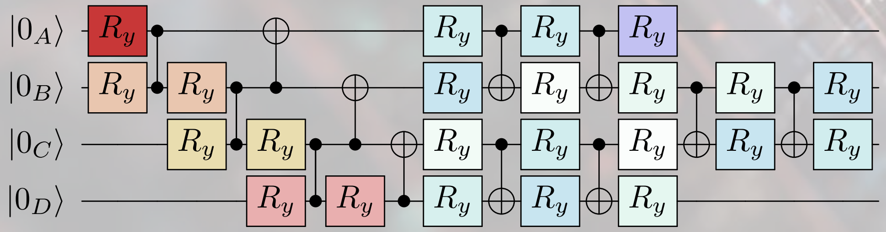
Quantum Algorithms for Large-Scale Photochemistry





Rob Parrish
Chemistry Simulations
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Primer:
Quantum Circuits – What are they good for?

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Classical Computing Timeline: Hardware *then* Software

1945

ENIAC comes online – Designed for ballistics computations

1946

John von Neumann promptly coopts ENIAC for H-bomb simulations

1950

Jule Charney and coworkers perform first numerical weather forecast

1952

Grace Hopper initiates the development of COBOL

1956

First artificial intelligence conference held (Dartmouth)

1956

Dijkstra’s algorithm for shortest paths in graphs

1965

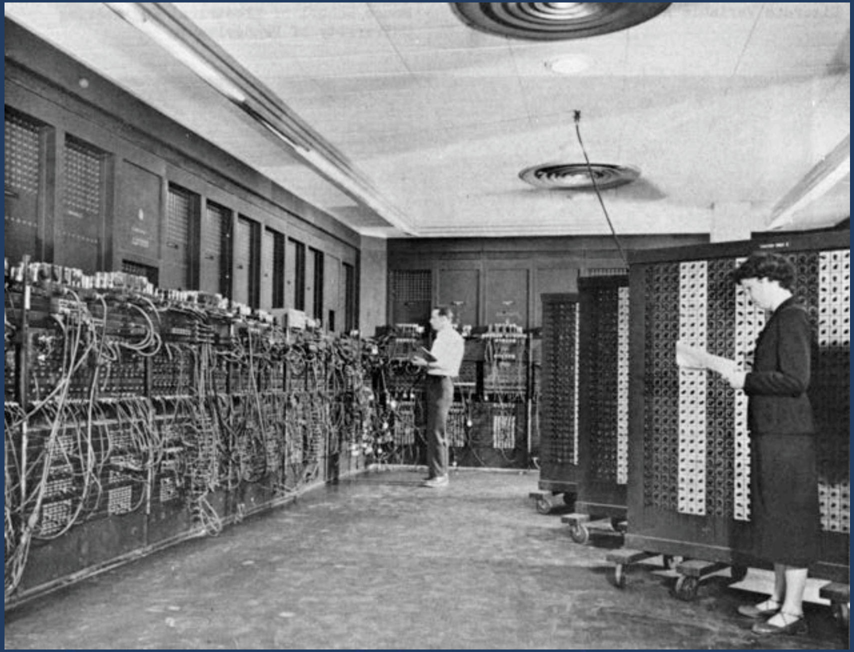
Fast Fourier Transform (Cooley Tukey)

1968

Mouse, Videoconferencing, etc debuted in “the Mother of all Demos”

1988-1992

Boeing designs the 777 fuselage entirely with CFD



ENIAC (U.S. Army Photo)

Classical Accelerator Timeline: Hardware *then* Software (but faster pace)

2007
CUDA released

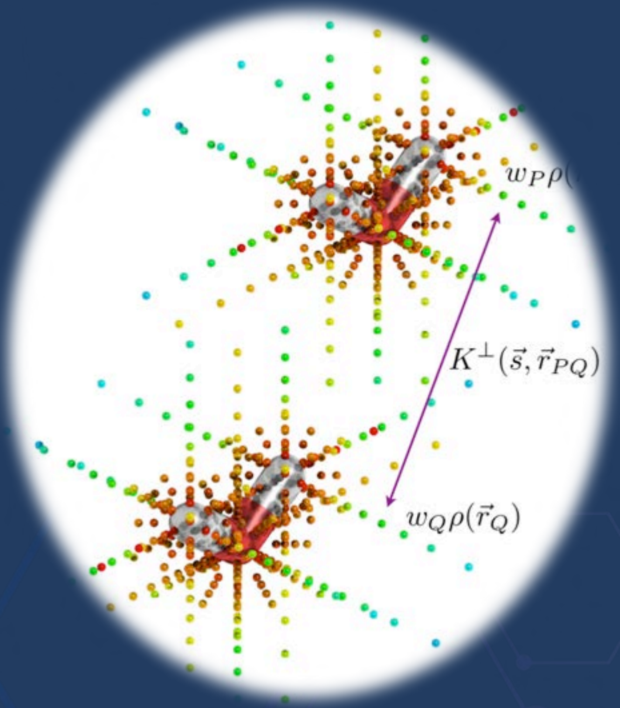
2006-2010
GPU-accelerated Folding@Home molecular mechanics library developed

2009-2012
GPU-accelerated TeraChem electronic structure package developed

2009
OpenCL released

2015
Tensorflow released – GPU and ASIC accelerated machine learning

2016
PyTorch released – GPU accelerated machine learning

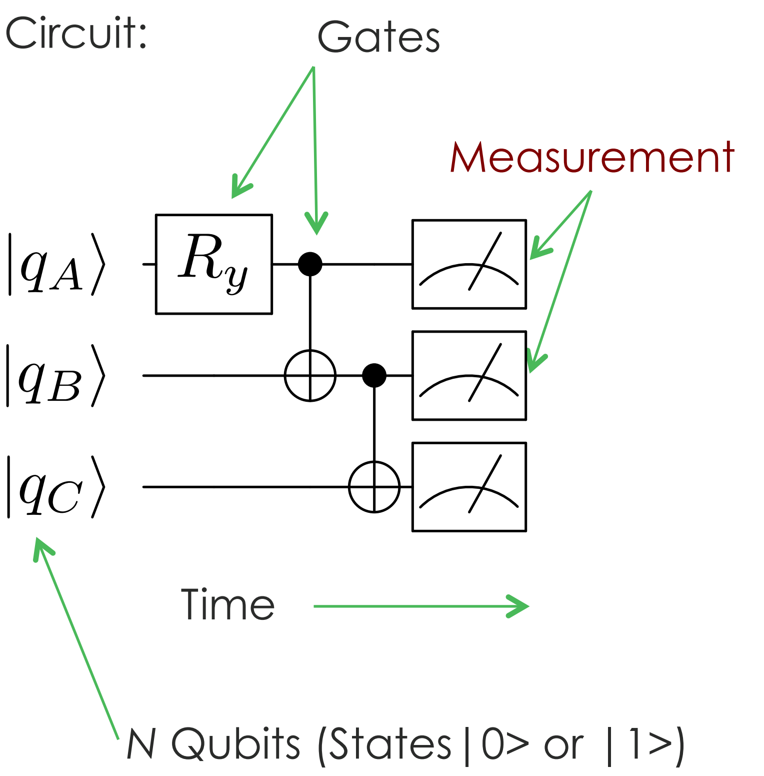


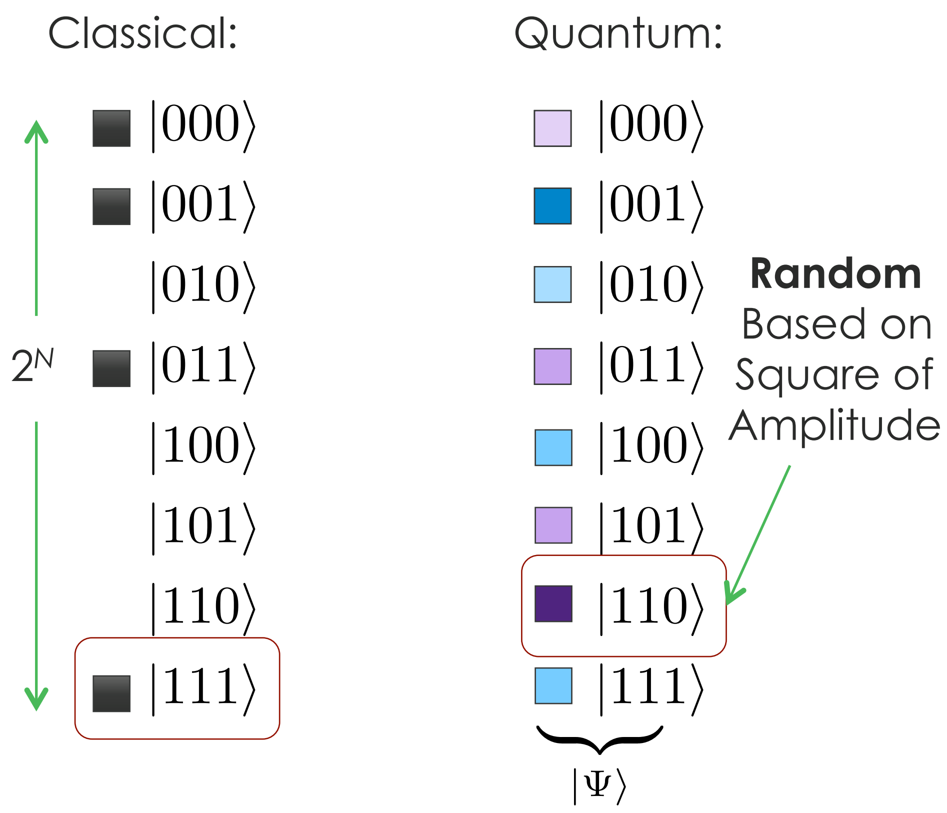
GPU-Accelerated X-Ray Scattering Simulation

Quantum Computing Timeline: Hardware and Software Together?

Goal: On the very day that the first medium-sized quantum computer is brought online, have quantum algorithms and industrial applications problems ready to run to obtain immediate advantage on that machine.

Quantum Circuits: Not Quite a Free Lunch





Quantum Circuits: Key Primitives

Diagonal Observables:

$$O(\theta) \equiv \langle \Psi(\theta) | \hat{O} | \Psi(\theta) \rangle$$

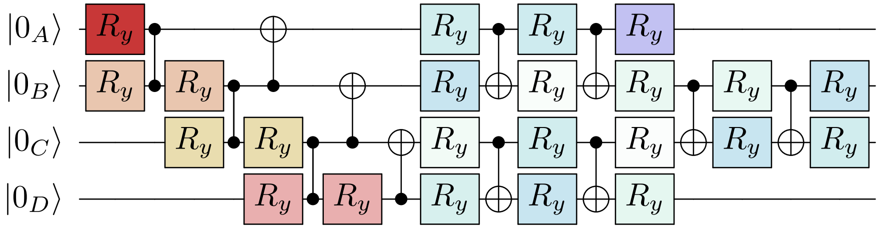
Transition Observables:

$$T(\theta) \equiv \langle \Psi(\theta) | \hat{O} | \Phi(\theta) \rangle$$

Gradients:

$$\vec{G}(\theta) \equiv \frac{\partial \langle \Psi(\theta) | \hat{O} | \Phi(\theta) \rangle}{\partial \theta}$$

|Ψ(θ)>: A Parametrized Circuit:



Ô: A Pauli-Sparse Operator:

$$\hat{O} = \sum_A \mathcal{X}_A \hat{X}_A + \mathcal{Z}_A \hat{X}_Z$$

$$+ \sum_{A,B} \mathcal{X}\mathcal{X}_{AB} \hat{X}_A \otimes \hat{X}_B + \mathcal{X}\mathcal{Z}_{AB} \hat{X}_A \otimes \hat{Z}_B$$

$$\mathcal{Z}\mathcal{X}_{AB} \hat{Z}_A \otimes \hat{X}_B + \mathcal{Z}\mathcal{Z}_{AB} \hat{Z}_A \otimes \hat{Z}_B + \ldots$$

Background:
Large-Scale Photochemistry

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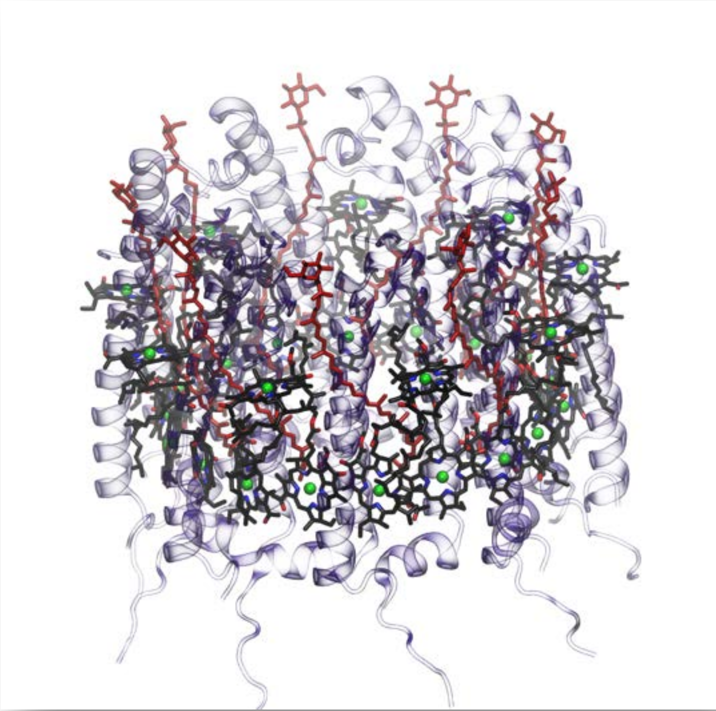
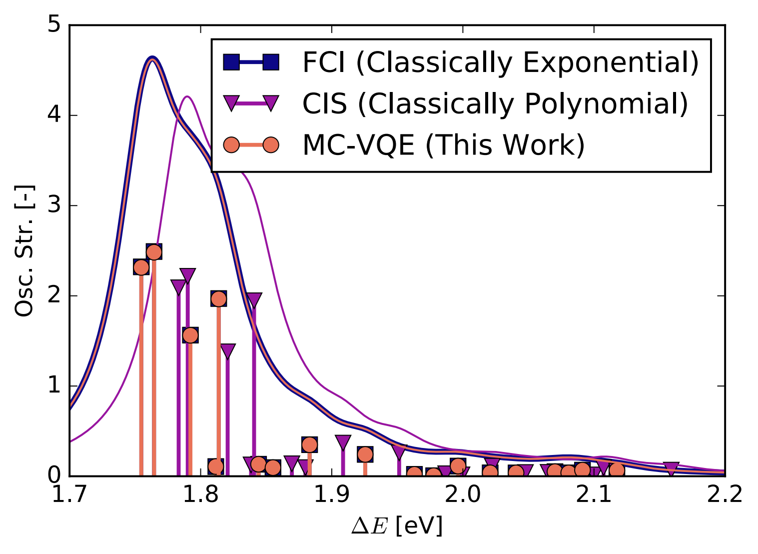
Target: Ground States + Excited States + Properties + Derivatives of Large Photoactive Molecules

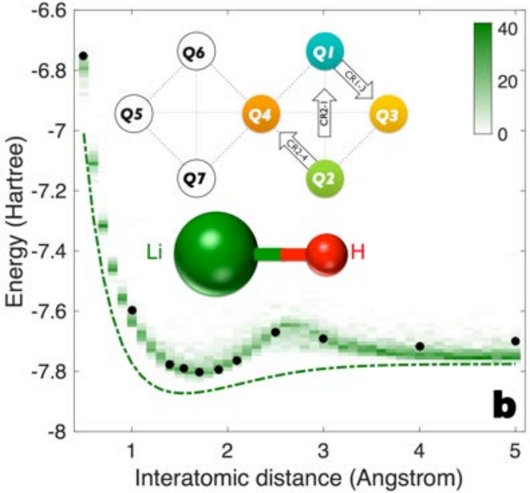




Challenges w/ Existing State of the Art

Untenably Deep Circuits and Low-Accuracy Excited States

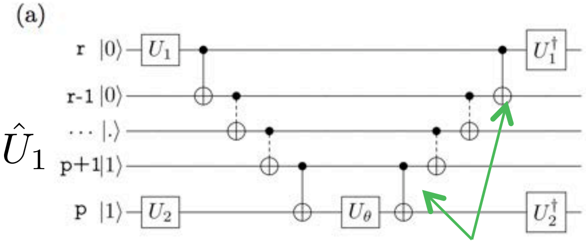
1-3 Atom (~2-6 Spin-Orbital) Experimental Realizations:[1]



Deep Fermionic Quantum Circuits:[2]

$$\hat{U}_{\mathrm{VQE}} \approx \exp\left(\sum_{ia} t_i^a \hat{a}^\dagger \hat{i} + \sum_{iajb} t_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{i}\hat{j} + \mathrm{H.C.}\right)$$

Quartic-Scaling Hamiltonian/VQE Entanglers

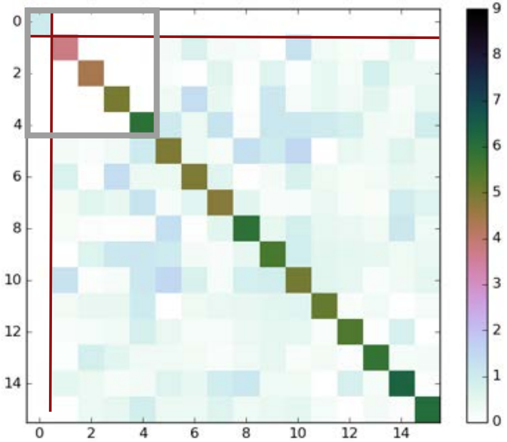


+Fermion Overhead (JW/KB)

$(\mathrm{U}_1, \mathrm{U}_2) = \{(\mathrm{Y}, \mathrm{H}), (\mathrm{H}, \mathrm{Y})\}$ $\left(\text{where } \mathrm{Y} = \mathrm{R}_x(-\frac{\pi}{2})\right)$

Existing QSE-VQE Algorithm for Excited States:[3]

$$|\Psi_\Theta\rangle \equiv \sum_{pq} C_{pq}^{\Theta} \{\hat{p}^\dagger \hat{q}\} \hat{U}_{\mathrm{VQE}} |0\rangle$$



[1]A. Kandala et al., *Nature* **549**, 242 (2017).
[2]P. Barkoutsos et al., *Phys. Rev. A*, **98**, 022322 (2018).
[3]J.R. McClean, M.E. Kimchi-Schwartz, J. Carter, and W.A. de Jong., *Phys. Rev. A*, **95**, 042308 (2017).

Topic 1: **MC-VQE+AIEM**

R.M. Parrish, E.G. Hohenstein, P. McMahon, and T.J. Martínez
Phys. Rev. Lett., **122**, 230401 (2019)
ArXiv: https://arxiv.org/abs/1901.01234

QCWARE

Quantum Computation of Electronic Transitions using a Variational Quantum Eigensolver

- **Authors:** R.M. Parrish, E.G. Hohenstein, P. McMahon, and T.J. Martínez
- **Key Results:**
  - Ground and excited state properties of molecular systems can be treated on the same footing and with the same efficiency for the first time using our novel "multistate, contracted" variational quantum eigensolver (MC-VQE).
  - Transition properties can be studied for the first time, which means that light-molecule interactions can now be studied with quantum computers.
  - The ab initio exciton model (AIEM) allows us to compress the representation of the electronic Hamiltonian significantly which means that molecular systems with thousands of atoms are now tractable.

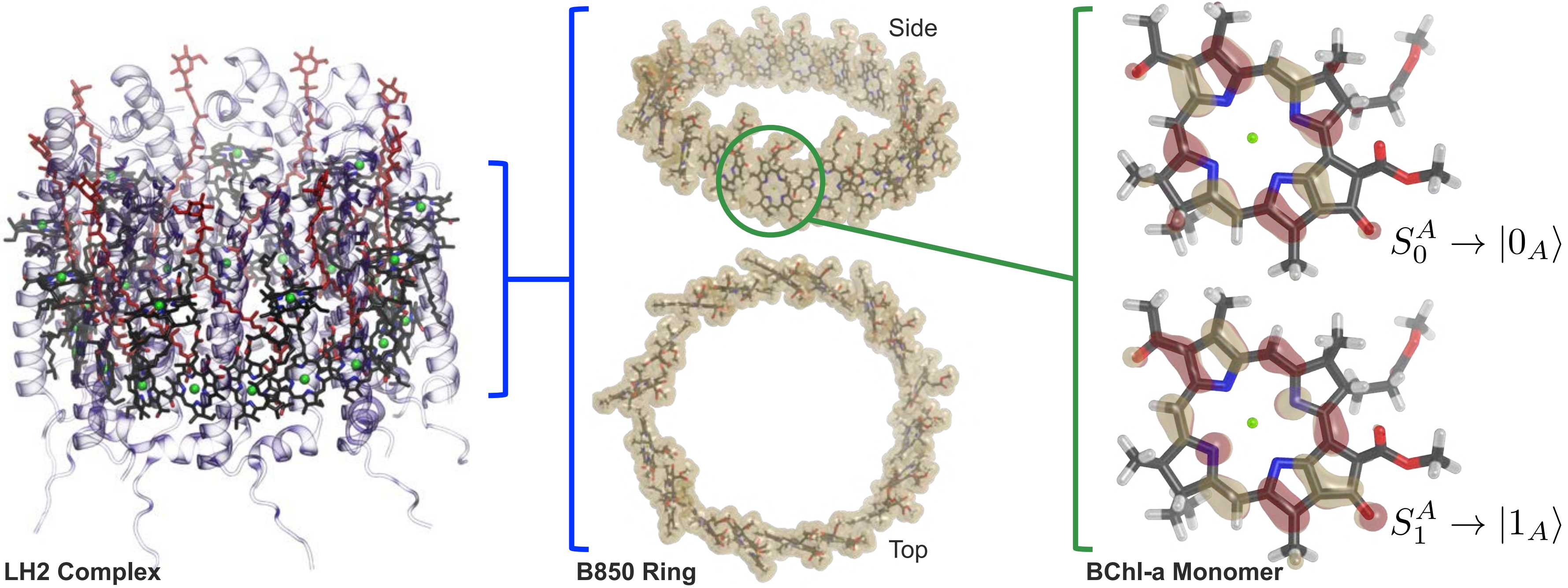
Phys. Rev. Lett., accepted (2019)
ArXiv: https://arxiv.org/abs/1901.01234

QC WARE + SLAC

Tool 1: Quantum Deployment of the *Ab Initio* Exciton Model (AIEM)[1]

Minimizing Quantum Circuit Depth/Connectivity by Classical Compression

Photosystem: Photoactive Component: Monomer States (TD-DFT):

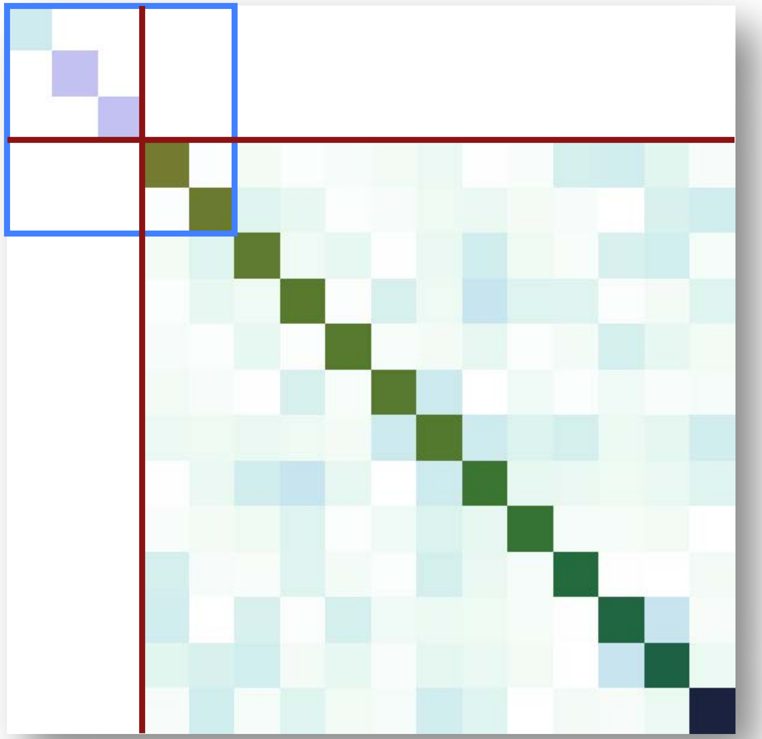


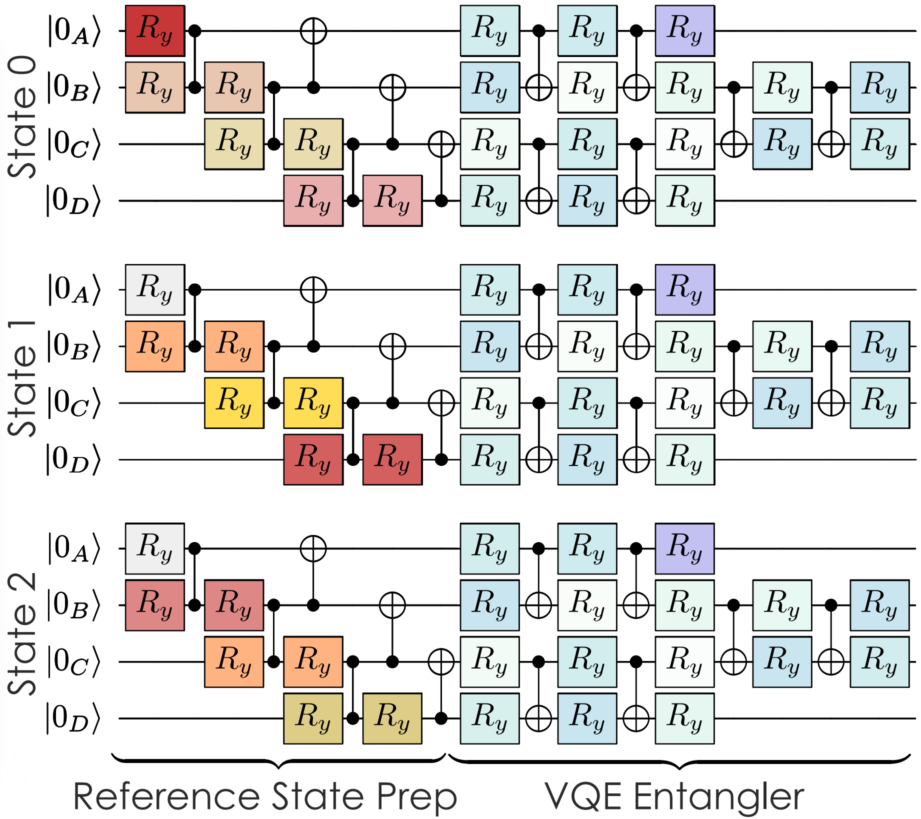
1x Qubit per Monomer!!

[1]A. Sisto, D.R. Glowacki, and T.J. Martínez, *Acc. Chem. Res.*, **47**, 2857 (2014).
X. Li, R.M. Parrish, S.I.L. Kokkila-Schumacher, and T.J. Martínez, *J. Chem. Theory Comput.*, **13**, 3493 (2017).

Tool 2: A Multistate, Contracted Variational Quantum Eigensolver (MC-VQE)

A New Quantum Algorithm for the Balanced Treatment of Ground/Excited States





Required Technical Tools

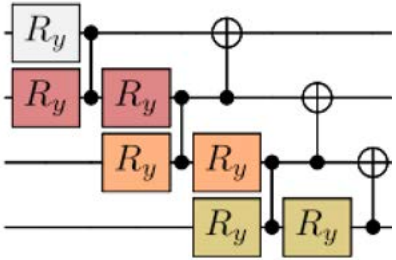
Mapping Electronic Structure Concepts to Quantum Circuits

CIS Reference States:

$$|\Phi_\Theta\rangle \equiv \mu|000\ldots\rangle + \alpha|100\ldots\rangle + \beta|010\ldots\rangle + \gamma|001\ldots\rangle + \ldots$$

$$: \sqrt{\mu^2 + \alpha^2 + \beta^2 + \gamma^2 \ldots} = 1$$

CIS State Preparation Circuit:[1]



- N Parameters (R_y gates)
- $O(N)$ Gates
- $O(N)$ Depth

Transition Matrix Elements:

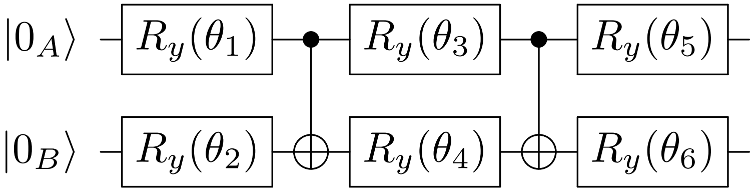
$$2H_{\Theta\neq\Theta'} = \left(\langle\Phi_\Theta| + \langle\Phi_{\Theta'}|\right)\hat{U}^\dagger\hat{H}\hat{U}\left(|\Phi_\Theta\rangle + |\Phi_{\Theta'}\rangle\right)/2 - \left(\langle\Phi_\Theta| - \langle\Phi_{\Theta'}|\right)\hat{U}^\dagger\hat{H}\hat{U}\left(|\Phi_\Theta\rangle - |\Phi_{\Theta'}\rangle\right)/2$$

"Interfering" Reference States:

$$|\chi^\pm_{\Theta\Theta'}\rangle \equiv \left(|\Phi_\Theta\rangle \pm |\Phi_{\Theta'}\rangle\right)/\sqrt{2}$$

Recipe: change CIS coefficients!

***SO*(4) VQE Entanglers:**[2]

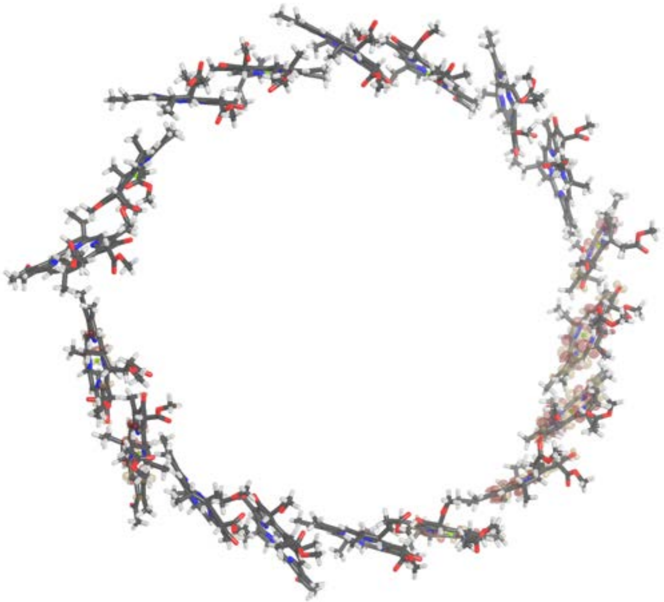


[1]Inspiration from $|W_N>$ states: F. Diker, arXiv preprint, arXiv:1606.09290 (2016).
[2]First Presented in: H.-R. Wei and Y.-M. Di, arXiv preprint, arXiv:1203.0722 (2012).

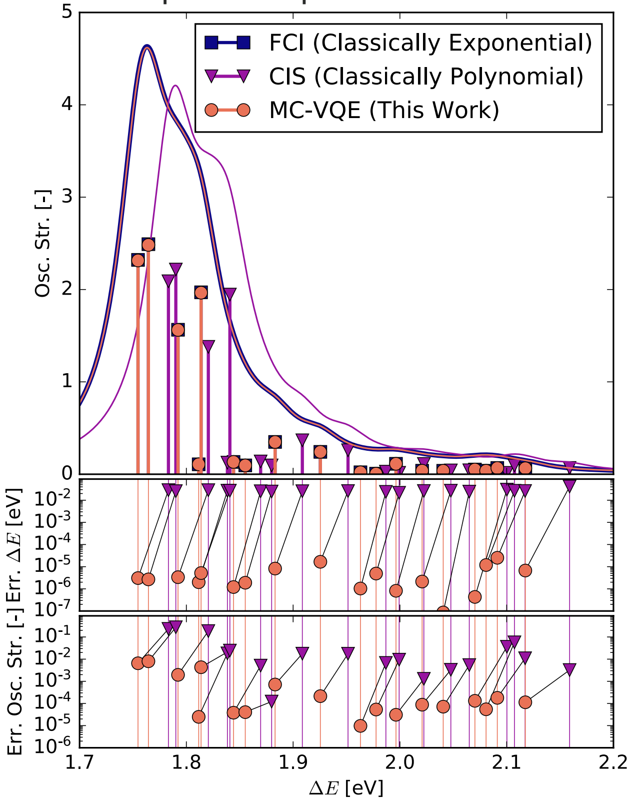
Preliminary Results

Simulated Quantum Circuit Deployment of MC-VQE+AIEM

$S_0 \rightarrow S_1$ Difference Density (red +/tan -):



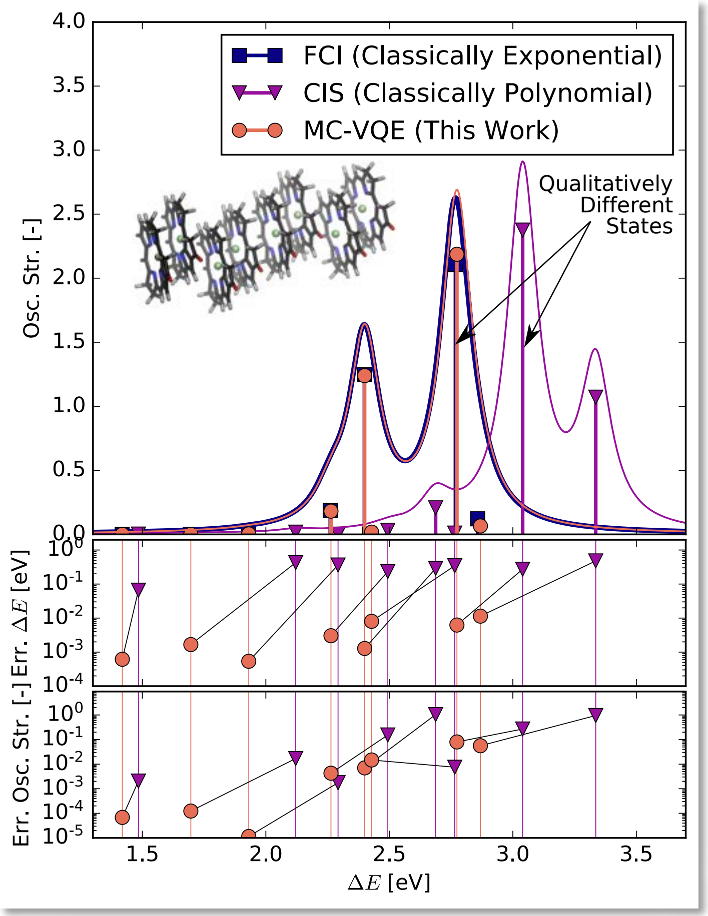
Absorption Spectrum:



N=18 B850 Ring of LH2. Monomer states from ωPBE(ω=0.3)/6-31G*. Nearest-Neighbor Dipole Interactions.
R.M. Parrish, E.G. Hohenstein, P.L. McMahon, and T.J. Martínez, https://arxiv.org/abs/1901.01234.pdf (2019).

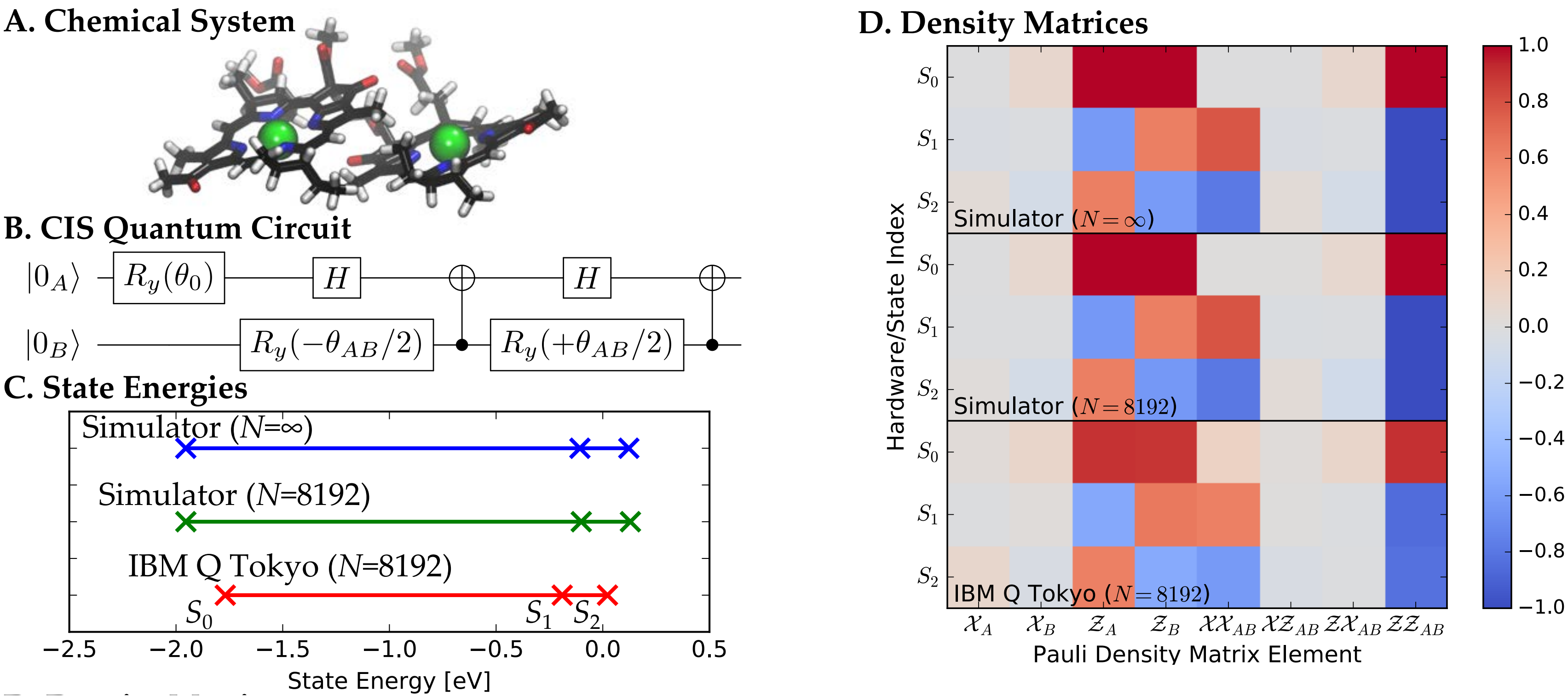
A Case Where CIS/TD-DFT Qualitatively Fail

H-Aggregate *N*=8 Stack of BChl-a: Highly multi-reference/multi-excitonic



Initial Hardware Deployment

CIS State Preparation on IBM Q 20 Tokyo



More tests underway!

Topic 2: **MC-VQE+AIEM Gradients**

R.M. Parrish, E.G. Hohenstein, P. McMahon, and T.J. Martínez

ArXiv: https://arxiv.org/abs/1906.08728

QCWARE

Hybrid Quantum/Classical Derivative Theory: Analytical Gradients and Excited-State Dynamics for the Multistate Contracted Variational Quantum Eigensolver

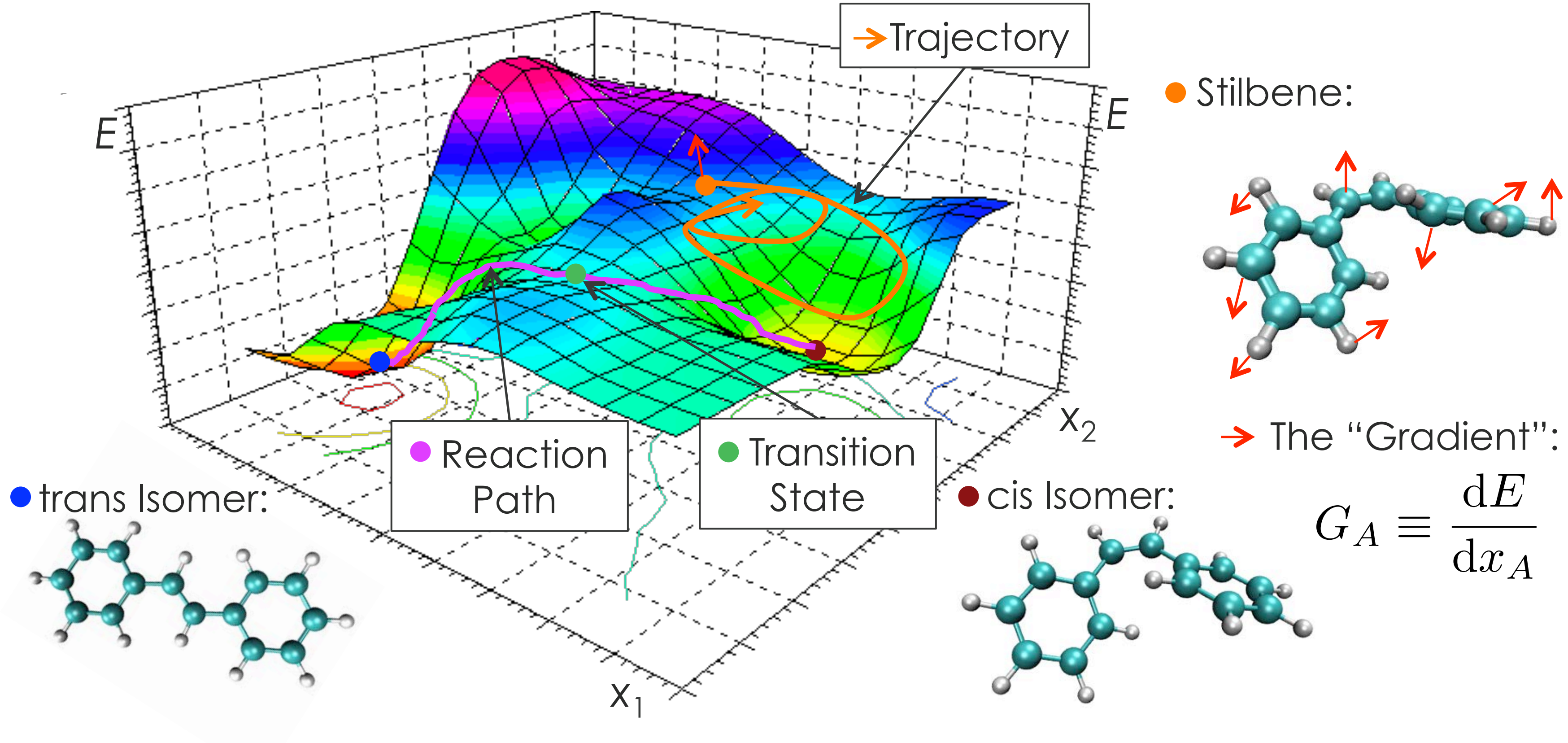
- **Authors:** R.M. Parrish, E.G. Hohenstein, P. McMahon, and T.J. Martínez
- **Key Results:**
  - Ground and excited state gradients of MC-VQE+AIEM energies can be computed with a limited number of additional quantum measurements.
  - The Lagrangian formalism efficiently decouples the quantum and classical portions of the computation, allowing for the number of quantum measurements to be made to be independent of the number of atoms.
  - The quantum response equations involve the solution of the SA-VQE response equations, and require evaluation (or contraction with) the SA-VQE Hessian.
  - The parameter shift method provides the needed quantum gradient pieces.

ArXiv: https://arxiv.org/abs/1906.08721

QC WARE + SLAC

Analytical Nuclear Gradients

The key to efficient exploration of the potential energy landscape



$$G_A \equiv \frac{\mathrm{d}E}{\mathrm{d}x_A}$$

Reme ber: This plot is an illusion: Stilbene has 72 dimensions! Traveling through hyperspace ain't like dusting crops!

Lagrangian Formulation of Analytical Gradients

Beating the Wavefunction Response Problem

Energy Function:

$$E \equiv \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle$$

Wavefunction Parameters:

$$f(\theta) = 0$$

← Orbital Choices
Reference State Choices
State Averaging

Direct Gradient:

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\mathrm{d}E}{\mathrm{d}\hat{H}} \frac{\mathrm{d}\hat{H}}{\mathrm{d}x} + \frac{\mathrm{d}E}{\mathrm{d}\theta} \frac{\mathrm{d}\theta}{\mathrm{d}x}$$

"Hellmann-Feynman" (↑ $\frac{\mathrm{d}E}{\mathrm{d}\hat{H}}$) "Wavefunction Response" (↑ $\frac{\mathrm{d}\theta}{\mathrm{d}x}$)

Lagrangian Function:

$$\mathcal{L} \equiv \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle + \tilde{\theta} f(\theta)$$

Wavefunction Parameters:

$$\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}\tilde{\theta}} = 0 \Rightarrow \qquad f(\theta) = 0$$

Response Equations:

$$\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}\theta} = 0 \Rightarrow \frac{\mathrm{d}}{\mathrm{d}\theta} \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle + \tilde{\theta} \frac{\mathrm{d}}{\mathrm{d}\theta} f(\theta) = 0$$

Nuclear Gradient:

$$\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}x} = \frac{\mathrm{d}\mathcal{L}}{\mathrm{d}\hat{H}} \frac{\mathrm{d}\hat{H}}{\mathrm{d}x} + \underbrace{\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}\theta}}_{0} \frac{\mathrm{d}\theta}{\mathrm{d}x} + \underbrace{\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}\tilde{\theta}}}_{0} \frac{\mathrm{d}\tilde{\theta}}{\mathrm{d}x}$$

Favorite Lagrangian Reference: T.U. Helgaker, *IJQC*, **21**, 939 (1982) – 4 equations, ¾ pages, 16 references.

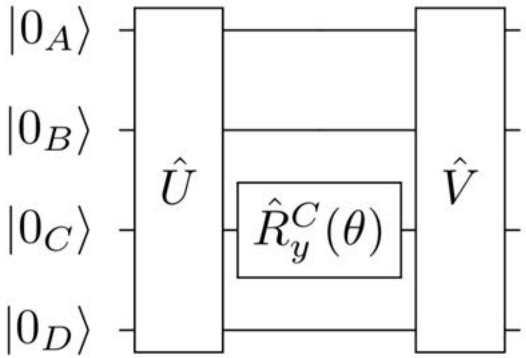
Parameter Shift Method

Efficient, Statistically Robust Quantum Derivatives

Observable Expectation Value:

$$O(\theta) = \langle \hat{O} \rangle = \langle \vec{0} | \hat{U}^\dagger \hat{R}_y^{C\dagger}(\theta) \hat{V}^\dagger \hat{O} \hat{V} \hat{R}_y^C(\theta) \hat{U} | \vec{0} \rangle$$

Quantum Circuit:



First Derivatives:

$$\frac{\partial O(\theta)}{\partial \theta} = O(\theta + \pi/4) - O(\theta - \pi/4)$$

$$\approx \frac{1}{2h}\left[O(\theta + h) - O(\theta - h)\right]$$

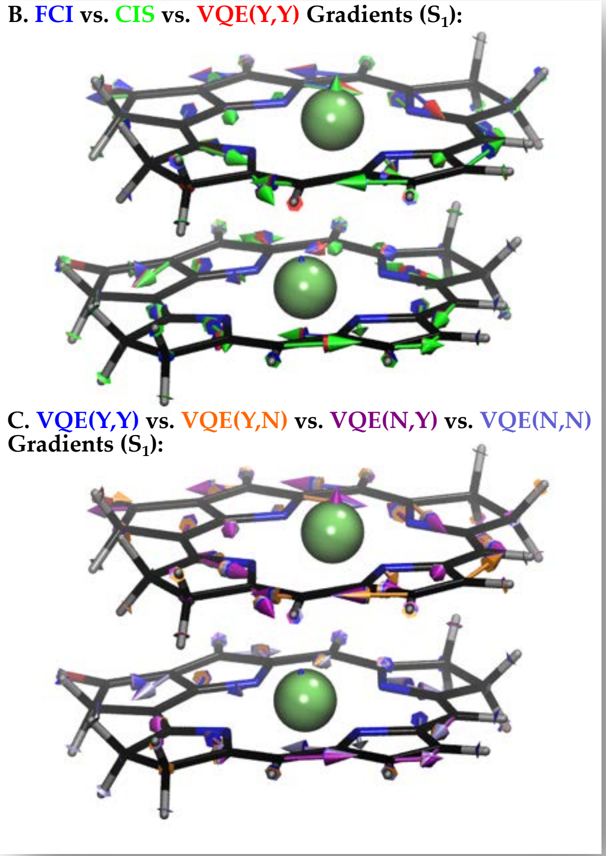
Second Derivatives:

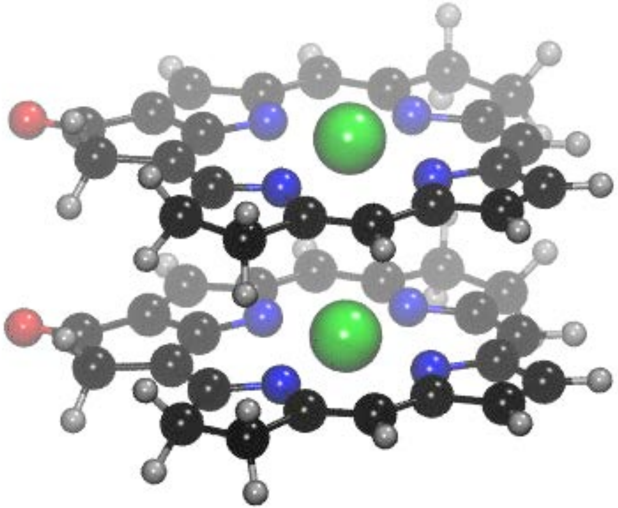
$$\frac{\partial^2 O(\theta)}{\partial \theta^2} = O(\theta + \pi/2) - 2O(\theta) + O(\theta - \pi/2)$$

$$\approx \frac{1}{4h^2}\left[O(\theta + 2h) - 2O(\theta) + O(\theta - 2h)\right]$$

MC-VQE+AIEM Analytical Gradients

150 Equations – yields exact forces with minimal additional quantum measurements





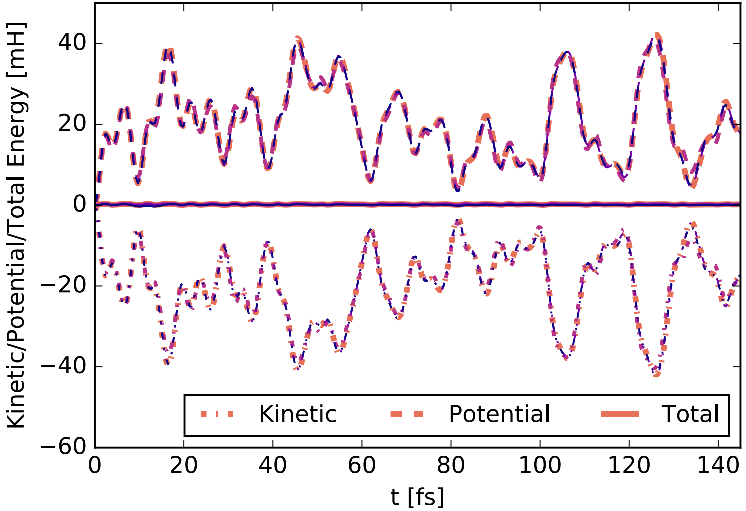
Example Excited State Dynamics with MC-VQE+AIEM

MC-VQE+AIEM Gradient Reference: R.M. Parrish, E.G. Hohenstein, P.L. McMahon, and T.J. Martinez, arXiv:1906.08728.

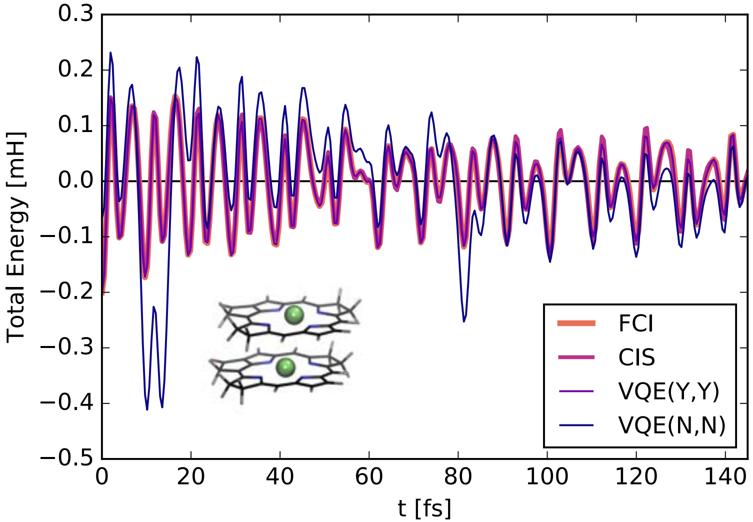
Detailed Dynamics Study

Self-Consistent Gradients/Lagrangian Formalism Needed for Convservation of Energy

Energy Profile vs. Time:



Total Energy:



NVE-VV w/ 20 au timestep

MC-VQE+AIEM Gradient Reference: R.M. Parrish, E.G. Hohenstein, P.L. McMahon, and T.J. Martinez, arXiv:1906.08728.

Crux: Represent solution as variational linear combination of ***different*** quantum circuit wavefunctions – combine in classical postprocessing

Topic 3: **QFD**

Same Day!

R.M. Parrish and P. McMahon
ArXiv: https://arxiv.org/abs/1909.08925

W. Huggins, J. Lee, U. Baek, B. O'Gormin, and K.B. Whaley
ArXiv: https://arxiv.org/abs/1909.09114

QCWARE

Quantum Filter Diagonalization: Quantum Eigendecomposition without Full Quantum Phase Estimation

- **Authors:** R.M. Parrish and P. McMahon
- **Key Results:**
  - A new variational ansatz is developed that represents the target wavefunction as a classical weighted linear combination of basis states that are prepared from multiple different quantum circuits.
  - The classical weights are determined by solving a generalized eigenproblem after all quantum matrix elements are obtained.
  - The (parallelizable) quantum matrix elements require evaluation of off-diagonal overlaps between different basis states via simple swap test circuits.
  - Using a basis of Trotterized time-propagated guess states, excellent accuracy is obtained for a case study problem even in the presence of considerable Trotterization error.

ArXiv: https://arxiv.org/abs/1909.08925

Problem Statement

Pauli-Sparse Hamiltonian:

$$\hat{H} \equiv \sum_{A} \mathcal{Z}_A \hat{Z}_A + \mathcal{X}_A \hat{X}_A$$
$$+ \sum_{A>B} \mathcal{Z}\mathcal{Z}_{AB} \hat{Z}_A \otimes \hat{Z}_B + \mathcal{Z}\mathcal{X}_{AB} \hat{Z}_A \otimes \hat{X}_B$$
$$+ \mathcal{X}\mathcal{Z}_{AB} \hat{X}_A \otimes \hat{Z}_B + \mathcal{X}\mathcal{X}_{AB} \hat{X}_A \otimes \hat{X}_B + \ldots$$

Schrödinger Equation:

$$\hat{H} | \Psi^{\Theta} \rangle = E^{\Theta} | \Psi^{\Theta} \rangle : \ \langle \Psi^{\Theta} | \Psi^{\Theta'} \rangle = \delta_{\Theta\Theta'}$$

Transition Properties:

$$O^{\Theta\Theta'} \equiv \langle \Psi^{\Theta} | \hat{O} | \Psi^{\Theta'} \rangle$$

QFD Ansatz and Generalized Eigenproblem (Classical)

Ansatz:

$$|\Psi^{\Theta}\rangle \equiv \sum_{\Xi k} C_{\Xi k}^{\Theta} e^{-i2\pi k\hat{H}/\kappa}|\Phi_{\Xi}\rangle \equiv \sum_{\Xi k} C_{\Xi k}^{\Theta}|\Gamma_{\Xi k}\rangle$$

Variational Generalized Eigenproblem:

$$\sum_{\Xi' k'} \mathcal{H}_{\Xi k,\Xi' k'} C_{\Xi' k'}^{\Theta} = \sum_{\Xi' k'} \mathcal{S}_{\Xi k,\Xi' k'} C_{\Xi' k'}^{\Theta} E^{\Theta} :$$

$$\sum_{\Xi k}\sum_{\Xi' k'} C_{\Xi k}^{*\Theta} \mathcal{S}_{\Xi k,\Xi' k'} C_{\Xi' k'}^{\Theta'} = \delta_{\Theta\Theta'}$$

Hamiltonian Matrix Elements:

$$\mathcal{H}_{\Xi k,\Xi' k'} \equiv \langle\Gamma_{\Xi k}|\hat{H}|\Gamma_{\Xi' k'}\rangle$$

$$= \langle\Phi_{\Xi}|e^{+i2\pi k\hat{H}/\kappa}\hat{H}e^{-i2\pi k'\hat{H}/\kappa}|\Phi_{\Xi'}\rangle$$

Overlap Matrix Elements:

$$\mathcal{S}_{\Xi k,\Xi' k'} \equiv \langle\Gamma_{\Xi k}|\Gamma_{\Xi' k'}\rangle$$

$$= \langle\Phi_{\Xi}|e^{+i2\pi k\hat{H}/\kappa}e^{-i2\pi k'\hat{H}/\kappa}|\Phi_{\Xi'}\rangle$$

QFD Transition Properties

Transition Properties:

$$\langle \Psi^{\Theta} | \hat{O} | \Psi^{\Theta'} \rangle = \sum_{\Xi k} \sum_{\Xi' k'} C^{*\Theta}_{\Xi k} \mathcal{O}_{\Xi k, \Xi' k'} C^{\Theta'}_{\Xi' k'}$$

Transition Operator Matrix Elements:

$$\mathcal{O}_{\Xi k, \Xi' k'} \equiv \langle \Gamma_{\Xi k} | \hat{O} | \Gamma_{\Xi' k'} \rangle$$

$$= \langle \Phi_{\Xi} | e^{+i2\pi k \hat{H}/\kappa} \hat{O} e^{-i2\pi k' \hat{H}/\kappa} | \Phi_{\Xi'} \rangle$$

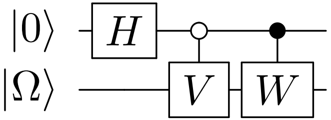
QFD Quantum Matrix Elements

Desired Transition Observable:

$$|A\rangle \equiv \hat{V}|\Omega\rangle \qquad |B\rangle \equiv \hat{W}|\Omega\rangle \qquad \langle A|\hat{O}|B\rangle \equiv \langle\Omega|\hat{V}^\dagger\hat{O}\hat{W}|\Omega\rangle$$

1-Ancilla Swap Test Circuit:

$|\aleph\rangle \equiv$



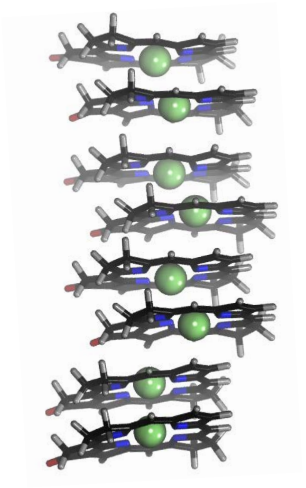
$$= \frac{1}{\sqrt{2}}\left[|0\rangle \otimes \hat{V}|\Omega\rangle + |1\rangle \otimes \hat{W}|\Omega\rangle\right]$$

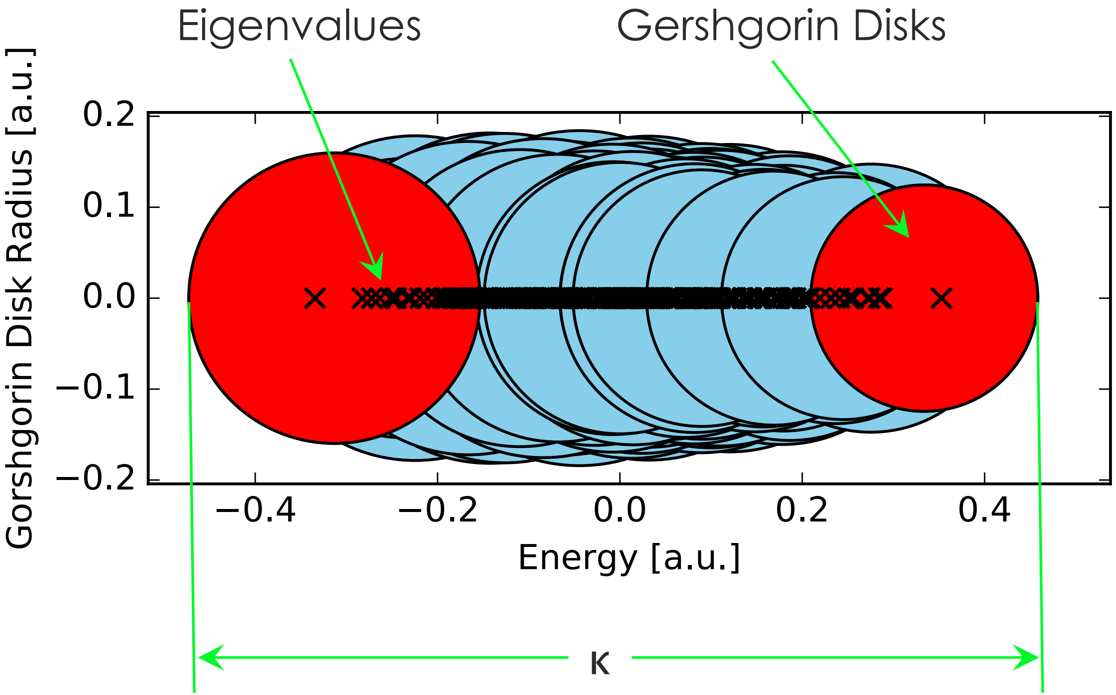
Resolved Observable:

$$\langle A|\hat{O}|B\rangle = \langle\aleph|\hat{X} \otimes \hat{O}|\aleph\rangle + i\langle\aleph|\hat{Y} \otimes \hat{O}|\aleph\rangle$$

QFD Hamiltonian Scaling (Gershgorin Circles)

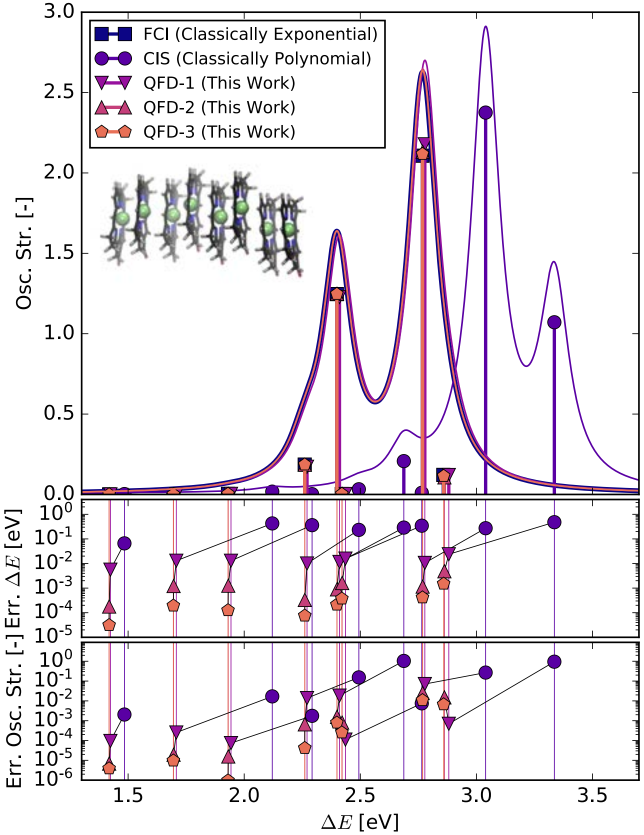
N=8 BChl-a Stack:



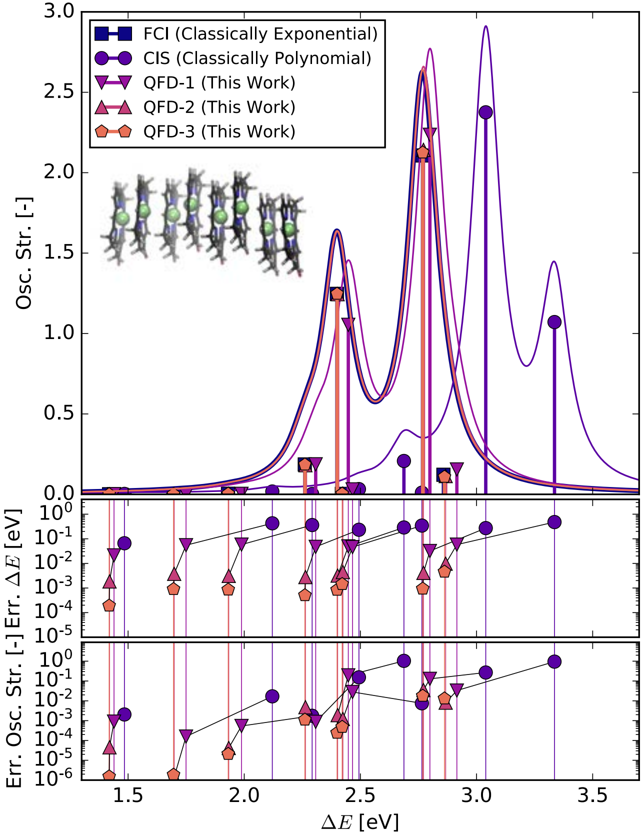


QFD Ansatz Demonstration

Exact U:



Trotterized U:



(Ideal Quantum Circuits, infinite statistical sampling limit)

Acknowledgements

Ed Hohenstein

Peter McMahon

Todd Martínez

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Chemistry Simulations

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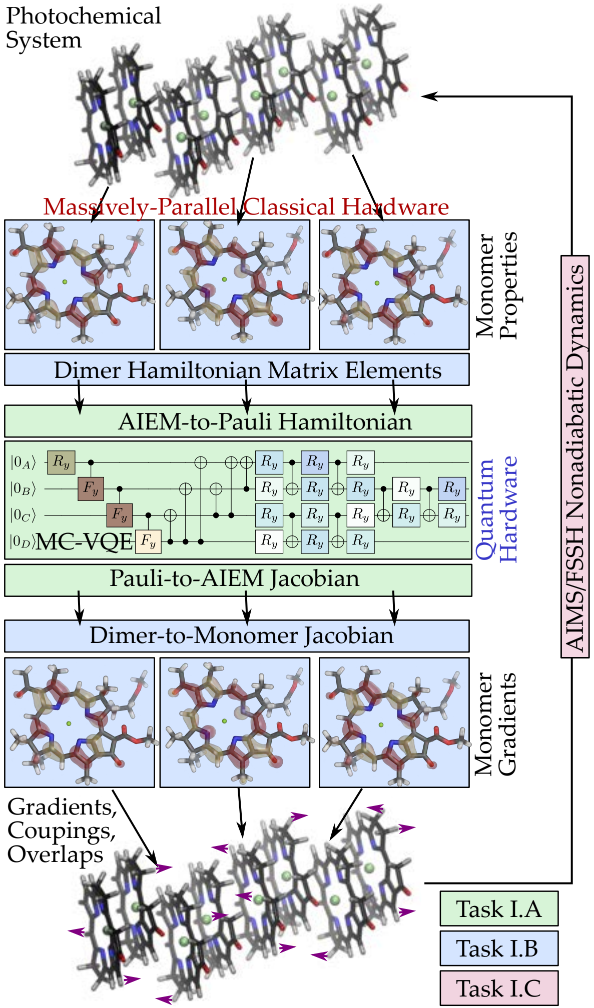
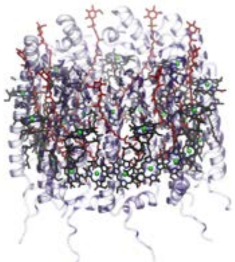
Task I: Hybrid Quantum/Classical Photodynamics

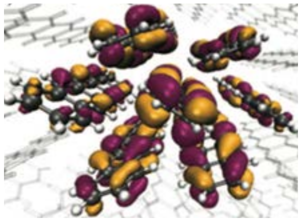


Task II: Photochemistry Simulations Applications

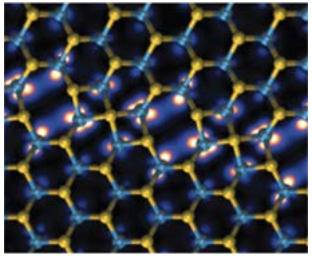
Electronic Energy Transfer:



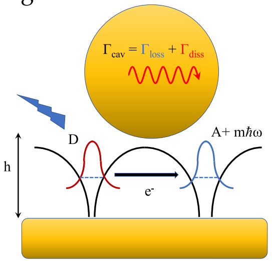
Singlet Fission:



Low-Dimensional Materials:

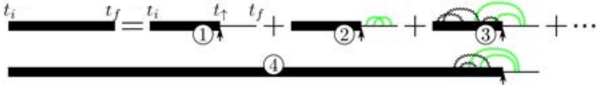


Light-Matter Interactions:



Task III: Benchmark/Validation Methods

"Inchworm" Quantum Monte Carlo:



Tensor Product/Network Quantum Circuit Simulation: