

Quantum Chemistry

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Motivation for quantum chemistry

Ground state estimation

Simplification of problem representation

Qubit representation of orbitals

Variational quantum eigensolver

VQE ansatz

Quantum chemistry

Catalysis

- | N_2 to NH_3
- | Haber-Bosch process: energy intensive.
- | Nitrogen fixation via nitrogenase: room temperature, efficient.
- | FeMoco: iron molybdenum cofactor, 60 electrons in 110 spin orbitals. [McArdle et al., 2020].

Superconductors

- | Hubbard model

Important, and hard. Why?

Schrödinger equation

Dynamics: interchange of potential and kinetic energy

$$\left| i \frac{d}{dt} j(t) \right\rangle = H j(t) \left| \right\rangle$$

$$\left| \frac{d}{dt} j(t) \right\rangle = -i H j(t) \left| \right\rangle$$

| Hamiltonian H describes dynamics, is a Hermitian matrix

The Hamiltonian for a molecule

Hamiltonian: energy = kinetic energy + potential energy

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

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

| R_i are nuclei positions

| M_i are nuclei masses

| Z_i are nuclei charges

| r_i are electron positions

Units: hartree

| Above equation normalized to electron mass and charge

| 1 hartree = $\frac{1}{m_e e^2 a_0^2}$

| m_e mass of electron

| e charge of electron

| a_0 Bohr radius

[McArdle et al., 2020, Cao et al., 2019, O'Malley et al., 2016]

Map of topics

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What problem to solve: statics vs. dynamics

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

Schrödinger equation

Dynamics

$$i\hbar \frac{d}{dt} |j(t)\rangle = H |j(t)\rangle$$

$$\frac{d}{dt} |j(t)\rangle = \frac{i}{\hbar} H |j(t)\rangle$$

| Hamiltonian H describes dynamics, is a Hermitian matrix

Statics

| If H is constant for a time step, then the solution to the above PDE is:

$$|j(t)\rangle = U(t) |j(0)\rangle, \text{ where } U(t) = \exp\left(-\frac{i}{\hbar} Ht\right)$$

$$U(t) = \exp\left(-\frac{i}{\hbar} Et\right)$$

Computing the ground state energy

- | The eigenstates and eigenvalues of the Hamiltonian tell us a lot about molecule's properties.

Figure: [Lanyon et al., 2010]

Computing the ground state energy

- | The eigenstates and eigenvalues of the Hamiltonian dictate almost all of a molecule's properties.
- | Reaction rate: $\text{rate} \propto \exp\left(-\frac{E}{k_B T}\right)$
- | Determining E to within $1 : 6 \cdot 10^{-3}$ hartree ≈ 43 meV will find reaction rate to within one order of magnitude. This is called chemical accuracy.
- | 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]

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Simplifications / mappings

Born-Oppenheimer approximation

Simplification: nuclei are three orders of magnitude more massive than electron, so treat nuclei as fixed; electrons move.

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

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

| R_i are nuclei positions

| Z_i are nuclei charges

| r_i are electron positions

(normalized to electron mass and charge)

To vary positions of nuclei, perform new calculation with new nuclei positions.

Figure: [Lanyon et al., 2010]

Simplifications / mappings

What will the state vector encode?

First quantization: real-space discretization

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} \frac{V_{ij}}{r_{ij}} + \sum_{i,j>i} \frac{1}{r_{ij}}$$

| Direct finite difference of space

Molecular basis set / Hartree Fock.

- | In molecules with many orbitals and electrons, the orbitals classified as: unoccupied, active space, or frozen.
- | Active space: the subset of degrees of freedom containing the essential quantum behavior

Figure: Credit: [Hempel et al., 2018]

Molecular basis set / Hartree Fock.

- | Hydrogen atom consists of a single 1s orbital, so use STO-3G (Slater-type orbital-3 Gaussians) basis set.
- | Uses three Gaussians with different parameters to approximate shape of 1s orbital.

Figure: Credit: McArdle. Quantum computational chemistry.

Molecular basis set / Hartree Fock.

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Figure: Credit: [McArdle et al., 2020]

Write in second quantized orbital basis

First quantization: real-space discretization

$$H = \sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + \sum_{i,j} \frac{z_i z_j}{|r_i - r_j|} + \sum_{i,j>i} \frac{1}{|r_i - r_j|}$$

| (direct finite difference of space)

Second quantization: incorporates knowledge of orbital occupancy

$$H = H_1 + H_2 = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

| a_p^\dagger is the fermionic creation operator for fermionic mode (spin orbital) p

| a_p is the fermionic annihilation operator for fermionic mode (spin orbital) p

Write in second quantized orbital basis

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Fermionic creation and annihilation operators

- | $f a_p^\dagger; a_q^\dagger g = f a_p; a_q g = 0$ Cannot simultaneously create or annihilate electrons from two orbitals p and q .
- | $f a_p; a_q^\dagger g = \delta_{pq}$ Evaluates to 1 if $p = q$.
- | $f a; b g = ab + ba$

Write in second quantized orbital basis

Second quantization: incorporates knowledge of orbital occupancy

$$H = H_1 + H_2 = \sum_{p;q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p;q;r;s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

- | a_p^\dagger is the fermionic creation operator for fermionic mode (spin orbital) p
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Numerical coefficients regarding orbital geometry, nuclear/electron attraction/repulsion can now be precomputed:

Write in second quantized orbital basis

Second quantization: incorporates knowledge of orbital occupancy

$$H = H_1 + H_2 = \sum_{p;q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p;q;r;s} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

- | a_p^\dagger is the fermionic creation operator for fermionic mode (spin orbital) p
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For example, for hydrogen molecule in the STO-3G basis

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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

[Dirac, 1929]

- | The main difficulty is the electron-electron repulsion terms that sum over combinations of four orbitals.
- | This belongs to algorithms in N-body simulation; e.g., Hartree-Fock
- | Classical simulation would rely on approximations (electron mean field)
- | Simulation using classical computers only possible for ~30 electrons

Map of topics

Figure: [Cao et al., 2019]

Quantum computing for quantum chemistry

1. A molecule: has n electrons that represent n electrons
2. Classical computer: uses $O(k^n)$ bits to represent n electrons
3. Quantum computer: uses $O(n^p)$ qubits to represent n electrons

Explanation credit to Ken Brown, Duke, 2018

Figure: Credit: img ip.com

Quantum computing for quantum chemistry

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

Mapping to qubit Hamiltonian

1. Jordan-Wigner: $O(m)$ gates for m orbitals.
2. Parity: $O(m)$ gates for m orbitals.
3. Bravyi-Kitaev: $O(\log(m))$ gates for m orbitals.
4. BKSF
5. ...

Jordan-Wigner encoding

Jordan-Wigner

Each spin orbital represented by one qubit

- | $j0i$: unoccupied
- | $j1i$: occupied

Jordan-Wigner encoding: creation and annihilation operators

Creation operator

$$| \ a_j^\dagger : Z_0 \quad Z_{j-1} \quad | \ + \ | \$$

$$| \ + = \frac{X - iY}{2} = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$| \ i \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = | j1i \rangle \langle 0j |$$

$$| \ + j0i = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = | j1i \rangle$$

$$| \ + j1i = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$| \ f \ + ; \ +g = 0$$

Annihilation operator

$$| \ a_j : Z_0 \quad Z_{j-1} \quad | \ - \ | \$$

$$| \ - = \frac{X + iY}{2} = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} +$$

$$| \ i \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = | j0i \rangle \langle 1j |$$

$$| \ - j0i = \begin{pmatrix} 0 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$| \ - j1i = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = | j0i \rangle$$

$$| \ f \ - ; \ g = 0$$

$$f \ + ; \ g = 1$$

Jordan-Wigner encoding: creation and annihilation operators

For example, for hydrogen molecule in the STO-3G basis with the Jordan-Wigner encoding

Figure: Credit: [McArdle et al., 2020]

A $2^4 \times 2^4$ matrix that represents the Hamiltonian of a 4-qubit system, which in turn represents a 4-orbital model of hydrogen molecule

Simplifications / mappings

Map of topics

Figure: [Cao et al., 2019]

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Ground state estimation problem

The Hamiltonian

- | So far, we've constructed a quantum circuit that is a model of the Hamiltonian matrix of a molecule.
- | For N qubits representing N orbitals, the Hamiltonian is size $2^N \times 2^N$.

Smallest eigenvalue is the ground state energy

- | Hamiltonian H , what is smallest eigenvalue E_G
- | For eigenvector $|j\rangle$, $H|j\rangle = E_G|j\rangle$

Figure: Credit: wikimedia.org

Ground state estimation problem

The Hamiltonian

- | So far, we've constructed a quantum circuit that is a model of the Hamiltonian matrix of a molecule.
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Smallest eigenvalue is the ground state energy

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Several quantum algorithms possible

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

VQE [Peruzzo et al., 2014, McClean et al., 2016] most viable on near term machines.

Hermitian spectral theorem

Because Hamiltonian H is Hermitian, its eigenvectors form an orthonormal basis set

- | Eigenvectors $|j_0\rangle; |j_1\rangle; \dots; |j_{N-1}\rangle$.
- | Eigenvectors are orthogonal $\langle j | j' \rangle = \delta_{jj'}$
- | $\sum_{i=0}^{N-1} |j_i\rangle \langle j_i| = I_N$

Try to find the eigenvector and eigenvalue pair with the lowest eigenvalue.

Ritz's variational principle

Because eigenvectors of H form an orthogonal basis, any state vector is a linear combination of the eigenvectors

- | Let $|j_0\rangle, |j_1\rangle, \dots, |j_{N-1}\rangle$, be eigenvectors of H with eigenvalues E_0, E_1, \dots to E_{N-1}
- | So for any $|j\rangle$, $|j\rangle$ can be written as $C_0|j_0\rangle + C_1|j_1\rangle + \dots + C_{N-1}|j_{N-1}\rangle$, where $C_i = \langle j | j_i \rangle$, and $\sum_{i=0}^{N-1} |C_i|^2 = 1$

For any given vector $|j\rangle$, $\langle j | H | j \rangle = E_0$, the ground state energy

- | $\langle j | H | j \rangle = C_0 \langle j_0 | H | j_0 \rangle + C_1 \langle j_1 | H | j_1 \rangle + \dots + C_{N-1} \langle j_{N-1} | H | j_{N-1} \rangle = C_0^2 E_0 + C_1^2 E_1 + \dots + C_{N-1}^2 E_{N-1} \geq E_0$
- | So unless a state vector is the ground state, it will have expectation value larger than the minimum eigenvalue.

Variational quantum eigensolver

VQE is a quantum classical algorithm for finding eigenvalues of a Hamiltonian H variationally

- | The VQE part of quantum chemistry VQE is actually quite small.
- | Guess and check: any guess may be better, if worse discard.
- | Quantum computer prepares using variational parameters $\tilde{\theta}$ a trial state $|j(\tilde{\theta})\rangle = U(\tilde{\theta})|j_0\rangle$, this is the ansatz.

Use a classical optimizer to minimize the expectation value by varying the parameters θ

- | $\min_{\tilde{\theta}} \langle j(\tilde{\theta}) | H | j(\tilde{\theta}) \rangle$
- | Iterate.

Variational error suppression

Mix calibration with experiment

Ritz's variational principle also holds true for density matrices, which underpins the robustness against noise.

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VQE ansatz


Problem / physics ansatz


- | Enforces key properties of valid state vectors, such as constant electron count.
- | Unitary coupled cluster ansatz.
- | Truncation at single and double electron interactions gives UCCSD.
- | Large depth: UCCSD has n^4 parameters.

Hardware / machine ansatz

- | Use a parameterized circuit that best fits what the quantum computer machine can execute.
- | Hardware efficient ansatz would have varying number of electrons which do not correspond to physical reality.

 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.

 Peruzzo, A., McClean, J., Shadbolt, P., Yung, M.-H., Zhou, X.-Q., Love, P. J., Aspuru-Guzik, A., and O'Brien, J. L. (2014).
A variational eigenvalue solver on a photonic quantum processor.
Nature communications, 5:4213.

 Romero, J., Babbush, R., McClean, J. R., Hempel, C., Love, P. J., and Aspuru-Guzik, A. (2018).
Strategies for quantum computing molecular energies using the unitary coupled cluster ansatz.
Quantum Science and Technology, 4(1):014008.