

NISQ algorithms 2: VQE

Yipeng Huang

Rutgers University

November 4, 2020

Quantum chemistry

Problems in:

- ▶ Catalysis: molecular structure
- ▶ Material science
- ▶ Superconductors
- ▶ Condensed matter physics

Important, and hard. Why?

Schrödinger equation

- ▶ $i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$
- ▶ Hamiltonian H describes dynamics, is a Hermitian matrix
- ▶ If H is constant for a time step, then the solution to the above PDE is: $|\psi(t)\rangle = U(t) |\psi(0)\rangle$, where $U(t) = \exp(-\frac{i}{\hbar}Et)$

The Hamiltonian for a molecule

$$H = - \sum_i \frac{\Delta_{R_i}^2}{2M_i} - \sum_i \frac{\Delta_{r_i}^2}{2} - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j>i} \frac{Z_i Z_j}{|R_i - R_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}$$

- ▶ R_i are nuclei positions
- ▶ M_i are nuclei masses
- ▶ Z_i are nuclei charges
- ▶ r_i are electron positions

(normalized to electron mass and charge)

1. Nuclei have kinetic energy
2. Electrons have kinetic energy
3. Electrons are attracted to nuclei
4. Nuclei repel each other
5. Electrons repel each other

[McArdle et al., 2020, O'Malley et al., 2016]

Quantum mechanics difficult to classically simulate

"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

Quantum computing for quantum mechanics

- ▶ A molecule: has n electrons that represent n electrons
- ▶ Classical computer: uses $O(k^n)$ bits to represent n electrons
- ▶ Quantum computer: uses $O(n^P)$ qubits to represent n electrons



Figure: Credit: imgflip.com

Quantum computing for quantum mechanics

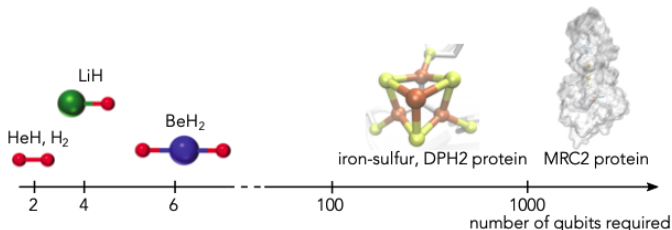


Figure 7: Qubit resources needed for quantum chemistry. Qubit numbers up to ten are based on existing experiments, whereas the resources for larger molecules are estimates. From left to right: hydrogen molecule, lithium hydride, beryllium hydride, iron sulphur (Fe-S) cluster in DPH2 complex of *Pyrococcus Horikoshii* (PDB entry code 3LZD), and Fe-S clusters sequence in cytochrome B560 subunit of mitochondria (PDB entry code 3SFD).

Figure: Credit: Moll et al. Quantum optimization using variational algorithms on near-term quantum devices.

Quantum chemistry and algorithms

- ▶ Quantum chemistry, algorithms, and the variational quantum eigensolver (VQE) are each broad research areas in scientific computation.
- ▶ In this class, we survey the most simple case studies.
- ▶ This is in contrast to QAOA, where we were able to study in more comprehensive detail.

[McArdle et al., 2020]

Decision 1: What problem to solve?

- ▶ Compute the ground state energy (lowest eigenvalue of Hamiltonian) (a.k.a. local Hamiltonian problem)
- ▶ Simulate the time dynamics of a quantum system.

Computing the ground state energy

- ▶ The eigenstates and eigenvalues of the Hamiltonian dictate almost all of a molecule's properties.

[McArdle et al., 2020]

Ground state energies / Hermitian spectral theorem

- ▶ Eigendecomposition of H : $H = \sum_{i=1}^N E_i |\phi_i\rangle \langle \phi_i|$
- ▶ If state $|\phi\rangle$ is an eigenvector of H , then $H|\phi\rangle = E|\phi\rangle$
- ▶ State $|\phi\rangle = |\phi\rangle \exp(-\frac{i}{\hbar}Et)$ is a solution to the Schrödinger equation. Exponent is purely imaginary. Only phase changes.

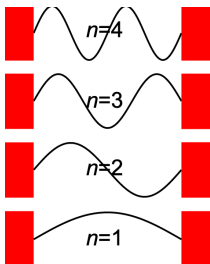


Figure: Credit: wikimedia.org

Computing the ground state energy

- ▶ The eigenstates and eigenvalues of the Hamiltonian dictate almost all of a molecule's properties.
- ▶ Reaction rate: $\text{rate} \propto \exp\left(-\Delta \frac{E}{k_B T}\right)$
- ▶ In most (temperature) conditions, ambient thermal energy not enough to move molecule's state from ground to first excited state.
- ▶ So, finding the ground state energy is an important fundamental problem.

[McArdle et al., 2020]

Difficult to classically simulate

"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. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

—Paul Dirac

Simplifications / mappings

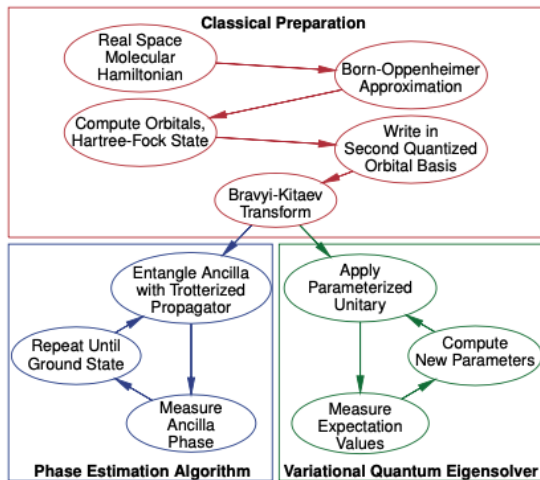


FIG. 5. A flowchart describing steps required to quantum compute molecular energies using both PEA and VQE.

Figure: Credit: OMalley et al. Scalable Quantum Simulation of Molecular Energies

Born-Oppenheimer approximation

Simplification: nuclei are fixed; electrons move.

$$H = - \sum_i \frac{\Delta_{r_i}^2}{2} - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}$$

- ▶ R_i are nuclei positions
- ▶ Z_i are nuclei charges
- ▶ r_i are electron positions

(normalized to electron mass and charge)

1. Electrons have kinetic energy
2. Electrons are attracted to nuclei
3. Electrons repel each other

Decision 2: Molecular basis set / Hartree Fock.

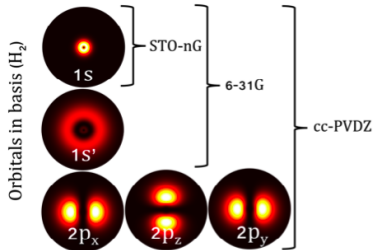


FIG. 1. The orbitals included in different basis sets for the Hydrogen atom. The $1s'$ orbital is often written as $2s$. The plots show the radial probability distributions for the true Hydrogenic orbitals, which the basis orbitals approximate.

Figure: Credit: McArdle. Quantum computational chemistry.

- ▶ Active space: the subset of degrees of freedom containing the essential quantum behavior
- ▶ Hydrogen atom consists of a single $1s$ orbital, so use Gaussian STO-3G basis set.

Decision 3: What quantization?

- ▶ First quantization

$$H = - \sum_i \frac{\Delta_{r_i}^2}{2} - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}$$

- ▶ Second quantization:

$$H = H_1 + H_2 = \sum_{\alpha,\beta=1}^M t_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta=1}^M u_{\alpha\beta\gamma\delta} a_{\alpha}^{\dagger} a_{\gamma}^{\dagger} a_{\delta} a_{\beta}$$

- ▶ a_{α}^{\dagger} is the fermionic creation operator for fermionic mode α
- ▶ a_{α} is the fermionic annihilation operator for fermionic mode α

[O'Malley et al., 2016, Kandala et al., 2017]

Decision 4: Mapping to qubit Hamiltonian?

1. Jordan-Wigner
2. Bravyi-Kitaev
3. BKSF
4. Parity
5. ...

Each of m qubits represents m orbitals, $|1\rangle =$ occupied, $|0\rangle =$ unoccupied.

Simplifications / mappings

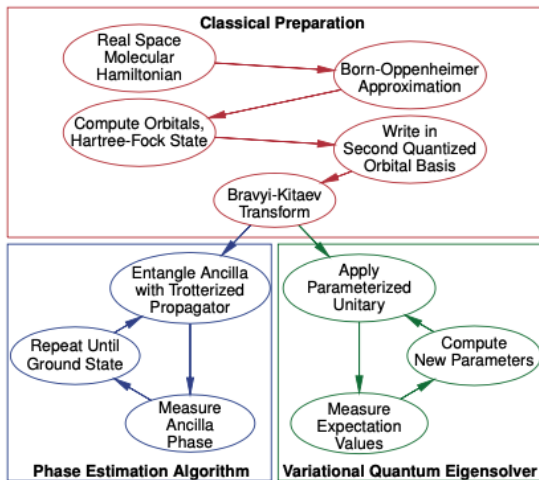


FIG. 5. A flowchart describing steps required to quantum compute molecular energies using both PEA and VQE.

Figure: Credit: OMalley et al. Scalable Quantum Simulation of Molecular Energies

Decision 5: Ground state estimation algorithm?

1. quantum phase estimation
2. quantum adiabatic evolution
3. quantum annealing
4. variational quantum eigensolver

VQE most viable on near term machines.

Ground state energies / Hermitian spectral theorem

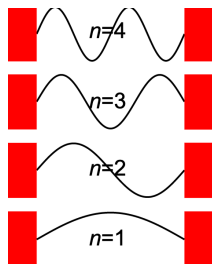


Figure: Credit: wikimedia.org

- ▶ Because H is Hermitian, its eigenvectors form an orthonormal basis set $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_N\rangle$.
- ▶ $\langle \phi_i | \phi_j \rangle = \delta_{ij}$
- ▶ $\sum_{i=1}^N |\phi_i\rangle \langle \phi_i| = I_N$

Ground state energies / Hermitian spectral theorem

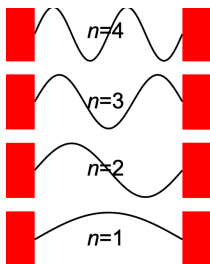


Figure: Credit: wikimedia.org

- ▶ Because H is Hermitian, its eigenvectors form an orthonormal basis set $|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_N\rangle$.
- ▶ Any other vector $|\psi\rangle$ can be phrased as a linear combination in $|\phi_i\rangle$ basis set.
- ▶ $|\psi\rangle = \sum_{i=1}^N c_i |\phi_i\rangle, c_i = \langle \phi_i | \psi \rangle$
- ▶ $\sum_{i=1}^N |c_i|^2 = 1$

Ground state estimation using the variational principle

- ▶ Hamiltonian H , what is smallest eigenvalue E_G



Kandala, A., Mezzacapo, A., Temme, K., Takita, M., Brink, M., Chow, J. M., and Gambetta, J. M. (2017).

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

Nature, 549(7671):242–246.



McArdle, S., Endo, S., Aspuru-Guzik, A., Benjamin, S. C., and Yuan, X. (2020).

Quantum computational chemistry.

Rev. Mod. Phys., 92:015003.



O'Malley, P. J., Babbush, R., Kivlichan, I. D., Romero, J., McClean, J. R., Barends, R., Kelly, J., Roushan, P., Tranter, A., Ding, N., et al. (2016).

Scalable quantum simulation of molecular energies.

Physical Review X, 6(3):031007.