Quantum simulations and quantum/computational chemistry

in MCC185: From quantum optics to Quantum Technology

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Outline

- Motivation – Goals
- Quantum Chemistry – Electronic Structure Theory
    - The case for Quantum Computing
- Digital Quantum Simulation/Computation
    - The Jordan-Wigner Mapping
    - Quantum Circuit Model
- Variational Quantum Eigensolver (VQE)
    - Wave function Ansätze

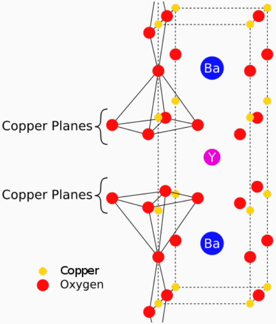
Motivation – Goals

Big Picture

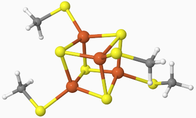
Learning goals:

- What is quantum computational chemistry (roughly)?
- Why is it worthwhile? What are limitations of “classical” approaches?
- Why and how can quantum computing help?
- How can we represent quantum chemical problems on quantum hardware?
- How can we solve it?
- Rough understanding of the variational quantum eigensolver as an example.

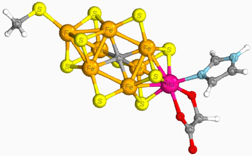
Ab Initio Quantum Chemistry – Electronic Structure Theory



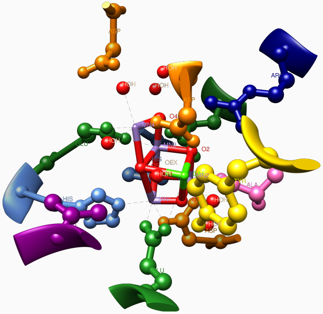
YBCO*: Unconventional high-T_c superconductivity



Iron-Sulfur clusters: electron transfer proteins



FeMo-cofactor: catalyst for N_2 reduction → improve Haber-Bosch process



Mn_4O_5Ca in Photosystem II: enable artificial photosynthesis process

Interesting systems/materials usually challenging for computational approaches!

Ab Initio Quantum Chemistry – Electronic Structure Theory

- Discover new materials/catalysts?
- Drug design?
- Chemical reactions for battery development?

→ $\sim$ 30% of high-performance computing for chemistry-related problems

- Q: What are you interested in?
- "Solving the puzzles of nature"?

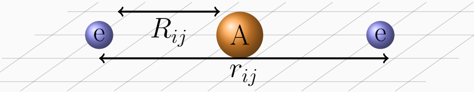
We need an accurate theoretical understanding at nano-scale for bottom-up materials design!

Quantum Chemistry – Electronic Structure Theory

Ab Initio Quantum Chemistry – Electronic Structure Theory

All necessary information of a quantum system contained in electronic molecular Hamiltonian (Born-Oppenheimer approx. and atomic units)

$$\hat{H} = \underbrace{-\sum_i \nabla^2_{\mathbf{r}_i}}_{\text{kinetic energy of e}^-} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\mathrm{e}^- - \mathrm{e}^-\ \text{repulsion}} - \underbrace{\sum_{I,j}\frac{Z_I}{|\mathbf{R}_I-\mathbf{r}_j|}}_{\text{Potential}}$$



Electronic properties: Ground- and low-lying excited state properties, energy differences, polarization, response functions, ...

Target: High / “chemical accuracy” to ensure predictability, interpretability and comparison with experimental results

Task: Solve the Schrödinger equation derived from first principles:

$$\hat{H}\,|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)\rangle = E_0\,|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)\rangle$$

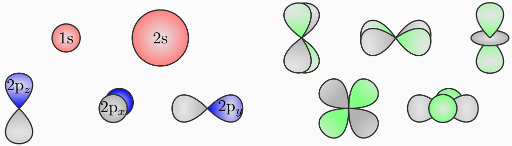
Ab Initio Quantum Chemistry – Electronic Structure Theory

Second quantized form of molecular Hamiltonian:

$$\hat{H} = \underbrace{\sum_{i,j} t_{ij} \sum_{\sigma=\uparrow,\downarrow} a^{\dagger}_{i,\sigma} a_{j,\sigma}}_{\text{kinetic/hopping term}} + \underbrace{\sum_{i,j,k,l} V_{ijkl} \sum_{\sigma,\tau=\uparrow\downarrow} a^{\dagger}_{i,\sigma} a^{\dagger}_{j,\tau} a_{l,\tau} a_{k,\sigma}}_{\text{e}^{-}\text{-e}^{-}\text{ interaction term}}$$

$a^{(\dagger)}_{i,\sigma}$ annihilates(creates) an electron with spin $\sigma = \{\uparrow, \downarrow\}$ in orbital i. The combination (i, σ) is often called “spin-orbital”.

We have to choose a **basis/orbitals** we perform our calculations in! In quantum chemistry: starting orbitals are most often “atomic-like” orbitals (for each atom):



(Anti-)Symmetric wave functions – Pauli exclusion principle

- For Fermions, the Pauli exclusion principle requires the wavefunction to be **anti-symmetric** under the exchange of two particles:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)$$

- While Bosonic wave functions are **symmetric** under the exchange of particles

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)$$

Occupation number representation – Commutation relations

- $a^\dagger_{i,\uparrow}$ creates an electron with up-spin, ↑, in orbital i, e.g. for 2 electrons in 2 orbitals (=4 spin-orbitals): $a^\dagger_{1,\uparrow} a^\dagger_{2,\downarrow} |vac\rangle = |1001\rangle$:

- Pauli-principle/(anti-)symmetry due do (anti-)commutation relations:

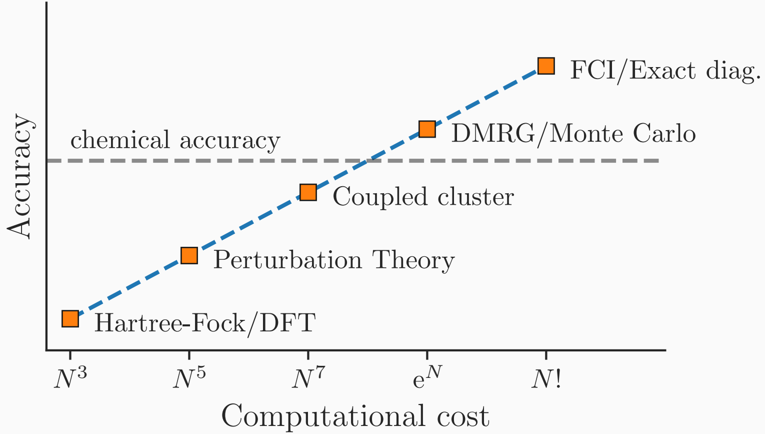
$$\left\{a_i\,, a_j\right\} = a_i a_j + a_j a_i = \left\{a^\dagger_i, a^\dagger_j\right\} = 0, \quad \left\{a_i, a^\dagger_j\right\} = \delta_{i,j} \quad \text{for Fermions}$$

$$\left[c_i\,, c_j\right] = c_i c_j - c_j c_i = 0, \quad \left[c_i, c^\dagger_j\right] = \delta_{i,j} \quad \text{for Bosons}$$

- *Exercise:* Convince yourself that anti-symmetry and Pauli exclusion principle (no two electrons with same quantum numbers) follow from anti-commutation property, e.g. for a 2 electron in 4 spin-orbital wave function, $|\Psi\rangle = a^\dagger_{1,\uparrow} a^\dagger_{1,\downarrow} |\mathbf{0}\rangle = |1100\rangle$

Computational approaches, cost and accuracy

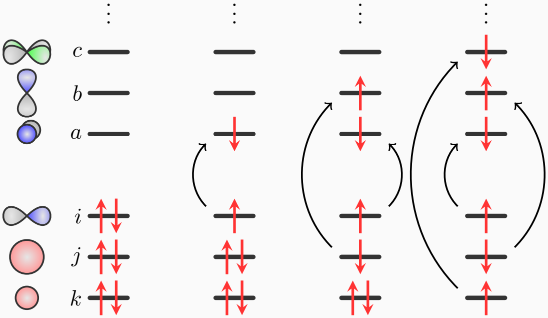
There is a long history and wide variety of computational approaches in quantum chemistry. Accuracy vs. computational cost:



Exponential scaling of Full Configuration Interaction (FCI)

FCI/Exact diagonalization (ED) ⇒ exact solution in a given basis: linear combination of determinants

$$|\Psi\rangle = |\Phi_{HF}\rangle + \sum_i c_i |\Phi_i\rangle$$



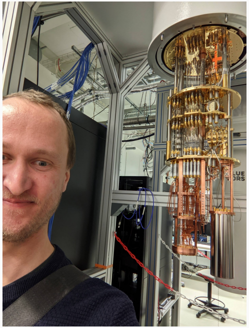
$$|\Phi_{HF}\rangle \quad + \quad |\Phi_i^a\rangle \quad + \quad |\Phi_{ij}^{ab}\rangle \quad + \quad |\Phi_{ijk}^{abc}\rangle + \cdots$$

All possible excitations from HF determinant

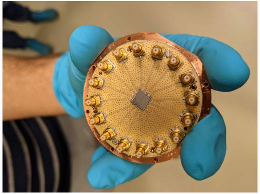
Number of possible states for given number of electrons, N, and orbitals, n: $\sim \binom{N}{n}$

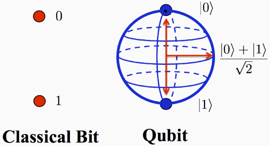
Mol.	#orbitals	#electrons	#states
H_2	2	2	4
LiH	4	4	36
Be_2	8	8	4900
H_2O	12	12	$\sim 8 \cdot 10^5$
C_2H_4	16	16	$\sim 16 \cdot 10^6$
F_2	18	18	$\sim 2 \cdot 10^9$

Quantum Computing



@ Chalmers





0011
0101
0110
1001
1010
1100

Exponentially scaling FCI $|\Psi\rangle \sim \binom{N}{n}$. n qubits can encode $\sim 2^n$ states. Quantum algorithms use **entanglement, superposition** and **interference** to find solution

$$\overbrace{(|0\rangle_1 + |1\rangle_1)}^{\text{qubit1}} \otimes \overbrace{(|0\rangle_2 + |1\rangle_2)}^{\text{qubit2}}$$
$$= |00\rangle + |01\rangle + |10\rangle + |11\rangle$$

$$|q_1\rangle \otimes |q_2\rangle \otimes |q_3\rangle =$$
$$= |000\rangle + |001\rangle + |010\rangle + |100\rangle$$
$$+ |011\rangle + |101\rangle + |110\rangle + |111\rangle$$

IBM Quantum Roadmap*

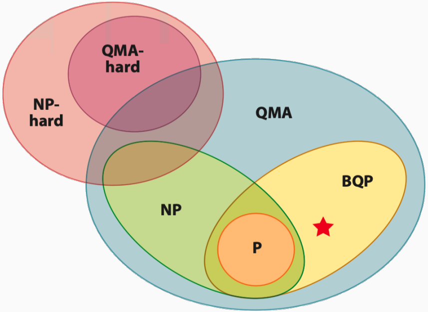
Year	2019	2020	2021	2022	2023	beyond
# qubits	27	65	127	433	1121	...

Benioff, J. Stat. Phys. **22** (5), 563 (1980); Feynman, Int. J. Theo. Phys. **21** (6/7), 467 (1982); Preskill, Quantum **2**, 79 (2018); * https://research.ibm.com/blog/ibm-quantum-roadmap

The case for quantum

Quantum chemistry potential use-case / killer-application of noisy intermediate-scale quantum (NISQ) devices and "quantum advantage" for relevant systems

- Efficient encoding of exponentially scaling wavefunction
- Effective measurement of Hamiltonian expectation values
- A system with > 60 qubits cannot be simulated with a classical computer
- A moderately-sized quantum processor (≈ 100 qubits) could outperform supercomputers for exact solutions
- **But how do we tackle the problem on quantum hardware?**

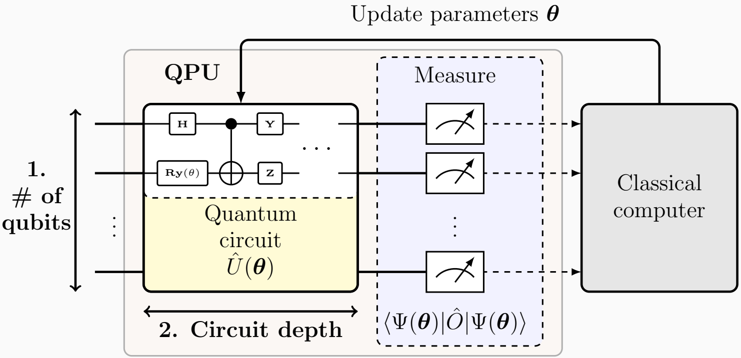


Kassal *et al.*, Annu. Rev. Phys. Chem. 2011. 62:185 (2010)

Overview: Quantum Chemistry on Quantum Computers

Current quantum hardware has many problems still: **noise, decoherence and limited number of qubits** – noisy intermediate-scale quantum (NISQ) era

Hybrid quantum-classical approach:



– Use pros of both classical and quantum hardware

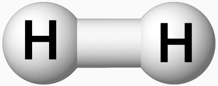
– Use **short-depth quantum circuits** that fit current hardware

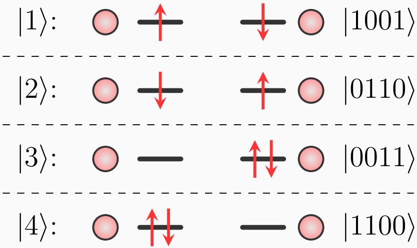
– Can **improve on classical estimates** by non-classical states

– Store quantum state with **exponentially fewer resources**

Example: Classic solution of hydrogen molecule – H_2

Hydrogen molecule in a “minimal” basis set: 1s orbital for each hydrogen.
4-dimensional Hilbert space for two electrons in two orbitals (4 spin-orbitals).





$|1\rangle$: $|1001\rangle$

$|2\rangle$: $|0110\rangle$

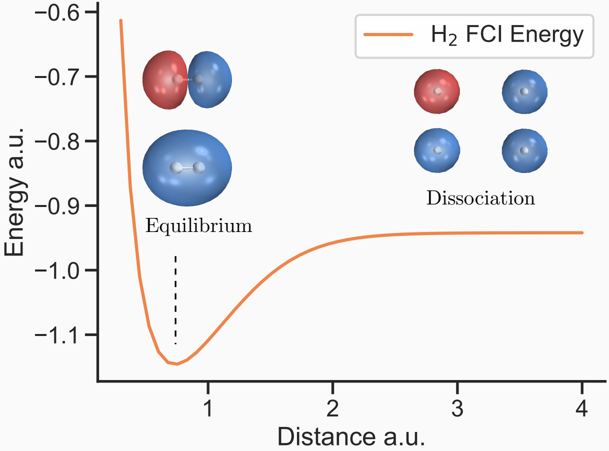
$|3\rangle$: $|0011\rangle$

$|4\rangle$: $|1100\rangle$

Construct matrix representation of quantum chemistry Hamiltonian in this basis,
$H_{ij} = \langle i| \hat{H} |j\rangle$, → diagonalize → exact solution in given basis

Jupyter Notebook

Example: Hydrogen molecule – H_2 – PES



Groundstate wavefunction at equilibrium: $|\Psi_0\rangle = 0.995\,|1100\rangle - 0.105\,|0011\rangle$

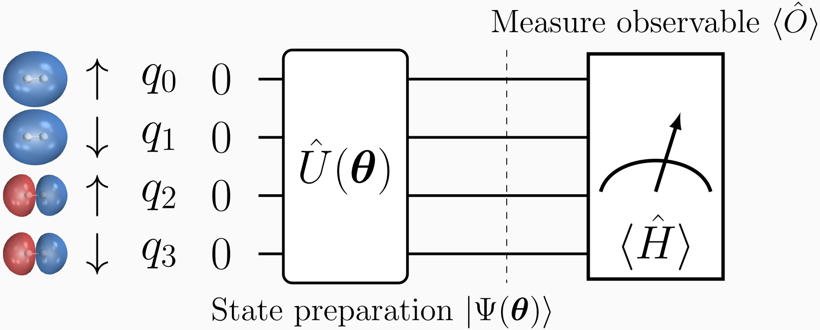
Groundstate wavefunction at dissociation: $|\Psi_0\rangle = \frac{1}{\sqrt{2}}\left(|1100\rangle - |0011\rangle\right)$

Digital Quantum Simulation/Computation

Digital Quantum Simulation/Computation

1. Map fermionic Hamiltonian onto quantum hardware/qubits
2. Use quantum algorithms to solve the problem at hand

Circuit model: Lines/wires represent qubits, operations/gates acting on it from left to right. Size of representable Hilbert space: 2^N



Encoding the problem on a quantum computer

Qubits can quite naturally store the occupation of an spin-orbital:
$|0\rangle$-state/$\left(\begin{smallmatrix}1\\0\end{smallmatrix}\right)$: empty, $|1\rangle$-state/$\left(\begin{smallmatrix}0\\1\end{smallmatrix}\right)$: occupied

Also: action of creation and annihilation operators representable by Pauli matrices:

$$\begin{aligned}\hat{a}^{\dagger}|0\rangle &= \begin{pmatrix}0 & 0\\1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{\hat{X}-i\hat{Y}}{2}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = |1\rangle\\ \hat{a}|1\rangle &= \begin{pmatrix}0 & 1\\0 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \frac{\hat{X}+i\hat{Y}}{2}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix} = |0\rangle\,,\end{aligned}$$

with the Pauli matrices

$$\hat{X} = \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix},\quad \hat{Y} = \begin{pmatrix}0 & -i\\i & 0\end{pmatrix},\quad \hat{Z} = \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

Anti-symmetry/Anti-commutation relations

However, electrons are **indistinguishable Fermions**, with anti-symmetric wavefunction and anti-commuting creation/annihilation operators!

$$\left\{a_i^\dagger, a_j^\dagger\right\} = 0, \qquad a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger$$

Unlike **individually addressable** qubits, with Pauli operators:

$$\left(\frac{X_i - iY_i}{2}\right)\left(\frac{X_j - iY_j}{2}\right) = +\left(\frac{X_j - iY_j}{2}\right)\left(\frac{X_i - iY_i}{2}\right)$$

Exercise: Convince yourself of equation above, $\{\sigma_i, \sigma_j\} = 2\delta_{i,j}$

Task: We need to map the **fermionic** Hamiltonian to a **qubit** Hamiltonian in terms of Pauli operators, $\hat{H} = \sum_i c_i \hat{P}_i$

Jordan Wigner Mapping

Note, however, that the following Pauli operators anti-commute:

$$\hat{Z}\hat{X} = -\hat{X}\hat{Z}, \qquad \hat{Z}\hat{Y} = -\hat{Y}\hat{Z}$$

Exercise: *convince yourself of equation above*

Jordan-Wigner encoding:

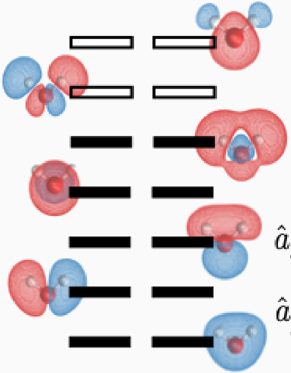
$$\begin{aligned} a_1^\dagger =& \frac{X_1 - iY_1}{2} \\ a_2^\dagger =& Z_1 \left(\frac{X_2 - iY_2}{2} \right) \\ a_3^\dagger =& Z_1 Z_2 \left(\frac{X_3 - iY_3}{2} \right) \\ a_i^\dagger =& \bigotimes_{j=1}^{i-1} Z_j \left(\frac{X_i - iY_i}{2} \right) \end{aligned}$$

- Fix anti-symmetry by tracking parity/phase before each creation/annihilation operator with $\hat{Z}_i$
- **Exercise:** Demonstrate anti-symmetry of JW-encoded $a_3^\dagger a_2^\dagger = -a_2^\dagger a_3^\dagger$!

JW Mapping – Recap

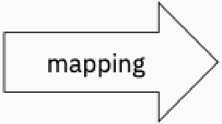
Fermions

$$\{a_i, a_i\} = 0,\ \{a_i^\dagger, a_i^\dagger\} = 0, \{a_i, a_i^\dagger\} = \delta_{i,j}$$

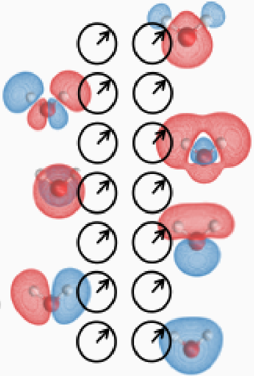


Spins

$$[\sigma_i, \sigma_i] = 0,\ [\sigma_i^\dagger, \sigma_i^\dagger] = 0, [\sigma_i, \sigma_j^\dagger] = \delta_{i,j}$$



mapping



Jordan-Wigner

$$\hat{a}_j = \bigotimes_{i=1}^{j-1} \hat{\sigma}_i^z \otimes (\hat{\sigma}_j^x + i\hat{\sigma}_j^y)$$

$$\hat{a}_j^\dagger = \bigotimes_{i=1}^{j-1} \hat{\sigma}_i^z \otimes (\hat{\sigma}_j^x - i\hat{\sigma}_j^y)$$

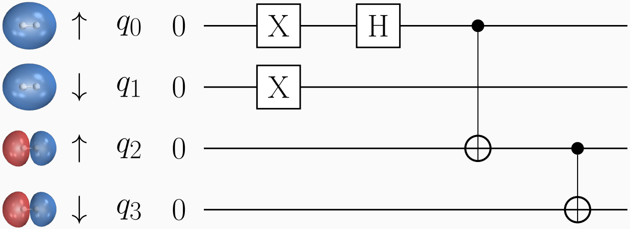
$$\hat{H}_{elec} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

$$\hat{H}_{elec} = \sum_i c_i \hat{P}_i$$

https://qiskit.org/documentation/nature/tutorials/01_electronic_structure.html

Quantum circuit model – details

Lines/wires represent qubits, operations/gates acting on it from left to right



Hadamard gate (H):

$$H = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

Controlled NOT (CNOT): target qubit ($\bigoplus$) is inverted if control qubit ($\cdot$) is $|1\rangle$.

Exercise: *what is the state* $|\Phi\rangle$ *at the end of the above circuit?*

In our case a qubit encodes the **occupation** of the associated spin-orbital

We will restrict ourselves to single-qubit **rotational gates**, e.g. $\hat{X}, \hat{Y}$, and 2-qubits **entangling gates**, like controlled NOT (CNOT) gates

Try: IBM Quantum Composer, IBM Quantum Lab

https://quantum-computing.ibm.com/

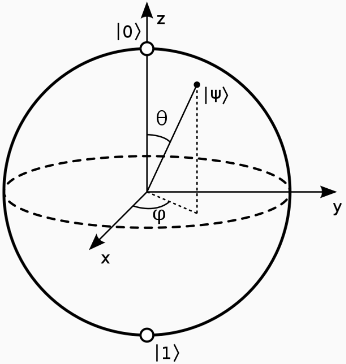
Parametrized gates

For flexibility, we need **parametrized** gates, e.g. rotation around axis:

$$R_X(\theta) = \exp(-i\frac{\theta}{2}\hat{X}) = \begin{pmatrix} \cos(\theta/2) & -i\sin(\theta/2) \\ -i\sin(\theta/2) & \cos(\theta/2) \end{pmatrix}$$

$$R_Y(\theta) = \exp(-i\frac{\theta}{2}\hat{Y}) = \begin{pmatrix} \cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & \cos(\theta/2) \end{pmatrix}$$

$$R_Z(\phi) = \exp -i\frac{\phi}{2}\hat{Z} = \begin{pmatrix} \exp(-i\phi/2) & 0 \\ 0 & \exp(i\phi/2) \end{pmatrix}$$



Can we express the groundstate wavefunction of H_2 with parametrized gates?

Groundstate wavefunction at dissociation: $|\Psi_0\rangle = \frac{1}{\sqrt{2}}(|1100\rangle - |0011\rangle)$

Try: IBM Quantum Composer

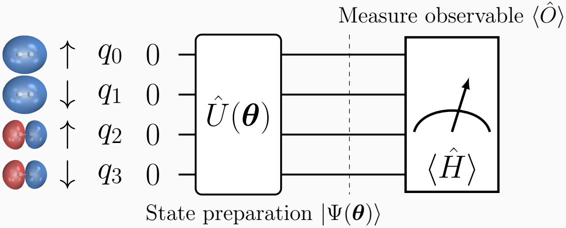
Parametrized gates – cont.

H_2 groundstate wavefunction at equilibrium:

$|\Psi_0\rangle = 0.995\,|1100\rangle - 0.105\,|0011\rangle + 0 \cdot |1001\rangle + 0 \cdot |0110\rangle$

Need a more general "Ansatz", $\hat{U}(\boldsymbol{\theta})\,|\mathbf{0}\rangle$:

$$\begin{aligned} |\Psi(\boldsymbol{\theta})\rangle &= \hat{U}(\boldsymbol{\theta})\,|0000\rangle \\ &\overset{!}{=} c_1\,|1100\rangle + c_2\,|0011\rangle \\ &+ c_3\,|1001\rangle + c_4\,|0110\rangle \end{aligned}$$



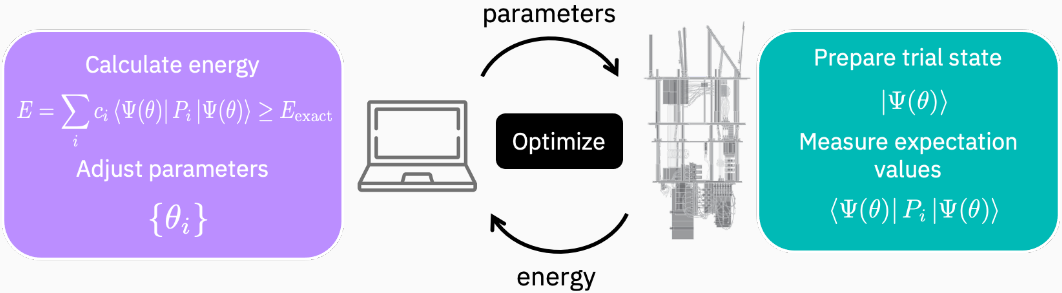
The variational quantum eigensolver (VQE) is an algorithm to find the **most optimal** parameters/angles $\boldsymbol{\theta}$ of a given Ansatz $\hat{U}(\boldsymbol{\theta})$ to minimize the energy expectation value,

$$E(\boldsymbol{\theta}) = \min_{\boldsymbol{\theta}} \langle\mathbf{0}|\,\hat{U}^\dagger(\boldsymbol{\theta})\hat{H}\hat{U}(\boldsymbol{\theta})\,|\mathbf{0}\rangle$$

Variational Quantum Eigensolver (VQE)

Hybrid quantum-classical algorithms – VQE

Leverage pros of both classical and quantum computers:



Calculate energy

$$E = \sum_i c_i \langle \Psi(\theta) | P_i | \Psi(\theta) \rangle \geq E_{\mathrm{exact}}$$

Adjust parameters

$$\{\theta_i\}$$

parameters

Optimize

energy

Prepare trial state

$$|\Psi(\theta)\rangle$$

Measure expectation values

$$\langle \Psi(\theta) | P_i | \Psi(\theta) \rangle$$

https://qiskit.org/documentation/nature/tutorials/01_electronic_structure.html; **VQE:** Peruzzo *et al.*, Nature Comm., **5**, 4213, (2014), McClean, *et al.*, New J. Phys. **18**, 023023 (2016)

Variational Quantum Eigensolver

Ground state, $|\Psi_0\rangle$, is fundamental in quantum chemistry and electronic structure theory → used to calculate all sort of properties, like reaction rates and reaction pathways

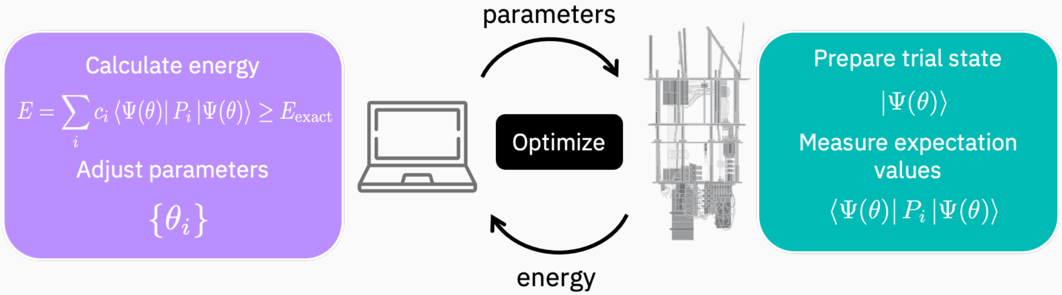
Our goal is to estimate: $\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle \quad \Rightarrow \langle\Psi_0|\,\hat{H}\,|\Psi_0\rangle = E_0$

Variational principle: an arbitrary state, $|\Psi(\boldsymbol{\theta})\rangle$, the expectation value of $\hat{H}$, will be an upper bound to E_0

$$\langle\Psi(\boldsymbol{\theta})|\,\hat{H}\,|\Psi(\boldsymbol{\theta})\rangle = E(\boldsymbol{\theta}) \geq E_0$$

Variational Quantum Eigensolver

VQE: Efficiently prepare and encode $|\Psi(\boldsymbol{\theta})\rangle$ with a suitable *Ansatz*, $\hat{U}(\boldsymbol{\theta})$, on **quantum hardware** and measure the expectation values of "Pauli strings", $\hat{P}_i$. Reconstruct the energy and update the parameters (with some optimizer) on a **classical computer**. Repeat until convergence of $E(\boldsymbol{\theta}) = \langle\Psi(\boldsymbol{\theta})|\,\hat{H}\,|\Psi(\boldsymbol{\theta})\rangle$



Calculate energy

$$E = \sum_i c_i \langle\Psi(\theta)|\,P_i\,|\Psi(\theta)\rangle \geq E_{\text{exact}}$$

Adjust parameters

$$\{\theta_i\}$$

parameters

Optimize

energy

Prepare trial state

$$|\Psi(\theta)\rangle$$

Measure expectation values

$$\langle\Psi(\theta)|\,P_i\,|\Psi(\theta)\rangle$$

Qiskit Tutorial, Example

Ansatz for the quantum chemistry wavefunction

In general: An **Ansatz** is a quantum circuit with parametrized gates

Desired in Ansätze:

- Expressive – spans large and correct portion of Hilbert space
- Small number of qubits
- Short-depth

→ **Hardware efficient**

Consideration due to noise and coherence times:

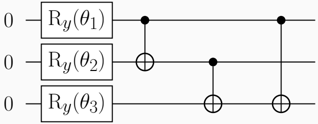
- Circuit depth
- Circuit connectivity
- Number of parameters
- Number of 2-qubit gates
- Gate types (Native to hardware?)

Ansatz for the quantum chemistry wavefunction

Hardware efficient Ansätze:

- Gates directly tailored for the quantum device
- Spans a very large portion of Fock space (inefficient)
- Large number of parameters, hard to optimize, “barren plateaus”

$$|\Psi(\boldsymbol{\theta})\rangle = \prod_{i}^{d} \left[\hat{U}_{ent}\hat{U}_{\mathrm{rot}}(\{\boldsymbol{\theta}_i\})\right] |\psi_{\mathrm{init}}\rangle$$



Chemically/Physically motivated:

- Chemistry-inspired exponential Ansatz: *Unitary coupled cluster Ansatz*
- Encode excitations of electrons between different orbitals, $|1100\rangle \rightarrow |0011\rangle$
- Not hardware efficient, deep circuits
- Less parameters, easier to optimize

$$|\Psi(\boldsymbol{\theta})\rangle = \mathrm{e}^{\hat{T}(\boldsymbol{\theta})-\hat{T}^{\dagger}(\boldsymbol{\theta})} |\psi_{HF}\rangle$$

Algorithms on quantum hardware

There is a variety of quantum algorithms for different kind of problems, most are for future **fault-tolerant** quantum hardware with many qubits and deep circuits.

- Shor's algorithm – Encryption
- Grover's algorithm – Database search
- Quantum Fourier Transformation
- Quantum Phase Estimation (QPE)
- *Quantum Approximate Optimization algorithm (QAOA)*
- *Quantum (Imaginary) Time Evolution*
- **Variational Quantum Eigensolver (VQE)**

On near-term intermediate-scale quantum (NISQ) hardware (low number of qubits and short circuits): **hybrid quantum-classical algorithms**

QPE: Kitaev, arXiv:quant-ph/9511026 (1995), Nielsen and Chuang, *Quantum computation and quantum information* (2001);

Further Topic

- Noise!
- Simulation – Noise-less / with noise model
- Calculations on real-hardware over the cloud
- Error mitigation, arXiv:2203.14756 (2022)
- Calculations/experiments on Chalmers devices
- Resource reduction, arXiv:2201.03049 (2022)
- Many more...

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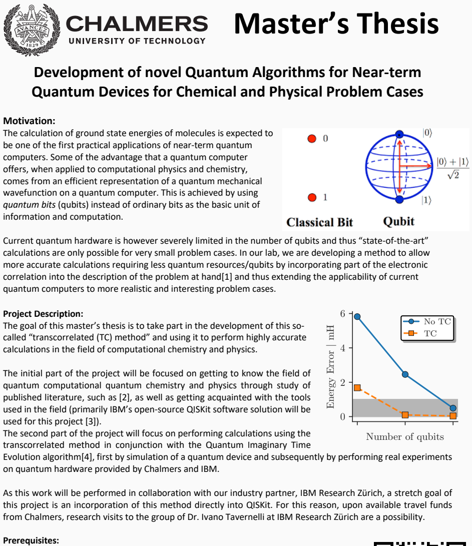


Master’s Thesis

Development of novel Quantum Algorithms for Near-term Quantum Devices for Chemical and Physical Problem Cases

Motivation:

The calculation of ground state energies of molecules is expected to be one of the first practical applications of near-term quantum computers. Some of the advantage that a quantum computer offers, when applied to computational physics and chemistry, comes from an efficient representation of a quantum mechanical wavefunction on a quantum computer. This is achieved by using *quantum bits* (qubits) instead of ordinary bits as the basic unit of information and computation.

Current quantum hardware is however severely limited in the number of qubits and thus “state-of-the-art” calculations are only possible for very small problem cases. In our lab, we are developing a method to allow more accurate calculations requiring less quantum resources/qubits by incorporating part of the electronic correlation into the description of the problem at hand[1] and thus extending the applicability of current quantum computers to more realistic and interesting problem cases.

Project Description:

The goal of this master’s thesis is to take part in the development of this so-called “transcorrelated (TC) method” and using it to perform highly accurate calculations in the field of computational chemistry and physics.

The initial part of the project will be focused on getting to know the field of quantum computational quantum chemistry and physics through study of published literature, such as [2], as well as getting acquainted with the tools used in the field (primarily IBM’s open-source QISKit software solution will be used for this project [3]).

The second part of the project will focus on performing calculations using the transcorrelated method in conjunction with the Quantum Imaginary Time Evolution algorithm[4], first by simulation of a quantum device and subsequently by performing real experiments on quantum hardware provided by Chalmers and IBM.

As this work will be performed in collaboration with our industry partner, IBM Research Zürich, a stretch goal of this project is an incorporation of this method directly into QISKit. For this reason, upon available travel funds from Chalmers, research visits to the group of Dr. Ivano Tavernelli at IBM Research Zürich are a possibility.

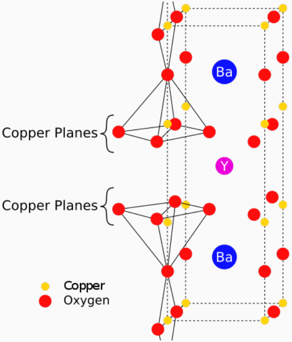
Prerequisites:

Time for questions!

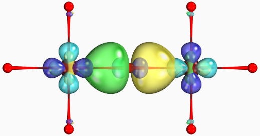
$$t_{ij} = \int \phi_i^*(\mathbf{r}) \left(\nabla_{\mathbf{r}}^2 - \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|} \right) \phi_j(\mathbf{r}) d\mathbf{r}$$

$$V_{ijkl} = \int \int \frac{\phi_i^*(\mathbf{r}_1)\phi_k^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

Application: High-T$_C$ Superconductors and the Hubbard Model

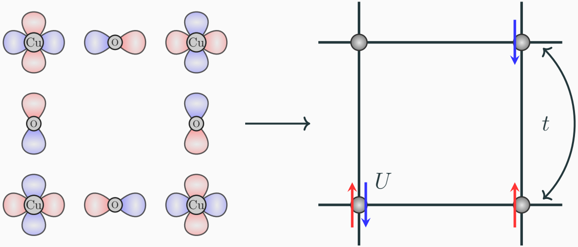


YBCO



Cu-O-Cu

Mapping to an effective lattice model:



The Hubbard Hamiltonian

$$\hat{H} = -t \sum_{\langle i,j \rangle,\sigma} \left(c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

Strong interaction $\Rightarrow$ highly multiconfigurational

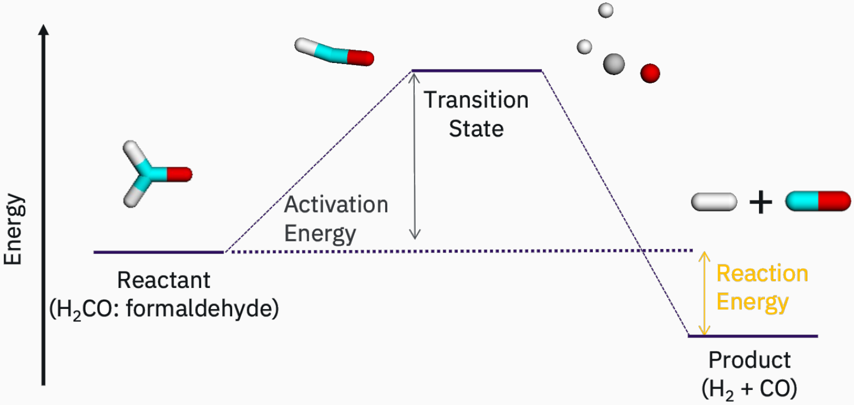
Hubbard, 1963; Kanamori, 1963; Gutzwiller; 1963; Anderson, 1987; Emery, 1987; Zhang and Rice, 1988; Bednorz and Müller, 1986

Effective Model – Solid State Physics

Not restricted to *ab initio* electronic structure theory – quantum chemistry

- Hubbard-like model
- Electron-phonon model
- Impurity model
- Heisenberg/spin model

Chemical reactions – high accuracy

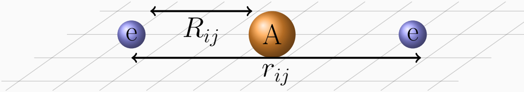


In chemistry, it is important to calculate the energy of molecules within **chemical accuracy**, which is required to predict reaction rates:

$k_B T \approx 1\ kcal/mol \approx 0.043\ eV$

First Quantization

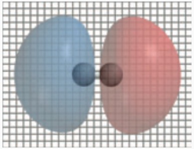
First Quantization → real-space grid necessary

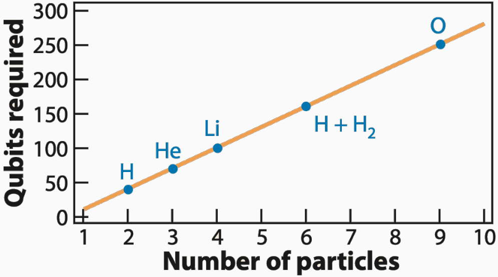


$$\hat{H} = -\sum_i \nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,j}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_j|}$$

$$|\Psi\rangle = |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)\rangle\,, \quad \mathbf{r}_i \in \mathbb{R}^3$$

Wave-function encoding:
on a grid of 2^n sites per dimension





Kassal *et al.*, Annu. Rev. Phys. Chem. 2011. 62:185 (2010)

Qubits required to represent
the wave function:
3n per particle

Slater Determinants

- Simplest way to approximate wavefunctions is to express them as products (Hartree-product) of single particle wavefunctions (orbitals):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

- But this wave function is **not symmetric** → not suitable for fermionic wave functions
- Anti-symmetric property via **Slater determinant (SD)**:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \vdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

- *Exercise:* Convince yourself of anti-symmetry of a two-particle SD: $\Psi(\mathbf{r}_1, \mathbf{r}_2)$