Quantum Chemistry Benchmark for Quantum Computing

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Introduction

Leadership Computing Facility (OLCF)

- Titan Architecture: Cray XK7
  (18,688 AMD Opteron 6274 16-core CPUs, 18,688 Nvidia Tesla K20X GPUs)
  17.59 petaFLOPS
- Ranking TOP500: #3, June 2016
- Summit (IBM): 200 PFLOPS (2018)

Spallation Neutron Source (SNS) & Center for Nanophase Material Science (CNMS)

- SNS is an accelerator-based neutron source in Oak Ridge
- The brightest neutron beam in the world
- Neutron scattering experiments
- User facility (semiannual calls)
Quantum Computing is a DOE priority

Ref. BES Roundtable report “Opportunities in Chemical in Materials Sciences, 2017
Opportunities in Chemical and Materials Sciences

- Controlling the Quantum Dynamics of Nonequilibrium Chemical and Materials Systems

Water-splitting reaction on a catalytic surface:
1. harvesting light energy to form charge carriers
2. proton-coupled electron transfer (PCET) processes
3. multiple pathways, and excited states
4. time-dependent Schrödinger equation (non-adiabatic)
5. unfeasible with classical computers.

- Embedding Quantum Hardware in Classical Frameworks

- Hybrid model and computing
- Separation of problem between “easy” and “hard” part
- Interfacing

Ref. BES Roundtable report “Opportunities in Chemical in Materials Sciences, 2017
Quantum chemistry hierarchy: Pople diagram

Relation between basis set and levels of theory typically used in quantum chemistry.

**Level of Theory**

```
HF/SCF  MP2  MP4  CCSD (T)  CCSD (T)-F12  FULL CI

Increasing description of electron correlation
- Double excitations
- Perturbative of triple excitations

Larger basis set increases flexibility to describe wave function/ electron density
- Valence electrons
- Diffusion function
- Polarization function
- Higher-angular momentum orbitals

Increasing an accuracy Increasing CPU time

EXACT
```

Basis Set (Atomic Orbitals)

- Pople basis set
  - 6-31G(d)
  - 6-31+G(d,p)
  - 6-311++G(2df,pd)
- Dunning basis sets
  - (aug)-cc-pVDZ
  - (aug)-cc-pVTZ
  - (aug)-cc-pVQZ
- Infinite Basis set

https://en.wikipedia.org/wiki/Pople_diagram
Recent work (IBM group)

Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets

Abhinav Kandala\textsuperscript{1*}, Antonio Mezzacapo\textsuperscript{1*}, Kristan Temme\textsuperscript{1}, Maika Takita\textsuperscript{1}, Markus Brink\textsuperscript{1}, Jerry M. Chow\textsuperscript{1} & Jay M. Gambetta\textsuperscript{1}

## Recent Related Work

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<th>Authors</th>
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<tr>
<td>Kandala et. al.</td>
<td>Hardware efficient VQE for small molecules and quantum magnets</td>
<td>Uses hardware-efficient trial state consisting of alternating layers of Euler rotations and entanglers. Applied to $H_2$, LiH, and BeH$_2$</td>
</tr>
<tr>
<td>Kandala et. al.</td>
<td>Extending the computational reach of a noisy supercomputing quantum processor</td>
<td>Extends Kandala 2017 with readout error correction and zero-noise error extrapolation, which enables increasing the levels of entanglement</td>
</tr>
<tr>
<td>Ryabinkin et. al.</td>
<td>Qubit coupled-cluster method</td>
<td>Uses energy response estimators for ranking importance of entanglers; <strong>Ground state energy of $H_2$ and LiH</strong> numerically calculated to chemical accuracy.</td>
</tr>
<tr>
<td>Ryabinkin et. al.</td>
<td>Constrained variational quantum eigensolver</td>
<td>Adds a penalty functional with constraining operators to the Hamiltonian, which eliminates kinks in the PSE; demonstrated on Rigetti hardware for $H_2$ and $H_2^0$</td>
</tr>
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<td>Romero et. al.</td>
<td>Strategies of quantum computing molecular energies using the unitary coupled cluster ansatz</td>
<td>Reduce parameters and qubits through 1) pre-screening of cluster amplitudes, 2) active space approximation</td>
</tr>
<tr>
<td>Bonet-Monroig et.</td>
<td>Low-cost error mitigation by symmetry verification</td>
<td>Inserts symmetries into circuits for error mitigation; order of magnitude error reduction for $H_2$ ground state dissociation curve (using simulator)</td>
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Motivation for quantum chemistry benchmark

- Diversity of Quantum Processing Units (QPU):
  - superconducting, ion traps, optical, …

- Progress measures in hardware specific metrics:
  - capacity of the quantum register
  - fidelity of the available instructions
  - connectivity between register elements
  - depth and width of quantum program execution
  - coherence times / accuracy in observing the generated outcome

- How does this translates to practical use?
  - gap between domain and quantum computer scientists / hardware vendors
  - set of quantum chemistry problems ➔ guideline for the development
  - XACC ➔ aid the transition between quantum and classical computing
XACC (eXtreme-scale ACCelerator) software framework

- Alex Mc Caskey (computer scientist)
mccaskeyaj@ornl.gov
Quantum Programming Landscape

IBM QPU(s)

Rigetti QPU(s)

Google QPU(s)

D-Wave QPU(s)

Aqua

Grove

PyQuil

Quil

Openfermion (probably spans more)

Cirq

Google low-level instruction set

D-Wave Ocean

D-Wave SAPI

D-Wave QMI

Terra

OpenQasm

(+ others)
Quantum Programming Landscape - What Challenges arise here?

- **Lack of code portability**
  - Users must re-express codes/programs in the vendor’s DSL (python data structures)
  - Users have to learn N-frameworks for N QPUs
- **Lack of Integration**
  - Simulator from Vendor X not immediately usable from code written for Vendor Y
- **Lack of in-line error mitigation** tools
  - Left as onerous post-processing task for user
- **Very difficult to enable benchmark suite across QPUs**
  - see above lack of code portability…
- **Requires N*M compilers for N QPLs and M QPUs**
- **Oh yea, and the access model**
  - Remote (makes sense, scarce resource)
  - Queue single QPU executions (ouch)
Learn from classical compiler architectures

- Code portability and integration are no problem
- Error mitigation through operations on the IR and Backend Decoration
- Benchmarking possible since backend hardware is abstracted away.
- Requires N compilers to map to M QPUs
import xacc

xacc.Initialize()

xacc.setOptions({'ibm-backend': 'ibmq_20_tokyo',
                 'ro-error-file': 'READOUTERROR_FILE.json'})

# Get access to the Accelerator you want
# Can be ibm, rigetti, tnqvm, local-ibm, etc...
qpu = xacc.getAccelerator('ibm')

# Allocate some qubits to execute on
# This is the AcceleratorBuffer instance
qubits = qpu.createBuffer('q', 2)

# To turn on Readout-Error correction, decorate
# the Accelerator with the ro-error AcceleratorDecorator
qpu = xacc.getAcceleratorDecorator('ro-error', qpu)

# Annotate functions that are to be
# run on the QPU
@xacc.qpu(accelerator=qpu)
def entangle(buffer):
    H(0)
    CNOT(0, 1)
    Measure(0, 0)
    Measure(1, 1)

# Execute, gather results
entangle(qubits)

# Print the bit counts
print('Counts: ', qubits.getMeasurementCounts())

# Print the whole buffer as JSON
print(qubits)

xacc.Finalize()
Extend Decorators for Algorithmic Primitives like VQE

```python
@vqe.qpu.vqe(accelerator=qpu, observable=h2_ham, optimizer='scipy-COBYLA', options={'disp': True, 'maxiter': 10, 'tol': 1e-4})
def uccsdH2(buffer, *args):
    xacc(uccsd, n_qubits=4, n_electrons=2)

uccsdH2(buffer, 0.0, -0.05)

print('VQE Energy = ', buffer.getInformation('vqe-energy'))
print('VQE Angles = ', buffer.getInformation('vqe-angles'))
print(buffer)
```
XACC Python JIT Compiler and the IRGenerator

• Goals
  – Provide a mechanism for programming complex circuits / QUBOs parameterized by high-level user input
• How’s it done?
  – PyXACCCompiler interprets custom xacc() instruction
    • first argument is the name of the IRGenerator
    • subsequent arguments are the list of user input
XACC documentation and information:

- Check the XACC project at:
  - [https://github.com/eclipse/xacc](https://github.com/eclipse/xacc)
  - [https://xacc.readthedocs.io](https://xacc.readthedocs.io)


- Contact:
  - [xacc-dev@eclipse.org](mailto:xacc-dev@eclipse.org),
  - [mccaskeyaj@ornl.gov](mailto:mccaskeyaj@ornl.gov)

- Funding: ORNL LDRD, DOE Testbed Pathfinder, DOE Quantum Algorithms Teams, DOE Early Career Research Program
Benchmarking Quantum Computers

• What is a quantum computing benchmark?
  – There is no **Linpack equivalent**
  – Propose algorithm and application specific benchmarks
    • VQE-based algorithms: QML, QChem, Nuclear Physics

• With wide **variety of QCs**, need a programing mechanism that spans available hardware
  – XACC was designed for this

• The need for an **executable benchmark suite**
  – Reproducible software across QCs
  – QC vendor downloads and executes suite to provide QC-specific metric analysis
  – PyQuil, Cirq, Qiskit don’t provide that

---

**E? E_correlation? ...**
**Compared across QPUs?**
Quantum chemistry benchmark

• XACC framework (Python API)
• Molecular systems: H$_2$, LiH, NaH, KH, RbH
• Ansatz circuits
• VQE optimizers
• Error mitigation techniques
Mapping a Chemistry Problem onto a Quantum Computer

Typical Chemistry Problem Workflow

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

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

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

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

5. Select Problem and Algorithm
   - Energies, properties, etc.
   - Quantum phase estimation
   - Variational quantum eigensolver (and ansatz)

6. Map to Hardware

Ref. BES Roundtable report “Opportunities in Chemical in Materials Sciences, 2017"
General many-body problem for fermions (Hilbert spaces)

- Particles are spin $\frac{1}{2}$ fermions
- Many-body wave function is fully anti-symmetric
- Certain quantum numbers will be conserved
  - total angular momentum
  - Number of electrons
- Hamiltonian will be non-relativistic (usually)
- We (usually) work in second quantization

Fock space with $N$ single particle states and $A$ particles.

$$a_\alpha^+ |0\rangle = |1\rangle \quad a_\alpha |0\rangle = 0 \quad a_\alpha |1\rangle = |0\rangle \quad a_\alpha^+ |1\rangle = 0$$

$$a_\alpha^+ a_\beta^+ = -a_\beta^+ a_\alpha^+ \quad a_\alpha a_\beta = -a_\beta a_\alpha \quad a_\alpha^+ a_\beta + a_\beta a_\alpha^+ = \delta_{\alpha\beta}$$

$$|\Phi\rangle = a_1^+ a_2^+ \cdots a_A^+ |0\rangle = |11\cdots10000\rangle$$

$$1 = \sum_{\alpha=0}^{N-1} |\Psi_\alpha\rangle \langle\Psi_\alpha|; \langle\Psi_\alpha|\Psi_\beta\rangle = \delta_{\alpha\beta}$$
Example: 2 particles in 4 states

Many-body basis states

\[
|\Phi_0\rangle = |0000\rangle
|\Phi_1\rangle = |1000\rangle
|\Phi_2\rangle = |0100\rangle
|\Phi_3\rangle = |0010\rangle
|\Phi_4\rangle = |0001\rangle
|\Phi_5\rangle = |0000\rangle
\]

Hartree-Fock state

\[
I = 0 \quad a_2^+ a_1^+ |\Phi_0\rangle = |1100\rangle
I = 1 \quad a_3^+ a_1^+ |\Phi_0\rangle = |1010\rangle
I = 2 \quad a_4^+ a_1^+ |\Phi_0\rangle = |1001\rangle
I = 3 \quad a_3^+ a_2^+ |\Phi_0\rangle = |0110\rangle
I = 4 \quad a_4^+ a_2^+ |\Phi_0\rangle = |0101\rangle
I = 5 \quad a_4^+ a_3^+ |\Phi_0\rangle = |0011\rangle
\]

Correlated wave function:
linear combination of basis states

\[
|\Psi\rangle = (b_\alpha + b_{a_1}^{a_i} a_2^+ a_i + b_{a_2}^{abij} a_3^+ a_3^+ a_i a_j + \cdots) |\Phi_0\rangle
\]

\[
\langle \Psi|H|\Psi\rangle
\]

Solve for b's by diagonalizing the Hamiltonian matrix

\[
N = \text{number of single-particle states}
\]

\[
C(N,n) = \frac{N!}{(N-n)!n!}
\]

\[
C(100,10) = 1.7 \times 10^{13}
\]

\[
C(1000,100) = 6 \times 10^{139}
\]

Oops. These are HUGE numbers

Source: David Dean (ORNL)
Example: LiH, STO-3G basis set

LiH model:
- 4 electrons
- 6 orbitals
- 12 spinorbitals

Possible combinations:
- All electrons & orbitals: $\binom{12}{4} = 495$
- Freeze lowest 2e: $\binom{10}{2} = 45$
All electrons case:

\[ H = H_0 + H_1 + H_2 \]
\[ = H_0 + \sum_{p,q} p^+ q \cdot \tilde{h}_q^p + \frac{1}{4} \sum_{p,q,r,s} p^+ q^+ r s \cdot \tilde{g}_{sr}^{pq} \]

\( H_0 \) - nuclear repulsion (0-electrons)

\( h_p^q \) - core Hamiltonian (1-electron):
(kinetic energy + interaction with core ions)

\( g_{pq}^{rs} \) - antisymmetrized 2-electron repulsion integrals

\[ \tilde{g}_{sr}^{pq} = \langle p, q|s, r \rangle - \langle p, q|r, s \rangle \]

Valence electrons - runs over all spin-orbitals

Frozen core approximation:

Valence electrons \( \to \) delocalized chemical bonding

Core electrons \( \to \) localized near nucleus, not really involved in chemistry

\[ H = H_0' + H_1' + H_2' \]

\[ H_0' = E_{nucl} + \sum_a \left( \tilde{h}_a^p + \frac{1}{2} \sum_b \tilde{g}_{ab} \right) \]

\[ H_1' = \sum_{p,q} p^+ q \cdot \left( \tilde{h}_q^p + \frac{1}{2} \sum_a \tilde{g}_{a,q}^{aq} \right) \]

\[ H_2' = \frac{1}{4} \sum_{p,q,r,s} p^+ q^+ r s \cdot \tilde{g}_{sr}^{pq} \]

excitations

mean field interaction with frozen electrons (new term)

p,q,r,s - active spin-orbitals

a,b - inactive spin-orbitals of frozen core
### Requirements for UCCSD ansatz

Coupled–cluster (CC) methods ➔ gold standard method in quantum chemistry

Accuracy: HF < MPn < CC < Full Configuration Interaction (FCI)

<table>
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<tr>
<th>Molecule</th>
<th>No. of electrons</th>
<th>No. of spinorbitls STO-3G</th>
<th>FCI space size</th>
<th>UCCSD ansatz requirements</th>
<th>#params</th>
<th>#instructions</th>
<th>depth</th>
<th>#CNOTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH(fc)*</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>158</td>
<td>101</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>LiH(fc)*</td>
<td>2</td>
<td>10</td>
<td>45</td>
<td>14</td>
<td>6,258</td>
<td>4,673</td>
<td>3,680</td>
<td></td>
</tr>
<tr>
<td>LiH</td>
<td>4</td>
<td>12</td>
<td>495</td>
<td>44</td>
<td>41,892</td>
<td>30,487</td>
<td>26,112</td>
<td></td>
</tr>
<tr>
<td>NaH</td>
<td>12</td>
<td>20</td>
<td>125,970</td>
<td>324</td>
<td>616,428</td>
<td>N/A</td>
<td>441,600</td>
<td></td>
</tr>
<tr>
<td>KH</td>
<td>20</td>
<td>28</td>
<td>3,108,105</td>
<td>860</td>
<td>2,213,940</td>
<td>N/A</td>
<td>1,710,080</td>
<td></td>
</tr>
<tr>
<td>RbH</td>
<td>38</td>
<td>48</td>
<td>6,540,715,896</td>
<td>4655</td>
<td>19,438,938</td>
<td>N/A</td>
<td>16,460,080</td>
<td></td>
</tr>
</tbody>
</table>
Benchmark (ongoing)

- Hydrogen-like molecules: LiH, NaH, KH, RbH with STO-3G basis
- Adjustable list of active orbitals (1 active orbital = 1 qubit)
- Frozen core Hamiltonian with 2 electrons, 4 orbital
- Ansatz:

UCC

HWE (HardWare Efficient)


**Benchmark**

- **Unitary Coupled Cluster Ansatz (UCC)**
  - primitive CC
  - one parameter (small search space)
  - not accurate (double excitation)
  - preserve symmetry ($N_{\text{electrons}}$)

  ![UCC Diagram]


- **Hardware Efficient Ansatz (HWE)**
  - “brute force”
  - can map to exact FCI energy
  - 20 parameters (large search space)
  - mixes states with different electron number

  ![HWE Diagram]

Benchmark results (ongoing)

- UCC requires a single parameter for 2 electrons, 4 orbitals (scan)
- Known energy ➔ hardware test

![Graphs of energy as a function of variational parameter φ for NaH, KH, and RbH on the reduced UCC ansatz on the 20-qubit IBM Tokyo QPU.](image)

The dependence of the energy as a function of the variational parameter φ for the reduced UCC ansatz on the 20-qubit IBM Tokyo QPU.
Variational Quantum Eigensolver

- Optimization method (classical): Nelder-Mead? Bayesian? Other?
- Starting point: Hartree-Fock? Perturbational amplitudes?
- Noiseless simulator

He atom, 6-311G basis (2 electrons, 6 spin orbitals)

Deuteron binding energy, UCCSD ansatz
Ref: Dumitrescu, PRL 120, 210501 (2018)
Summary

• XACC (eXtreme-scale ACCELERator) software framework.
• XACC follows a coprocessor machine model:
  - independent of the underlying quantum computing hardware
  - unified application programming interface.
  - enabling quantum programs to be executed on a variety of QPUs
• Metal hydrides: LiH, NaH, KH, RbH with STO-3G basis set
• Frozen core Hamiltonian and adjustable virtual space
• Test ansatizes, optimizers, error mitigation
• Exploit symmetries when possible
• Cross-disciplinary challenges ➔ teaming (knowledge transfer)!
• Bottleneck: Hardware ➔ noisy
Contributors

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Zach Parks (computer science student)
Shirley Moore (HPC, math)
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Thank you