

# Quantum Chemistry

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December 1, 2021

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Ground state estimation

Simplification of problem representation

Qubit representation of orbitals

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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

- ▶  $i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$
- ▶  $\frac{d}{dt} |\psi(t)\rangle = \frac{-i}{\hbar} H |\psi(t)\rangle$
- ▶ Hamiltonian  $H$  describes dynamics, is a Hermitian matrix

## The Hamiltonian for a molecule

Hamiltonian: energy = kinetic energy + potential energy

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

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
- ▶  $1 \text{ hartree} = \frac{\hbar^2}{m_e e^2 a_0^2}$
- ▶  $m_e$  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

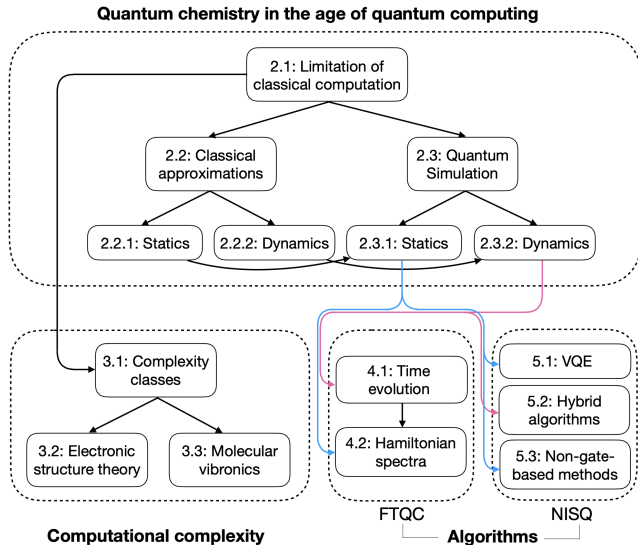


Figure: [Cao et al., 2019]

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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

- ▶  $i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$
- ▶  $\frac{d}{dt} |\psi(t)\rangle = \frac{-i}{\hbar} H |\psi(t)\rangle$
- ▶ 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:  
 $|\psi(t)\rangle = U(t) |\psi(0)\rangle$ , where  $U(t) = \exp(-\frac{i}{\hbar} H t)$
- ▶  $U(t) = \exp(-\frac{i}{\hbar} E t)$

# 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.
- ▶ Finding the minimum eigenvalue a large matrix is a fundamental problem primitive. The pagerank algorithm is also a lowest eigenvalue approximation.

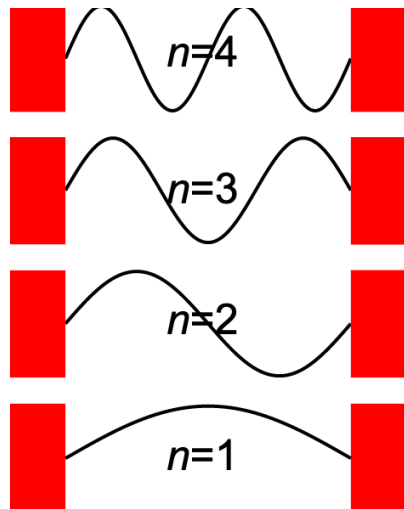


Figure: Credit: wikipedia.org

# Computing the ground state energy

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

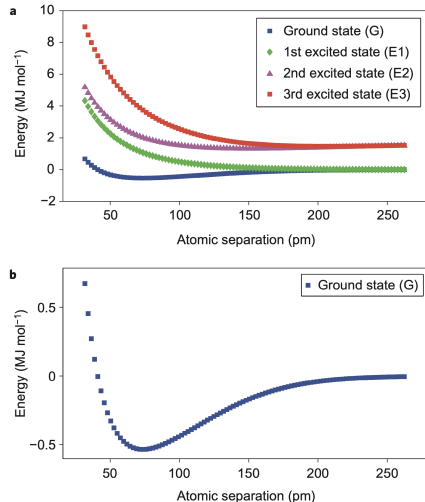


Figure: [Lanyon et al., 2010]

# Computing the ground state energy

- ▶ The eigenstates and eigenvalues of the Hamiltonian dictate almost all of a molecule's properties.
- ▶ Reaction rate:  $\text{rate} \propto \exp(-\Delta \frac{E}{k_B T})$
- ▶ Determining  $E$  to within  $1.6 \times 10^{-3}$  hartree  $\approx 43$  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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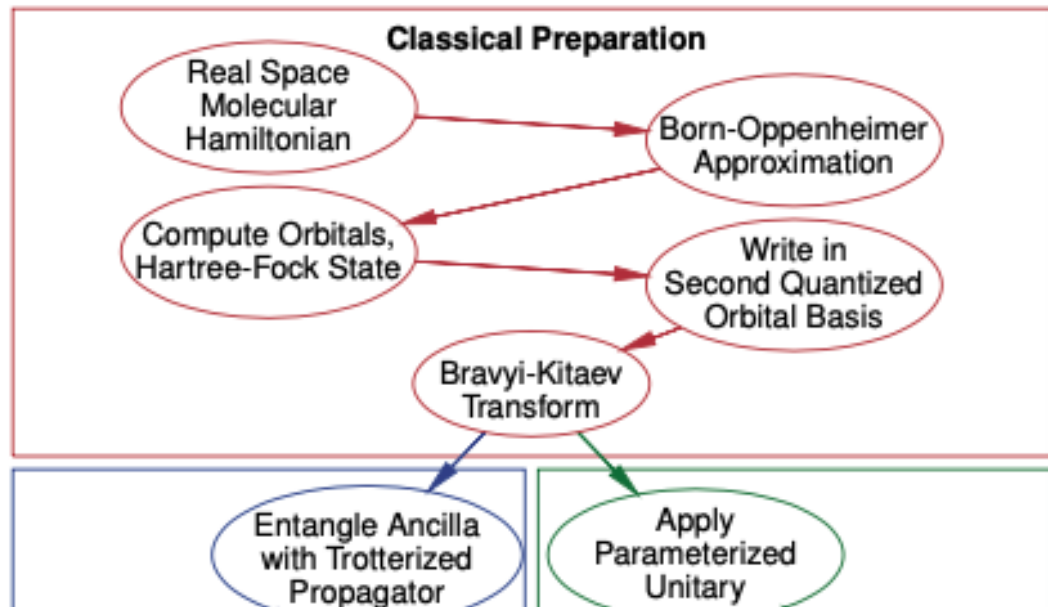
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## Simplifications / mappings



# Born-Oppenheimer approximation

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

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

1. Electrons have kinetic energy
2. PE: Electrons are attracted to nuclei
3. PE: Electrons repel each other
  - ▶  $R_i$  are nuclei positions
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(normalized to electron mass and charge)

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

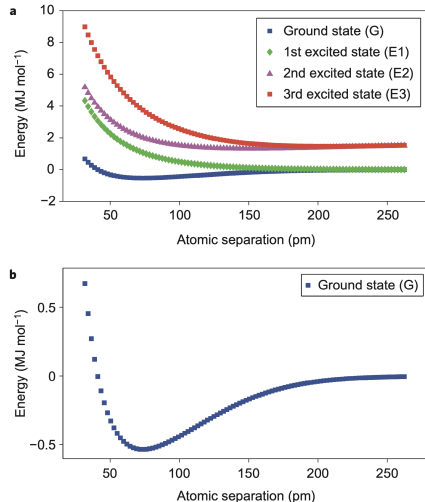
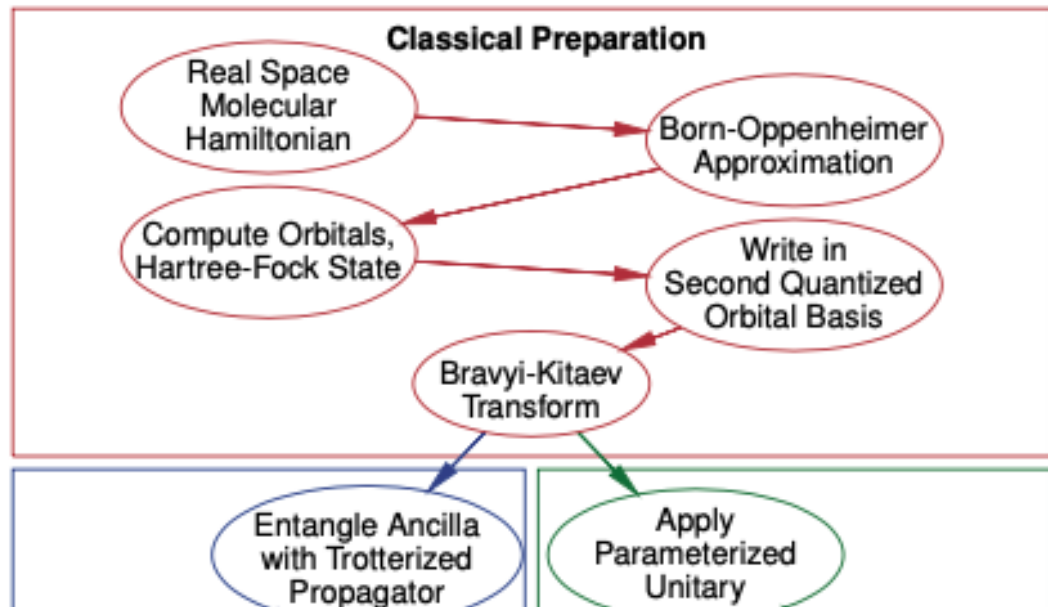


Figure: [Lanyon et al., 2010]

## Simplifications / mappings





# What will the state vector encode?

First quantization: real-space discretization

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

- Direct finite difference of space

# Molecular basis set / Hartree Fock.

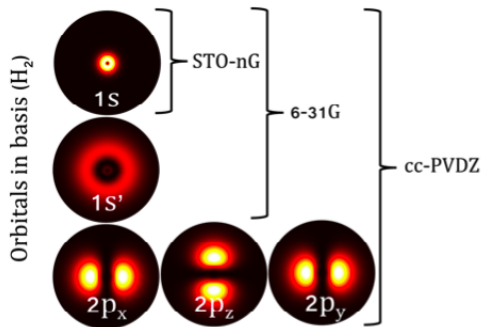


FIG. 4. The orbitals included in different basis sets for the Hydrogen atom. The 1s' orbital is often written as 2s. The plots show the radial probability distributions for the true Hydrogenic orbitals, which the basis orbitals approximate.

Figure: Credit: McArdle. Quantum computational chemistry.

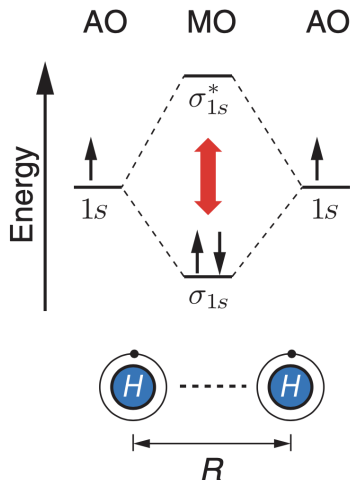
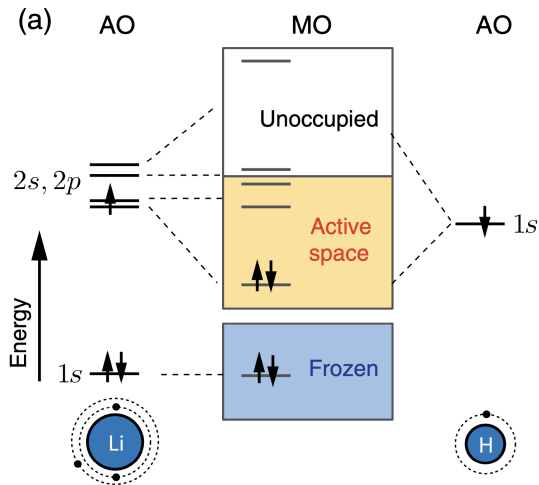


Figure: Credit: [Hempel et al., 2018]

# 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.

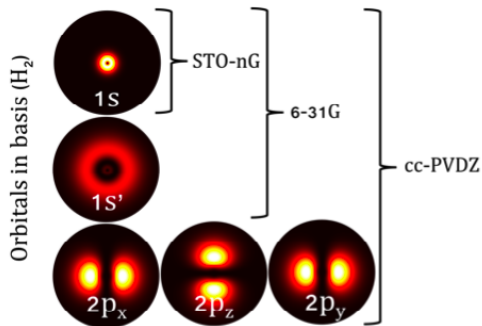


FIG. 4. The orbitals included in different basis sets for the Hydrogen atom. The  $1s'$  orbital is often written as  $2s$ . The plots show the radial probability distributions for the true Hydrogenic orbitals, which the basis orbitals approximate.

Figure: Credit: McArdle. Quantum computational chemistry.

- ▶ 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.

# Molecular basis set / Hartree Fock.

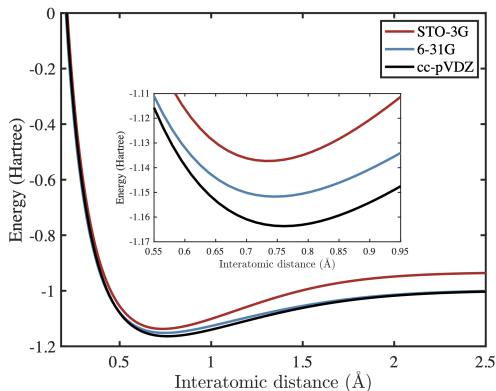


FIG. 14. Comparing the ground state dissociation curves of H<sub>2</sub> for a range of basis sets.

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

- ▶ 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.

# Write in second quantized orbital basis

First quantization: real-space discretization

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

- (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

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

## 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)  $p$
- ▶  $a_p$  is the fermionic annihilation operator for fermionic mode (spin orbital)  $p$

Numerical coefficients regarding orbital geometry, nuclear/electron attraction/repulsion can now be precomputed:

$$h_{pq} = \int d\sigma \varphi_p^*(\sigma) \left( -\frac{\nabla_{\vec{r}}^2}{2} - \sum_i \frac{Z_i}{|\vec{R}_i - \vec{r}|} \right) \varphi_q(\sigma) \quad (3)$$

$$h_{pqrs} = \int d\sigma_1 d\sigma_2 \frac{\varphi_p^*(\sigma_1) \varphi_q^*(\sigma_2) \varphi_s(\sigma_1) \varphi_r(\sigma_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (4)$$

$$h_{nuc} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \quad (5)$$



## 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)  $p$
- ▶  $a_p$  is the fermionic annihilation operator for fermionic mode (spin orbital)  $p$

For example, for hydrogen molecule in the STO-3G basis

$$\begin{aligned} H = & h_{00} a_0^\dagger a_0 + h_{11} a_1^\dagger a_1 + h_{22} a_2^\dagger a_2 + h_{33} a_3^\dagger a_3 \\ & + h_{0110} a_0^\dagger a_1^\dagger a_1 a_0 + h_{2332} a_2^\dagger a_3^\dagger a_3 a_2 + h_{0330} a_0^\dagger a_3^\dagger a_3 a_0 \\ & + h_{1221} a_1^\dagger a_2^\dagger a_2 a_1 + (h_{0220} - h_{0202}) a_0^\dagger a_2^\dagger a_2 a_0 \\ & + (h_{1331} - h_{1313}) a_1^\dagger a_3^\dagger a_3 a_1 + h_{0132} (a_0^\dagger a_1^\dagger a_3 a_2 + a_2^\dagger a_3^\dagger a_1 a_0) \\ & + h_{0312} (a_0^\dagger a_3^\dagger a_1 a_2 + a_2^\dagger a_1^\dagger a_3 a_0), \end{aligned}$$

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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  $\approx 30$  electrons

# Map of topics

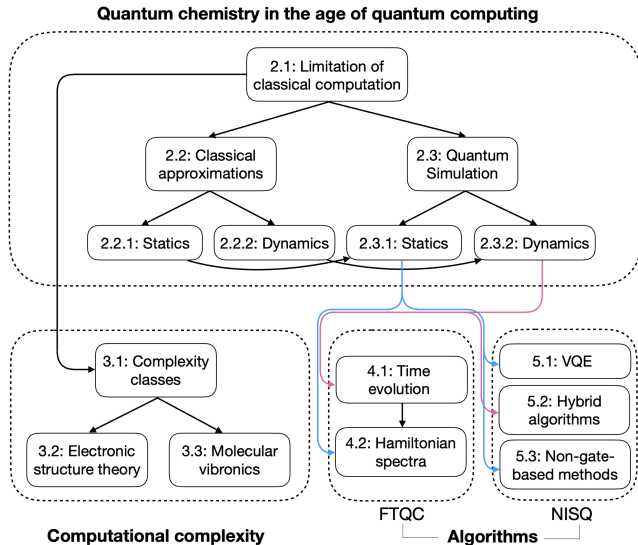


Figure: [Cao et al., 2019]

# 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: imgflip.com

# Quantum computing for quantum chemistry

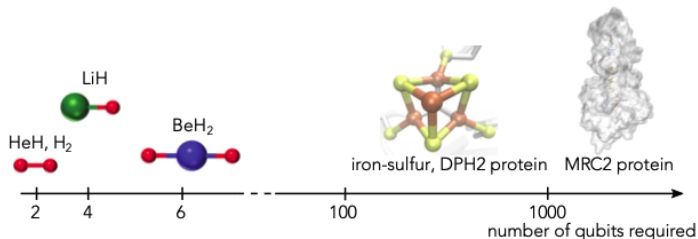


Figure 7: Qubit resources needed for quantum chemistry. Qubit numbers up to ten are based on existing experiments, whereas the resources for larger molecules are estimates. From left to right: hydrogen molecule, lithium hydride, beryllium hydride, iron sulphur (Fe-S) cluster in DPH2 complex of *Pyrococcus 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.

# 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

- ▶  $|0\rangle$ : unoccupied
- ▶  $|1\rangle$ : occupied



# Jordan-Wigner encoding: creation and annihilation operators

## Creation operator

- ▶  $a_j^\dagger: Z_0 \otimes \cdots \otimes Z_{j-1} \otimes \sigma_j^+ \otimes I$
- ▶  $\sigma^+ = \frac{X-iY}{2} = \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right) = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = |1\rangle \langle 0|$
- ▶  $\sigma^+ |0\rangle = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = |1\rangle$
- ▶  $\sigma^+ |1\rangle = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$
- ▶  $\{\sigma^+, \sigma^+\} = 0$

## Annihilation operator

- ▶  $a_j: Z_0 \otimes \cdots \otimes Z_{j-1} \otimes \sigma_j^- \otimes I$
- ▶  $\sigma^- = \frac{X+iY}{2} = \frac{1}{2} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right) = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = |0\rangle \langle 1|$
- ▶  $\sigma^- |0\rangle = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$
- ▶  $\sigma^- |1\rangle = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = |0\rangle$
- ▶  $\{\sigma^-, \sigma^-\} = 0$

$$\{\sigma^+, \sigma^-\} = I$$

# Jordan-Wigner encoding: creation and annihilation operators

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

$$\begin{aligned} H = & h_0 I + h_1 Z_0 + h_2 Z_1 + h_3 Z_2 + h_4 Z_3 + \\ & h_5 Z_0 Z_1 + h_6 Z_0 Z_2 + \\ & h_7 Z_1 Z_2 + h_8 Z_0 Z_3 + \\ & h_9 Z_1 Z_3 + h_{10} Z_2 Z_3 + \\ & h_{11} Y_0 Y_1 X_2 X_3 + h_{12} X_0 Y_1 Y_2 X_3 + \\ & h_{13} Y_0 X_1 X_2 Y_3 + h_{14} X_0 X_1 Y_2 Y_3. \end{aligned}$$

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

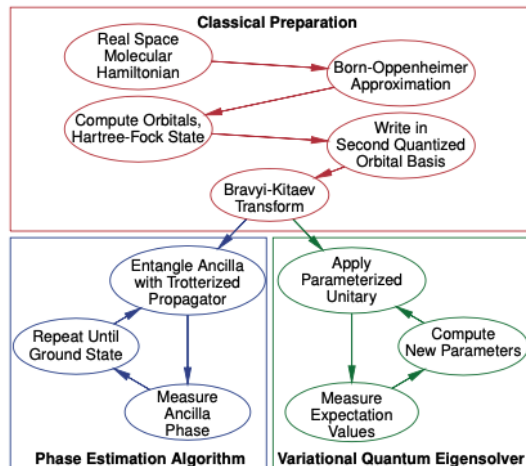


FIG. 5. A flowchart describing steps required to quantum compute molecular energies using both PEA and VQE.

# Map of topics

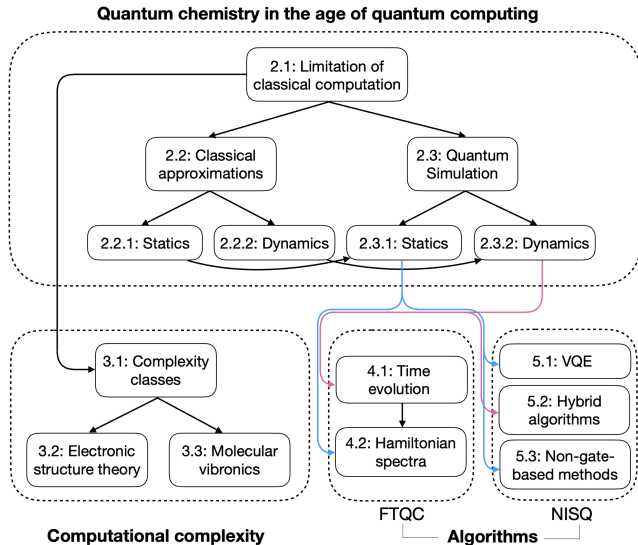


Figure: [Cao et al., 2019]

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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  $|\Psi\rangle$ ,  $H|\Psi\rangle = E_G|\Psi\rangle$

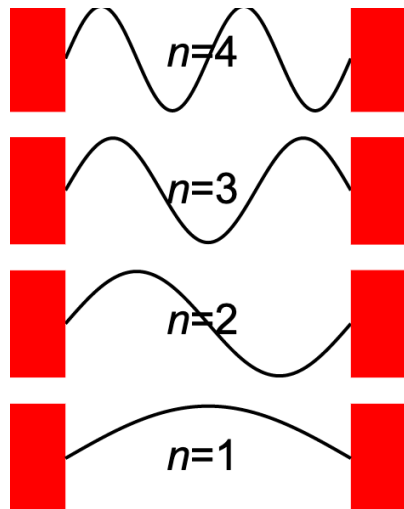


Figure: Credit: wikipedia.org

# Ground state estimation problem

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## Smallest eigenvalue is the ground state energy

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

## 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  $|\phi_0\rangle, |\phi_1\rangle, \dots, |\phi_{N-1}\rangle$ .
- ▶ Eigenvectors are orthogonal  $\langle\phi_i|\phi_j\rangle = \delta_{ij}$
- ▶  $\sum_{i=0}^{N-1} |\phi_i\rangle \langle\phi_i| = I_N$

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  $|\phi_0\rangle, |\phi_1\rangle \dots |\phi_{N-1}\rangle$ , be eigenvectors of  $H$  with eigenvalues  $E_0, E_1, \dots$  to  $E_{N-1}$
- ▶ So for any  $|\psi\rangle$ ,  $|\psi\rangle$  can be written as  $C_0 |\phi_0\rangle + C_1 |\phi_1\rangle + \dots + C_{N-1} |\phi_{N-1}\rangle$ , where  $C_i = \langle \phi_i | \psi \rangle$ , and  $\sum_{i=0}^{N-1} |C_i|^2 = 1$

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

- ▶  $\langle \psi | H | \psi \rangle = \left( C_0 \langle \phi_0 | + C_1 \langle \phi_1 | + \dots + C_{N-1} \langle \phi_{N-1} | \right) H \left( C_0 |\phi_0\rangle + C_1 |\phi_1\rangle + \dots + C_{N-1} |\phi_{N-1}\rangle \right) = C_0^2 E_0 + C_1^2 E_1 + \dots + C_{N-1}^2 E_{N-1} \geq E_0$
- ▶ 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  $\vec{\theta}$  a trial state  $|\psi(\vec{\theta})\rangle = U(\vec{\theta})|0\rangle^{\otimes N}$ , this is the ansatz.

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

- ▶  $\min_{\vec{\theta}} \langle 0 |^{\otimes N} U^\dagger(\vec{\theta}) H U(\vec{\theta}) | 0 \rangle^{\otimes N}$
- ▶ 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.



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