

# Quantum Chemistry

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Motivation for quantum chemistry

Ground state estimation

Simplification of problem representation

Quantum computing for quantum chemistry

Qubit representation of orbitals

# 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

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

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

| 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

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

- |  $i\hbar \frac{d}{dt} |j(t)\rangle = H |j(t)\rangle$
- |  $\frac{d}{dt} |j(t)\rangle = \frac{i}{\hbar} H |j(t)\rangle$
- | 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:  
 $|j(t)\rangle = U(t) |j(0)\rangle$ , where  $U(t) = \exp\left(-\frac{i}{\hbar} Ht\right)$
- |  $U(t) = \exp\left(-\frac{i}{\hbar} Et\right)$

# Ground state energies / Hermitian spectral theorem

- | Eigendecomposition of  $H$ :  
$$H = \sum_{i=1}^N E_i |j_i\rangle \langle i| h |ij\rangle$$
- | If state  $|j_i\rangle$  is an eigenvector of  $H$ , then  $H |j_i\rangle = E |j_i\rangle$
- | State  $|j_i\rangle = |j_i\rangle \exp(-\frac{i}{\hbar} E t)$  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: wikimedia.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:  $\text{rate} \propto \exp\left(-\frac{E}{k_B T}\right)$
- | Determining  $E$  to within  $1 : 6 \cdot 10^{-3}$  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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# Simplifications / mappings

# Born-Oppenheimer approximation

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

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

1. Electrons have kinetic energy
2. PE: Electrons are attracted to nuclei
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|  $R_i$  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.

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.

- | 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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- | Uses three Gaussians with different parameters to approximate shape of 1s orbital.

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  $q$ .
- |  $f a_p; a_q g = \delta_{pq}$  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.

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# 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

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

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

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

$$| \dots \rangle + j | 0 \rangle = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} | \dots \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = j | 1 \rangle$$

$$| \dots \rangle + j | 1 \rangle = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} | \dots \rangle = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

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

## Annihilation operator

$$| a_j : Z_0 \dots Z_{j-1} \rangle + | \dots \rangle$$

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

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

$$| \dots \rangle + j | 0 \rangle = \begin{pmatrix} 0 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} | \dots \rangle = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$| \dots \rangle + j | 1 \rangle = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} | \dots \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = j | 0 \rangle$$

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

$$| f \rangle + | g \rangle = | \dots \rangle$$

# 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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