

Quantum Chemistry

Yipeng Huang

Rutgers University

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Table of contents

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

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

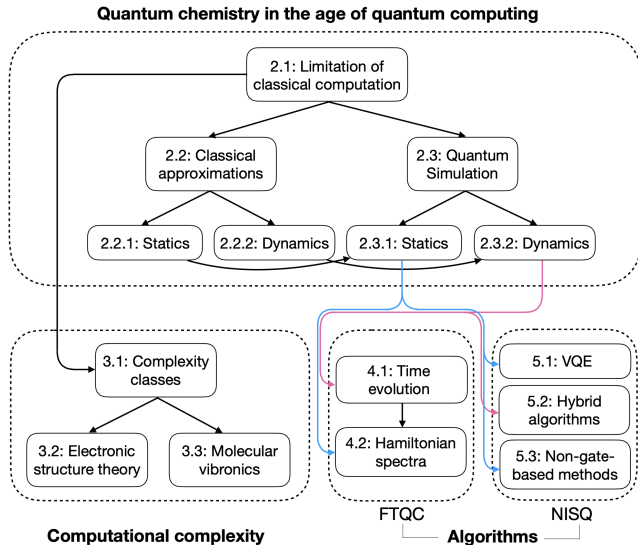


Figure: [Cao et al., 2019]

Table of contents

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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.

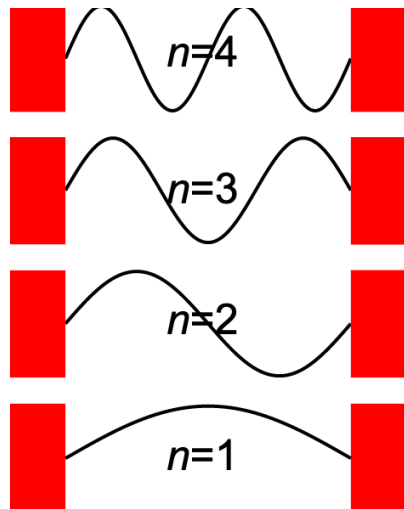


Figure: Credit: wikipedia.org

Computing the ground state energy

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

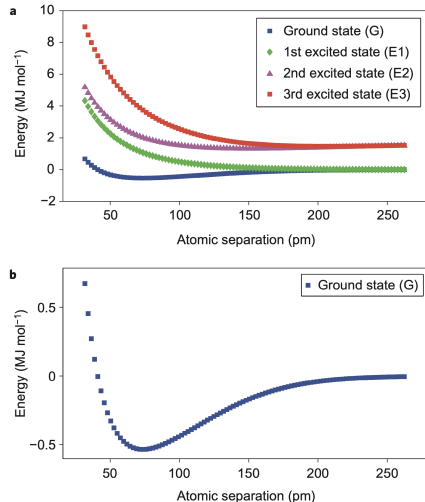


Figure: [Lanyon et al., 2010]

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 1.6×10^{-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]

Table of contents

Motivation for quantum chemistry

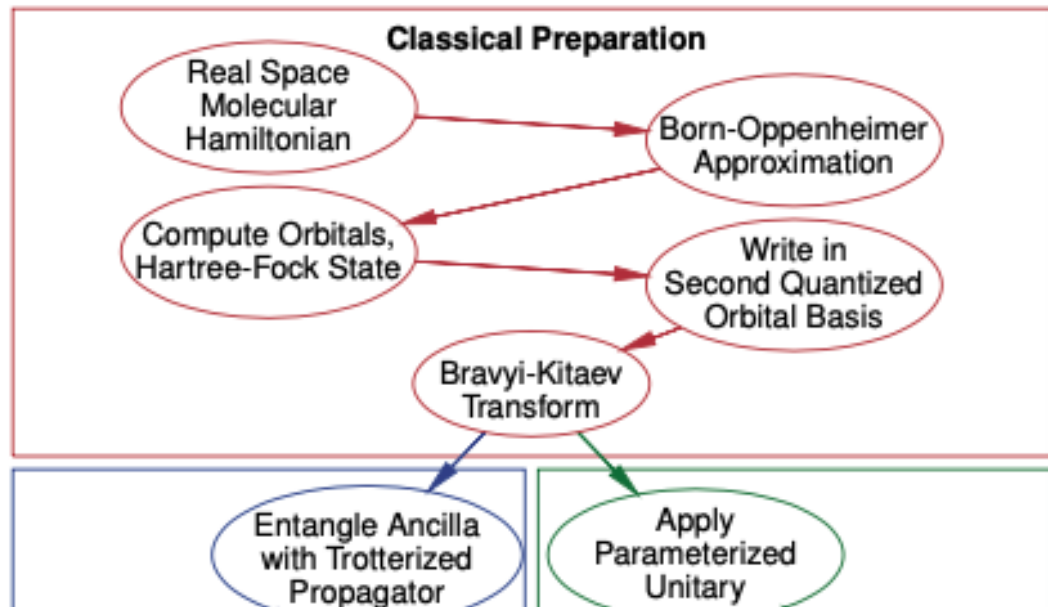
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Simplifications / mappings



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
 - ▶ 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.

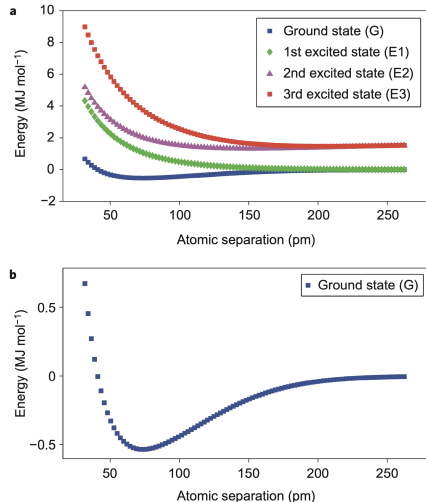
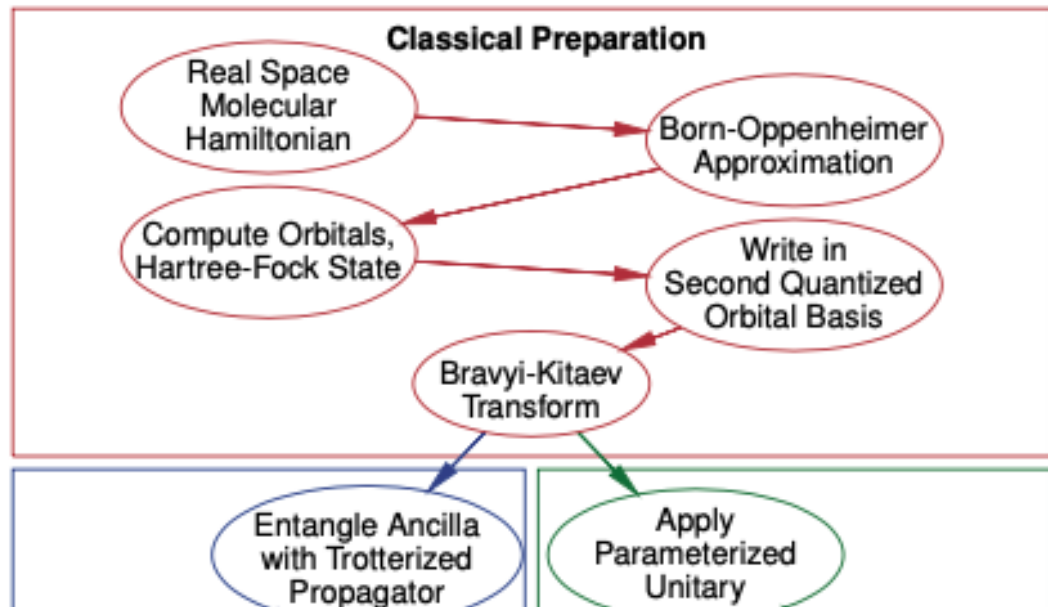


Figure: [Lanyon et al., 2010]

Simplifications / mappings



What will the state vector encode?

First quantization: real-space discretization

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

- Direct finite difference of space

Molecular basis set / Hartree Fock.

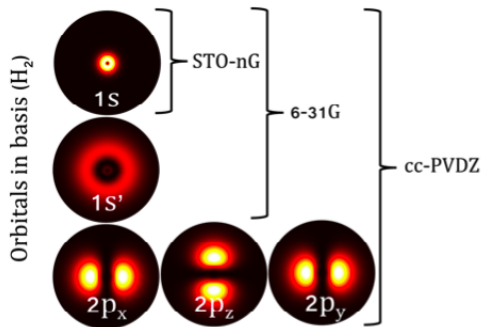


FIG. 4. The orbitals included in different basis sets for the Hydrogen atom. The 1s' orbital is often written as 2s. The plots show the radial probability distributions for the true Hydrogenic orbitals, which the basis orbitals approximate.

Figure: Credit: McArdle. Quantum computational chemistry.

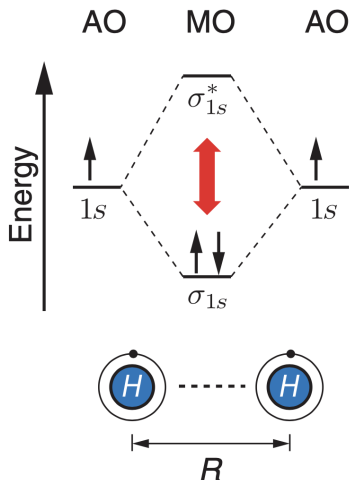
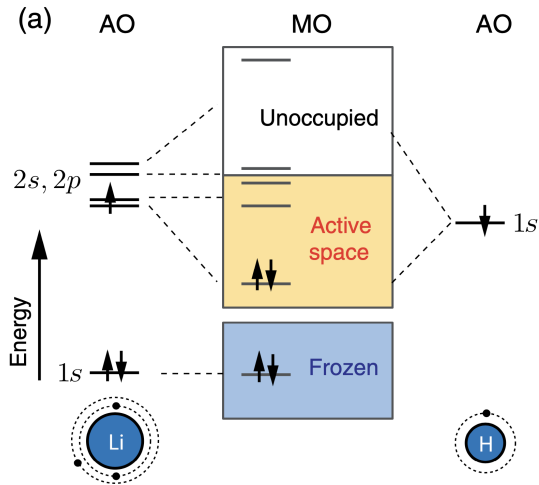


Figure: Credit: [Hempel et al., 2018]

Molecular basis set / Hartree Fock.



- ▶ In molecules with many orbitals and electrons, the orbitals are 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.

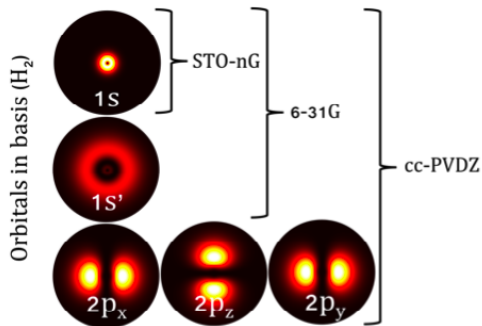


FIG. 4. The orbitals included in different basis sets for the Hydrogen atom. The $1s'$ orbital is often written as $2s$. The plots show the radial probability distributions for the true Hydrogenic orbitals, which the basis orbitals approximate.

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.

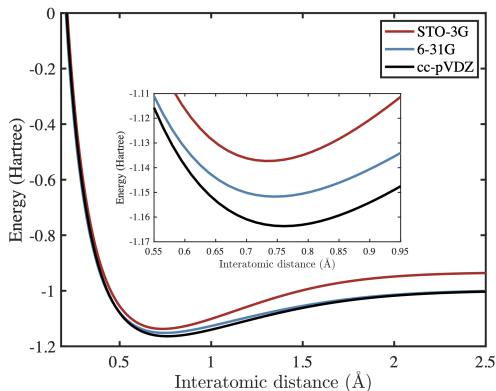


FIG. 14. Comparing the ground state dissociation curves of H₂ for a range of basis sets.

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

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

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 .
- ▶ $\{a_p, a_q^\dagger\} = \delta_{pq}$ Annihilates an electron in p and creates an electron in q if orbitals p and q are different.
- ▶ $\{a, b\} = ab + ba$

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:

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

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

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

Table of contents

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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

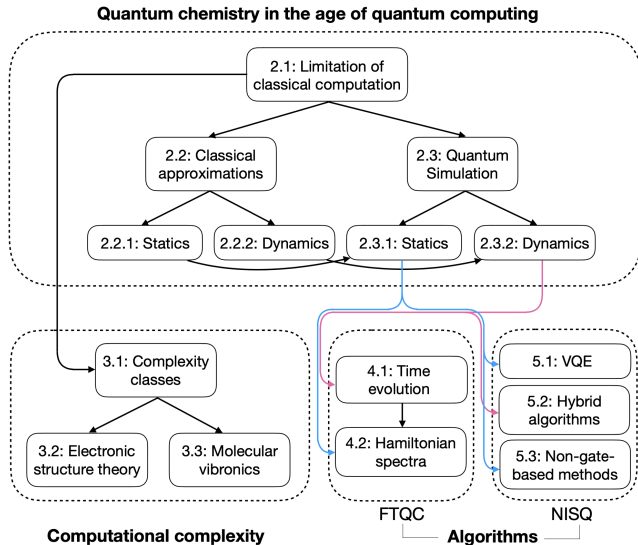


Figure: [Cao et al., 2019]

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: imgflip.com

Quantum computing for quantum chemistry

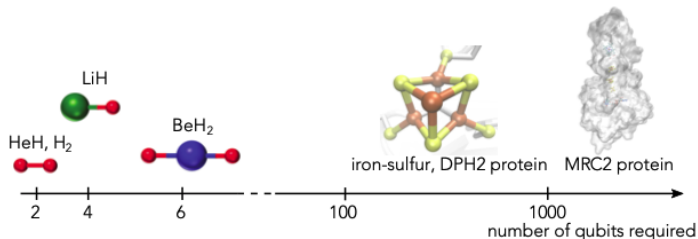


Figure 7: Qubit resources needed for quantum chemistry. Qubit numbers up to ten are based on existing experiments, whereas the resources for larger molecules are estimates. From left to right: hydrogen molecule, lithium hydride, beryllium hydride, iron sulphur (Fe-S) cluster in DPH2 complex of *Pyrococcus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

Table of contents

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Decision 4: Mapping to qubit Hamiltonian?

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

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



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