Simulating Chemistry on a Quantum Computer Part I

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IBM Quantum

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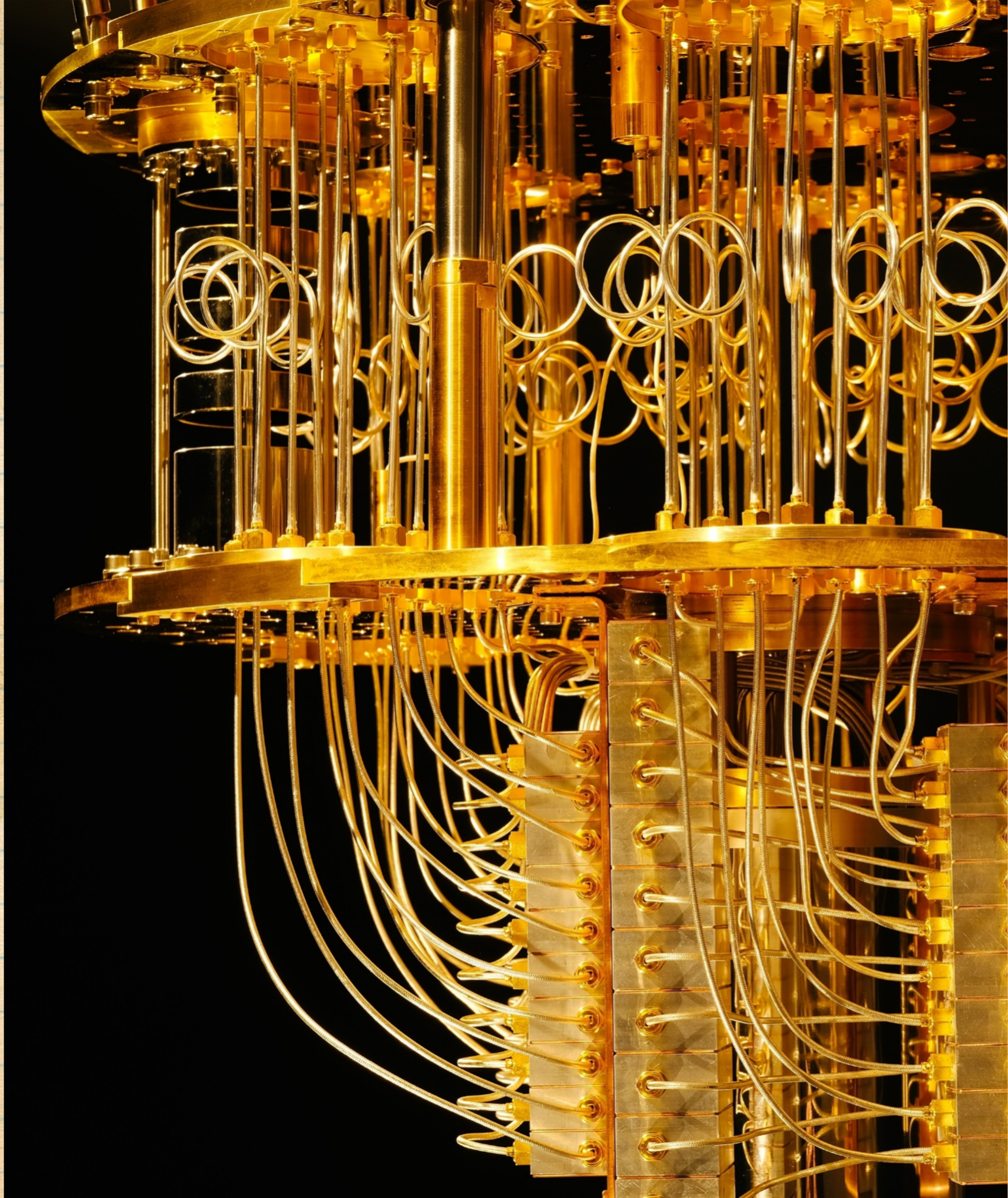

Topics covered

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Construct Qubit Hamiltonians for molecules

- **Second quantization notation**
- **Basics of fermion to qubit mappings**

Variational Quantum Algorithms

- **Why they work**
- **Popular Variational Wavefunctions**
- **Open challenges**

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THIS CLASS IS FOR YOU

Please

Ask questions!

Molecular Hamiltonians

Molecular Hamiltonians

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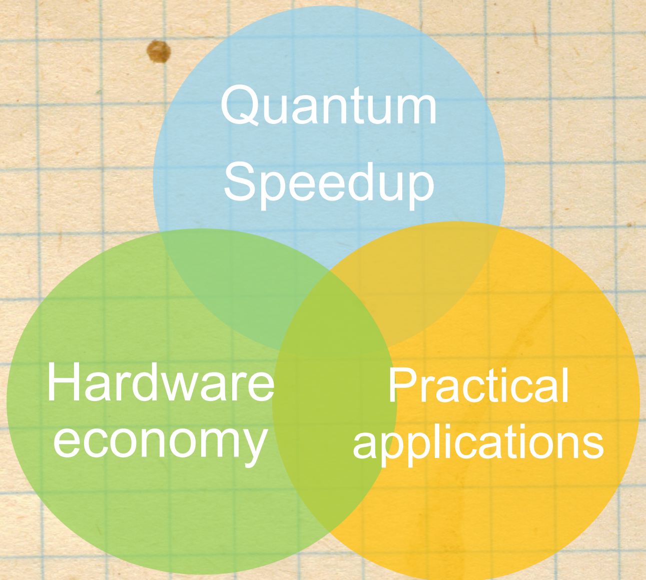
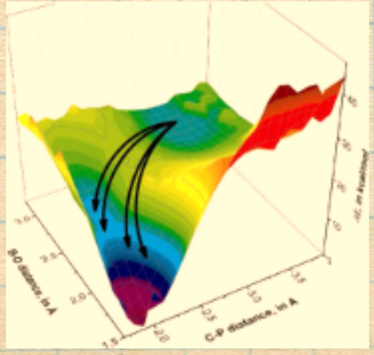
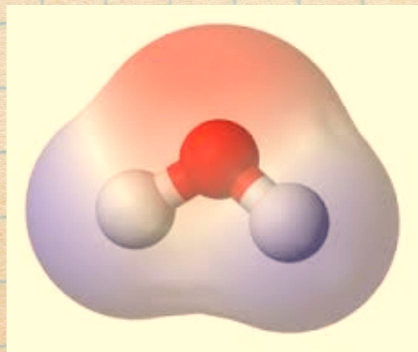


Quantum Chemistry: What can quantum computers do?

Reaction rates





Molecular structure

Molecular Hamiltonians

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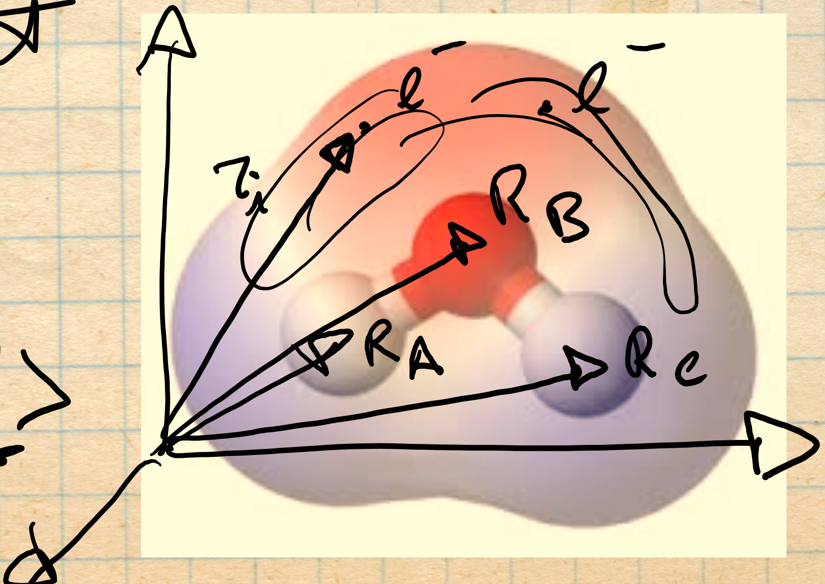
$$H = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{j>i} \frac{1}{r_{ij}} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

Electronic KE | Nuclear KE | Electron-nuclear Coulomb | Electron-electron Coulomb | Nuclear-nuclear Coulomb

Time-independent Schroedinger eq.

$$H|\Psi\rangle = E|\Psi\rangle$$



Molecular Hamiltonians

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$$H = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{j>i} \frac{1}{r_{ij}} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

Electronic KE | Nuclear KE | Electron-nuclear Coulomb | Electron-electron Coulomb | Nuclear-nuclear Coulomb

- H is an operator acting on quantum states
- H can be represented as a matrix
- We are interested in E_0

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

Molecular Hamiltonians

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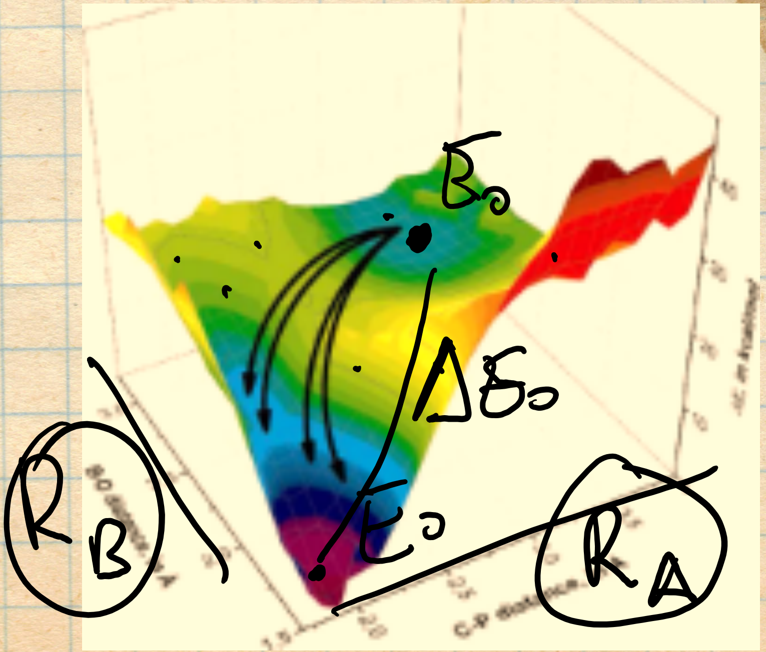
Classically – exponentially – hard problem

$$H = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{j>i}\frac{1}{r_{ij}} + \sum_{B>A}\frac{Z_A Z_B}{R_{AB}}$$

Reaction Rate

$O(\Delta E_0)$

$k \propto e$



$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$

Molecular Hamiltonians

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Energy shift

$$H = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \cancel{\sum_{A=1}^{M}\frac{1}{2M_A}}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{j>i}\frac{1}{r_{ij}} + \sum_{B>A}\frac{Z_A Z_B}{R_{AB}}$$

$\simeq 0$

- Born - Oppenhaimer approximation
- Problem of interacting electrons

Molecular Hamiltonians

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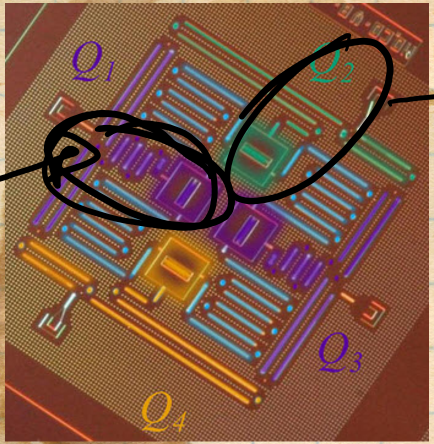
- Qubits are distinguishable

X_1



X_2

$$|\Psi_{Tot}\rangle = |X_1\rangle_1 |X_2\rangle_2$$

qubit 1 is in the X_1 state
qubit 2 is in the X_2 state

- Electrons (Fermions) are indistinguishable particles
identical

$$|\Psi_{tot}\rangle = \frac{1}{\sqrt{2}}\left(|X_1\rangle_1 |X_2\rangle_2 - |X_2\rangle_1 |X_1\rangle_2\right)$$

Antisymmetric

$$P_{1\to 2}|\Psi_{tot}\rangle = -|\Psi_{tot}\rangle$$

Why?
This is how nature works!!

Molecular Hamiltonians

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For N fermions

$$|\Psi_{tot}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |X_1\rangle_1 & \cdots & |X_1\rangle_N \\ \vdots & & \vdots \\ |X_N\rangle_1 & \cdots & |X_N\rangle_N \end{vmatrix}$$

$|X_1\rangle_1 |X_2\rangle_2 \cdots |X_N\rangle$

Slater determinant

- Single notation

$$|\Psi_{tot}\rangle = \sum |X_1 X_2 \cdots X_N\rangle = \begin{array}{c} X_1 X_2 \qquad\qquad X_N \\ |1111 \cdots 1\rangle \end{array} \to N \text{ electrons}$$

$$|1010 \cdots 01\rangle \quad n < N \text{ electrons}$$

Molecular Hamiltonians

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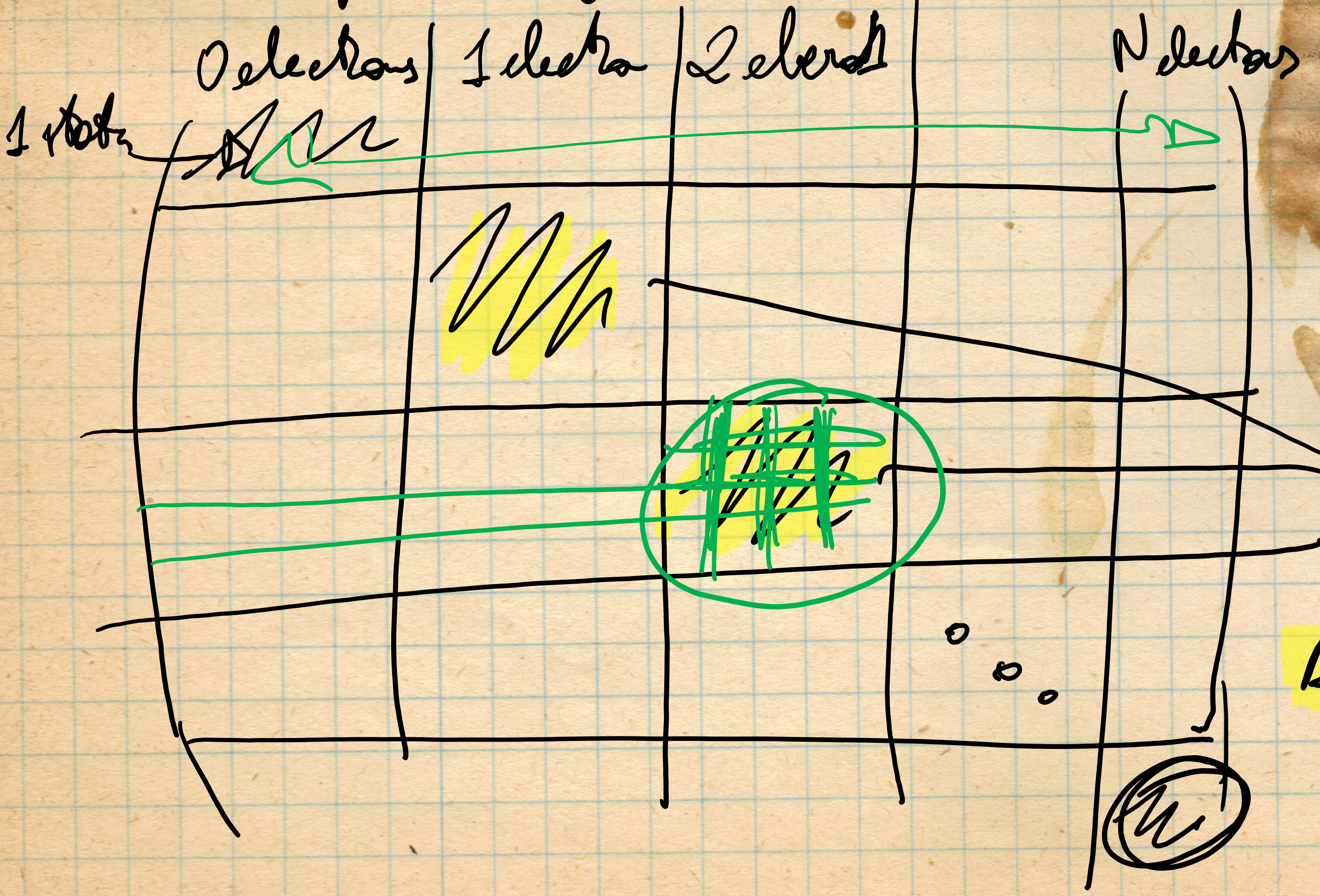
Fock Space of N orbitals



each n-particle subspace has # states

$$\binom{N}{n} = \frac{N!}{n!\,(N-n)!}$$

All together 2^N

N electrons in N orbitals

$|111\cdots1\rangle$

Molecular Hamiltonians

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- Creation / annihilation operators on the Fock space

$$a_i^\dagger | \ldots n_i \ldots \rangle = (1 - n_i)(-1)^{\sum_{j<i} n_j} | \ldots n+1 \ldots \rangle$$

$$a_i | \ldots n_i \ldots \rangle = n_i (-1)^{\sum_{j<i} n_j} | \ldots n-1 \ldots \rangle$$

- From this definition we can derive

$$\underbrace{a_i^\dagger a_j + a_j a_i^\dagger}_{} = \underline{\{a_i^\dagger, a_j\}} = \delta_{ij} \begin{cases} 1 & i=j \\ 0 & i \neq j \end{cases}$$

$$[a_i, a_j] = 0$$

$$[a_i^\dagger, a_j^\dagger] = 0$$

Molecular Hamiltonians

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- Definition of creation/annihilation operators $a_i^\dagger, a_i$
- Use them to build any operator on the Fock space

H

Molecular Hamiltonians

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$$H = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \cancel{\frac{1}{2M_A}} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{j>i} \frac{1}{r_{ij}} + \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

SHIFT

$$H_{\mathrm{e}} = -\sum_{i,j} \frac{1}{2} \langle i | \nabla_i^2 | j \rangle a_i^\dagger a_j + \sum_{i,j} \langle i | \frac{Z_A}{r_{iA}} | j \rangle a_i^\dagger a_j + \sum_{i,j,k,m} \langle i, j | \frac{1}{r_{ij}} | k, m \rangle a_i^\dagger a_j^\dagger a_k a_m$$

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

Molecular Hamiltonians

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$$H_\mathrm{e} = -\sum_{i,j} \frac{1}{2} \langle i | \nabla_i^2 | j \rangle a_i^\dagger a_j + \sum_{i,j} \langle i | \frac{Z_A}{r_{iA}} | j \rangle a_i^\dagger a_j + \sum_{i,j,k,m} \langle i, j | \frac{1}{r_{ij}} | k, m \rangle a_i^\dagger a_j^\dagger a_k a_m$$

fermionic orbitals

$$h_{pq} \equiv \int \mathrm{d}\mathbf{x}\, \chi_p^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 - \sum_\alpha \frac{Z_\alpha}{r_{\alpha,\mathbf{x}}} \right) \chi_q(\mathbf{x})$$

1-body integral

EFFICIENT CLASSICALLY

$$h_{pqrs} \equiv \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{\chi_p^*(\mathbf{x}_1)\chi_q^*(\mathbf{x}_2)\chi_r(\mathbf{x}_2)\chi_s(\mathbf{x}_1)}{r_{1,2}}$$

2-body integral

Molecular Hamiltonians

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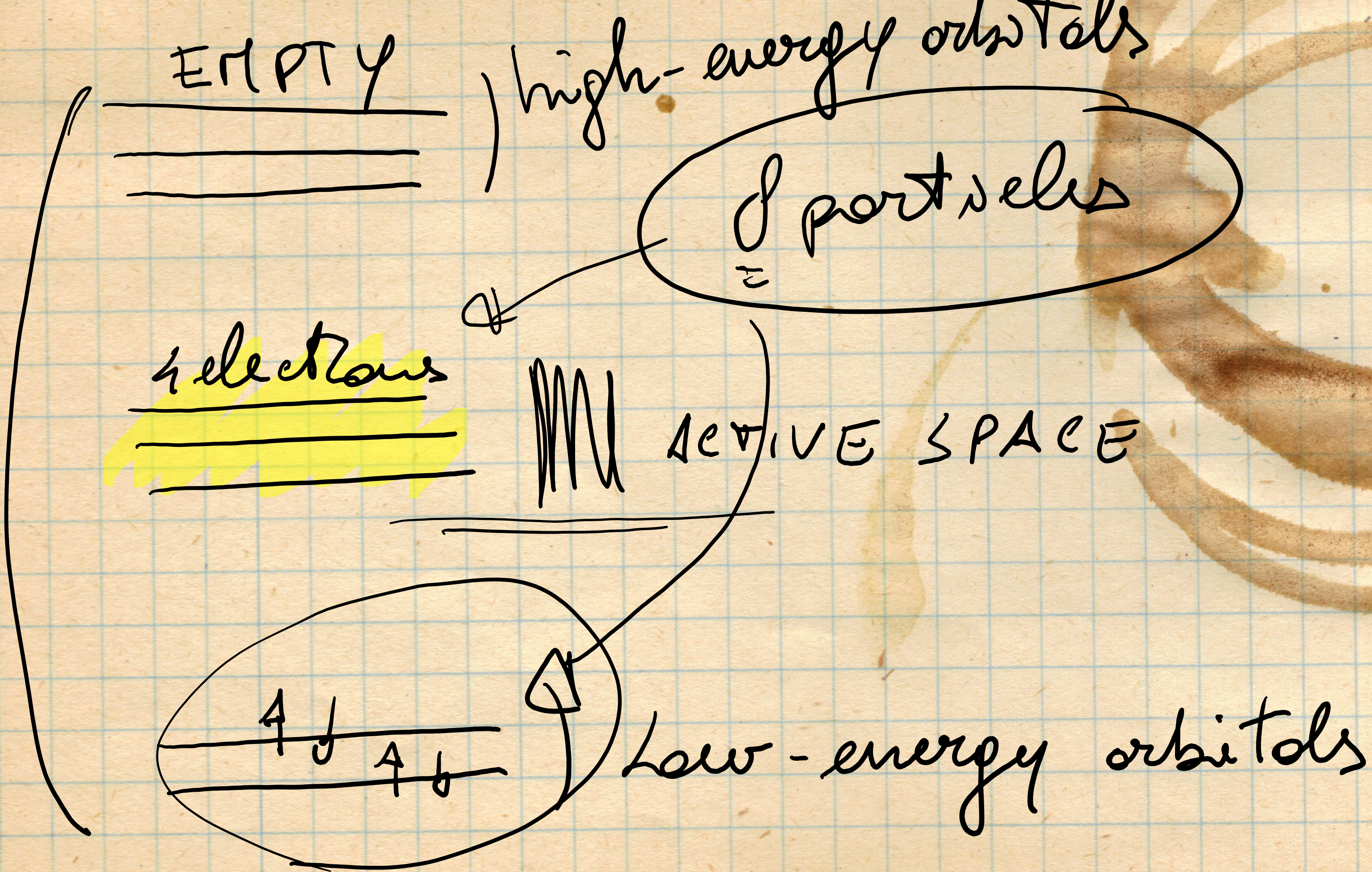

Molecular Hamiltonians

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- Ground state M particles

$$|\Psi\rangle = \sum_{|\vec{n}|=M} \psi_{\vec{n}} \, |n_1 n_2 \cdots n_N\rangle$$

- Freeze

$$|\Psi\rangle = \overset{\text{filled}}{|11\rangle} \otimes \sum_{|\vec{n}|=M-2} \psi_{\vec{n}} \, |n_1 n_2 \cdots n_N\rangle$$

Molecular Hamiltonians

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Frozen simplification rules

$$\frac{u'_{\alpha\beta\gamma\delta}}{2}a'^{\dagger}_{\alpha}a'^{\dagger}_{\gamma}a'_{\delta}a'_{\beta} \rightarrow \begin{cases} \frac{u'_{\alpha\beta\gamma\delta}}{2}a'^{\dagger}_{\gamma}a'_{\delta}, & \alpha=\beta, \alpha\in F, \{\gamma,\delta\}\notin F \\ \frac{u'_{\alpha\beta\gamma\delta}}{2}a'^{\dagger}_{\alpha}a'_{\beta}, & \gamma=\delta, \gamma\in F, \{\alpha,\beta\}\notin F \\ -\frac{u'_{\alpha\beta\gamma\delta}}{2}a'^{\dagger}_{\gamma}a'_{\beta}, & \alpha=\delta, \alpha\in F, \{\beta,\gamma\}\notin F \\ -\frac{u'_{\alpha\beta\gamma\delta}}{2}a'^{\dagger}_{\alpha}a'_{\delta}, & \gamma=\beta, \gamma\in F, \{\alpha,\delta\}\notin F \\ \frac{u'_{\alpha\beta\gamma\delta}}{2}I, & \alpha=\beta, \gamma=\delta, \alpha\neq\gamma, \{\alpha,\gamma\}\in F \\ -\frac{u'_{\alpha\beta\gamma\delta}}{2}I, & \alpha=\delta, \gamma=\beta, \alpha\neq\gamma, \{\alpha,\gamma\}\in F, \end{cases}$$

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Fermion to qubit mappings

Fermion to qubit mappings

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- Fock space has size 2^N
- Hilbert space of N qubits has also size 2^N

$\Downarrow$

MAPPING IS POSSIBLE

2 Ingredients

- Mapping between states : Slater det. to qub. states
- Reconstruct fermionic algebra in qubit lang.

Fermion to qubit mappings

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- Mapping states : Easy!

$|101001\rangle \longrightarrow |101001\rangle$

Fock space:
3 electrons on 6
fermionic modes

state of 6 qubits
3 of them excited

- Mapping a^+, a on 1 qubit : Easy

$a^+|0\rangle = |1\rangle \quad a|0\rangle = 0$

$a^+|1\rangle = 0 \quad a|1\rangle = |0\rangle$

$$\boxed{\begin{array}{l} a^+ \rightarrow \sigma^+ \\ a \rightarrow \sigma^- \end{array}}$$

act on 1 qubit

Fermion to qubit mappings

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$$a_i^{+} | \ldots n_i \ldots \rangle = (1 - n_i)(-1)^{\sum_{j<i} n_j^{\alpha}} | \ldots n_i \ldots \rangle$$

$$\boxed{a_i^{+} \longrightarrow \prod_{j<i} \sigma_j^z \, \sigma_i^{+}}$$

$$\sigma^z |1\rangle_z = - |1\rangle$$

$$\sigma^z |0\rangle_z = + |0\rangle$$

(JORDAN-WIGNER MAPPING)

~1920

Fermion to qubit mappings

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- Recover algebra $\{a_4^+, a_4\} = 1$

  4-mode system

$$\sigma_i^z \cdot \sigma_j^z = 1$$

$$\begin{cases} a_4^+ = \sigma_1^z \sigma_2^z \sigma_3^z \sigma_4^+ \\ a_4 = \sigma_1^z \sigma_2^z \sigma_3^z \sigma_4^- \end{cases}$$

$$a_4^+ a_4 + a_4 a_4^+ = \sigma_4^+ \sigma_4^- + \sigma_4^- \sigma_4^+ = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbb{1}$$

$$\sigma^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \sigma^+ \sigma^- = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\sigma^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \qquad \sigma^- \sigma^+ = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Fermion to qubit mappings

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$$a_i^{+} \longrightarrow \prod_{j<i} \sigma_j^{z} \, \sigma_i^{+}$$

$$a_N^{+} \longrightarrow \underbrace{O(N)}_{\Sigma}\text{-Local}$$

Very local

Very-non-local

BAD - Can we avoid this?

Fermion to qubit mappings

- Change mapping

$$q_1 = \underset{\text{mod } 2}{\text{sum}} \; \overset{1}{n_1} + \overset{1}{n_2} + \overset{0}{n_3} = 0$$

fermione SL. Det.

$$\begin{pmatrix} n_1 \\ n_2 \\ n_3 \\ n_4 \end{pmatrix} \quad \begin{pmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \end{pmatrix}$$

Valid mapping

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \quad \begin{pmatrix} 1 \\ 0 \\ 1 \\ 1 \end{pmatrix}$$

Fermion to qubit mappings

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· Parity Mapping

Parity Matrix

$$\underbrace{\begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{pmatrix}}_{\text{Invertible with operations mod 2}} \underbrace{\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix}}_{n} = \begin{pmatrix} a+b+c+d \\ b+c+d \\ c+d \\ d \end{pmatrix}$$

Parity of tot. # part.

Fermion to qubit mappings

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- JW Map - is $O(N)$ - local
- Parity mapping is $O(N)$ - local
- Bravyi - Kitaev (~2000) is $O(\log(N))$ - local

Define a binary matrix

$$\beta_1 = (1) \qquad 1 \text{ qubit} \quad 1$$

$$\beta_{2^{x+1}} = \left(\begin{array}{c|c} \beta_{2^x} & 11\cdots1 \\ \hline & \beta_{2^x} \end{array}\right) \qquad 2 \text{ qubits} \quad \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$$

4 qubits $\begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{pmatrix}$

Fermion to qubit mappings

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Ho do we write the action of fermionic creation and annihilation operators in these scrambled bases? Let’s identify three sets of qubits for each fermionic mode i:
The parity set, The update set, The flip set

The parity set: tells us the set of qubits that encodes the parity of the fermionic modes with index less than i. The parity of this set of qubits will give us the global phase $P(j)$

The update set: the set of qubits that must be flipped when the fermionic mode i change occupation $U(j)$

The flip set: the set of qubits that determines whether qubit i has the same or inverted parity with respect to fermionic mode i $F(j)$

$\rho(j) = P / F$

$$a_j^\dagger \equiv X_{U(j)} \otimes \hat{\Pi}_j^+ \otimes Z_{R(j)} = \tfrac{1}{2}(X_{U(j)} \otimes X_j \otimes Z_{P(j)} - iX_{U(j)} \otimes Y_j \otimes Z_{\rho(j)})$$

$$a_j \equiv X_{U(j)} \otimes \hat{\Pi}_j^- \otimes Z_{R(j)} = \tfrac{1}{2}(X_{U(j)} \otimes X_j \otimes Z_{P(j)} + iX_{U(j)} \otimes Y_j \otimes Z_{\rho(j)})$$

QISKIT
implementation

Fermion to qubit mappings

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H_2 Hamiltonian (4 fermionic modes): 4–qubit to 1–qubit

σ_1^z	σ_2^z	σ_3^z	σ_4^z
$\sigma_1^z\sigma_2^z$	$\sigma_1^z\sigma_3^z$	$\sigma_1^z\sigma_4^z$	
$\sigma_2^z\sigma_3^z$	$\sigma_2^z\sigma_4^z$	$\sigma_3^z\sigma_4^z$	
$\sigma_1^y\sigma_2^y\sigma_3^x\sigma_4^x$	$\sigma_1^x\sigma_2^y\sigma_3^y\sigma_4^x$	$\sigma_1^y\sigma_2^x\sigma_3^x\sigma_4^y$	$\sigma_1^x\sigma_2^x\sigma_3^y\sigma_4^y$

Independent Pauli Symmetries:

$$\boldsymbol{\tau}_1 = \sigma_1^z\sigma_2^z$$
$$\boldsymbol{\tau}_2 = \sigma_1^z\sigma_3^z$$
$$\boldsymbol{\tau}_3 = \sigma_1^z\sigma_4^z$$

QISKIT FUNCTION

3 single-qubit Pauli with commutation rules

$$(\sigma_{i+1}^x, \boldsymbol{\tau}_i)$$

$$\sigma_{q(i)}^x \boldsymbol{\tau}_j = (-1)^{\delta_{i,j}}\, \boldsymbol{\tau}_j \sigma_{q(i)}^x$$

Build 3 Clifford operators

$$U_1 = \frac{1}{\sqrt{2}}\left(\sigma_2^x + \sigma_1^z\sigma_2^z\right)$$
$$U_2 = \frac{1}{\sqrt{2}}\left(\sigma_3^x + \sigma_1^z\sigma_3^z\right)$$
$$U_3 = \frac{1}{\sqrt{2}}\left(\sigma_4^x + \sigma_1^z\sigma_4^z\right)$$

Apply the Clifford unitaries to the H2 Hamiltonian

σ_1^z	$\sigma_1^z\sigma_2^x$	$\sigma_1^z\sigma_3^x$	$\sigma_1^z\sigma_4^x$
σ_2^x	σ_3^x	σ_4^x	
$\sigma_2^x\sigma_3^x$	$\sigma_2^x\sigma_4^x$	$\sigma_3^x\sigma_4^x$	
$\sigma_1^x\sigma_3^x\sigma_4^x$	$\sigma_1^x\sigma_4^x$	$\sigma_1^x\sigma_2^x\sigma_3^x$	$\sigma_1^x\sigma_2^x$

BLOCK-DIAGONAL W.R.TO QUBITS 2, 3, 4

Fermion to qubit mappings

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	Spin Orbitals M	Jordan-Wigner	Parity	Binary Tree
H_2	4	$(\sigma_1^x, \sigma_1^z\sigma_4^z)$ $(\sigma_2^x, \sigma_2^z\sigma_4^z)$ $(\sigma_3^x, \sigma_3^z\sigma_4^z)$	(σ_2^x, σ_2^z) $(\sigma_1^x, \sigma_1^z\sigma_3^z)$ (σ_4^x, σ_4^z)	(σ_2^x, σ_2^z) $(\sigma_1^x, \sigma_1^z\sigma_3^z)$ (σ_4^x, σ_4^z)
LiH	12	$(\sigma_1^x, \sigma_1^z\sigma_2^z\sigma_3^z\sigma_6^z\sigma_{10}^z\sigma_{11}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_{10}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_{11}^z)$ $(\sigma_7^x, \sigma_7^z\sigma_8^z\sigma_9^z\sigma_{10}^z\sigma_{11}^z\sigma_{12}^z)$	(σ_6^x, σ_6^z) $(\sigma_3^x, \sigma_3^z\sigma_5^z\sigma_9^z\sigma_{11}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_5^z\sigma_{10}^z\sigma_{11}^z)$ $(\sigma_{12}^x, \sigma_{12}^z)$	$(\sigma_4^x, \sigma_4^z\sigma_6^z)$ $(\sigma_2^x, \sigma_2^z\sigma_3^z\sigma_6^z\sigma_9^z\sigma_{10}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_{11}^z)$ $(\sigma_8^x, \sigma_8^z\sigma_{12}^z)$
BeH_2	14	$(\sigma_1^x, \sigma_1^z\sigma_2^z\sigma_3^z\sigma_6^z\sigma_7^z\sigma_{11}^z\sigma_{12}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_{11}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_{12}^z)$ $(\sigma_8^x, \sigma_8^z\sigma_9^z\sigma_{10}^z\sigma_{11}^z\sigma_{12}^z\sigma_{13}^z\sigma_{14}^z)$	(σ_7^x, σ_7^z) $(\sigma_3^x, \sigma_3^z\sigma_5^z\sigma_{10}^z\sigma_{12}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_5^z\sigma_{11}^z\sigma_{12}^z)$ $(\sigma_{14}^x, \sigma_{14}^z)$	$(\sigma_4^x, \sigma_4^z\sigma_6^z\sigma_7^z)$ $(\sigma_2^x, \sigma_2^z\sigma_3^z\sigma_6^z\sigma_7^z\sigma_{11}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_{10}^z\sigma_{11}^z\sigma_{12}^z)$ $(\sigma_8^x, \sigma_8^z\sigma_{12}^z\sigma_{14}^z)$
H_2O	14	$(\sigma_1^x, \sigma_1^z\sigma_2^z\sigma_3^z\sigma_5^z\sigma_6^z\sigma_7^z\sigma_{11}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_{11}^z)$ $(\sigma_8^x, \sigma_8^z\sigma_9^z\sigma_{10}^z\sigma_{11}^z\sigma_{12}^z\sigma_{13}^z\sigma_{14}^z)$	(σ_7^x, σ_7^z) $(\sigma_3^x, \sigma_3^z\sigma_4^z\sigma_{10}^z\sigma_{11}^z)$ $(\sigma_{14}^x, \sigma_{14}^z)$	$(\sigma_4^x, \sigma_4^z\sigma_6^z\sigma_7^z)$ $(\sigma_2^x, \sigma_2^z\sigma_3^z\sigma_6^z\sigma_7^z\sigma_{11}^z)$ $(\sigma_8^x, \sigma_8^z\sigma_{12}^z\sigma_{14}^z)$
NH_3	16	$(\sigma_1^x, \sigma_1^z\sigma_2^z\sigma_3^z\sigma_4^z\sigma_5^z\sigma_6^z\sigma_7^z\sigma_8^z)$ $(\sigma_9^x, \sigma_9^z\sigma_{10}^z\sigma_{11}^z\sigma_{12}^z\sigma_{13}^z\sigma_{14}^z\sigma_{15}^z\sigma_{16}^z)$	(σ_8^x, σ_8^z) $(\sigma_{16}^x, \sigma_{16}^z)$	(σ_8^x, σ_8^z) $(\sigma_{16}^x, \sigma_{16}^z)$
HCl	20	$(\sigma_1^x, \sigma_1^z\sigma_2^z\sigma_3^z\sigma_6^z\sigma_7^z\sigma_{10}^z\sigma_{14}^z\sigma_{15}^z\sigma_{18}^z\sigma_{19}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_8^z\sigma_{14}^z\sigma_{18}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_9^z\sigma_{15}^z\sigma_{19}^z)$ $(\sigma_{11}^x, \sigma_{11}^z\sigma_{12}^z\sigma_{13}^z\sigma_{14}^z\sigma_{15}^z\sigma_{16}^z\sigma_{17}^z\sigma_{18}^z\sigma_{19}^z\sigma_{20}^z)$	$(\sigma_{10}^x, \sigma_{10}^z)$ $(\sigma_3^x, \sigma_3^z\sigma_5^z\sigma_7^z\sigma_9^z\sigma_{13}^z\sigma_{15}^z\sigma_{17}^z\sigma_{19}^z)$ $(\sigma_4^x, \sigma_4^z\sigma_5^z\sigma_8^z\sigma_9^z\sigma_{14}^z\sigma_{15}^z\sigma_{18}^z\sigma_{19}^z)$ $(\sigma_{20}^x, \sigma_{20}^z)$	$(\sigma_8^x, \sigma_8^z\sigma_{10}^z)$ $(\sigma_2^x, \sigma_2^z\sigma_3^z\sigma_6^z\sigma_7^z\sigma_{10}^z\sigma_{13}^z\sigma_{14}^z\sigma_{17}^z\sigma_{18}^z)$ $(\sigma_5^x, \sigma_5^z\sigma_9^z\sigma_{15}^z\sigma_{19}^z)$ $(\sigma_{16}^x, \sigma_{16}^z\sigma_{20}^z)$

Variational circuits

Variational circuits

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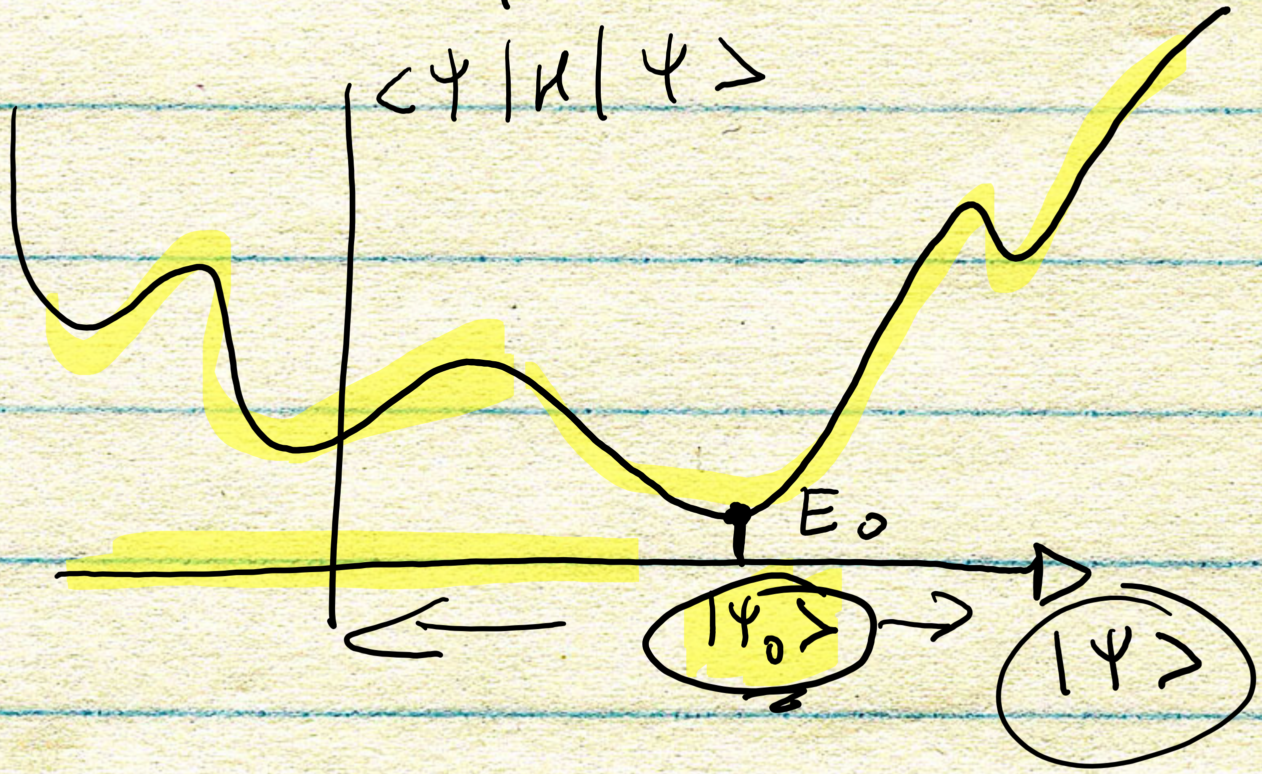
- Variational principle

$$E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$|\psi\rangle = \sum_i \alpha_{E_i} |\psi_{E_i}\rangle$$

$$H|\psi\rangle$$

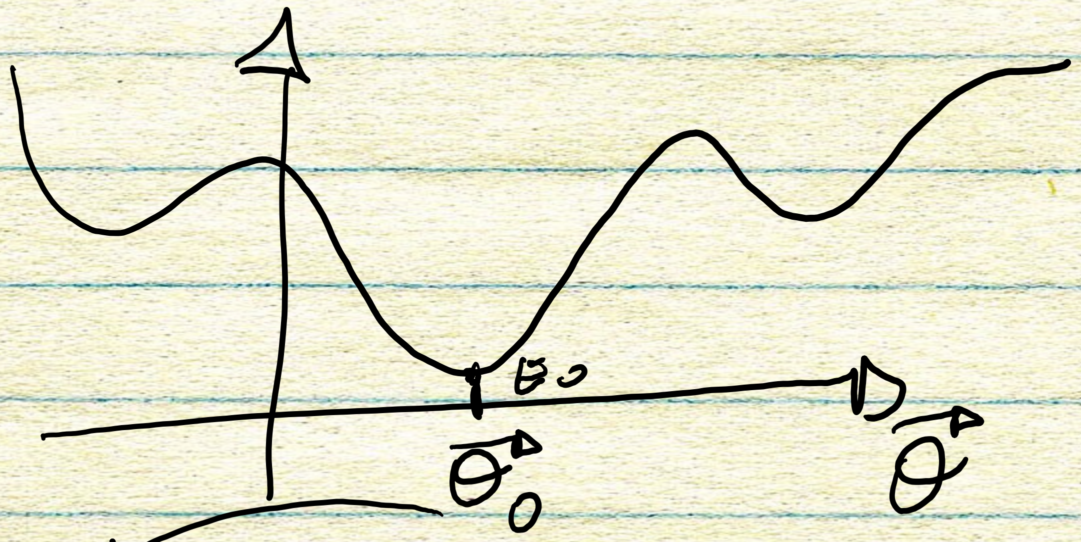
$$\langle \psi | H | \psi \rangle$$



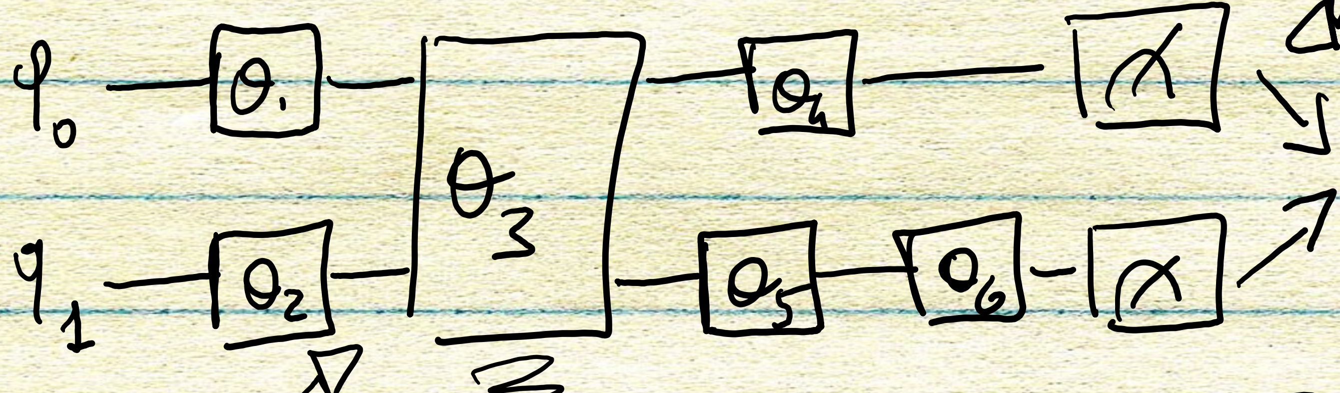
Variational circuits

IBM **Quantum**

Explore states $|\Psi\rangle$



$|\Psi(\vec{\theta})\rangle$



$\langle\Psi(\vec{\theta})|H|\Psi(\vec{\theta})\rangle$

$E_0 \leq \langle\Psi(\vec{\theta})|H|\Psi(\vec{\theta})\rangle$

rotation gates

Variational circuits

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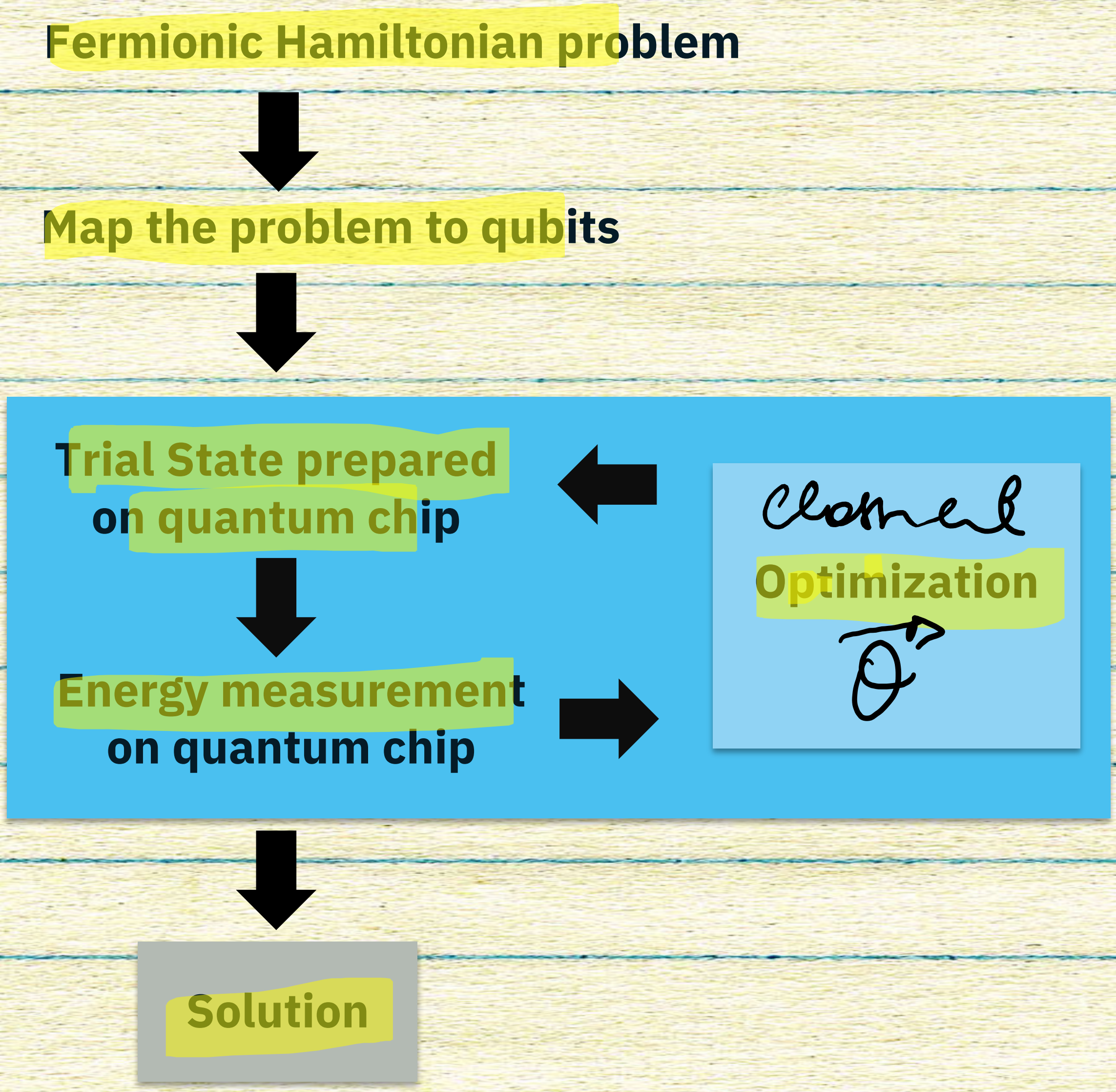

Variational circuits

IBM **Quantum**

- UCCSD Variational ansatz
- Inspired by classical computations

$\vec{t} \Leftrightarrow \vec{\theta}$

Reference state

$|\psi\rangle = e^{T - T^\dagger} |HF\rangle$

logical qubit state

$$T = \sum_{i=1}^{\eta} T_i$$ → RESTRICTING TO 1,2-BODY

$$T_1 = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} t_a^i a_a^\dagger a_i$$ → SINGLE

$$T_2 = \sum_{\substack{i > j \in \text{occ} \\ a > b \in \text{virt}}} t_{ab}^{ij} a_a^\dagger a_b^\dagger a_i a_j$$ → DOUBLE

Variational circuits

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$$|\Psi\rangle = e^{T - T^\dagger}|HF\rangle$$

2° step

1° step

$$T = \sum_{i=1}^{\eta} T_i$$

$$T_1 = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} t_a^i a_a^\dagger a_i$$

$$T_2 = \sum_{\substack{i > j \in \text{occ} \\ a > b \in \text{virt}}} t_{ab}^{ij} a_a^\dagger a_b^\dagger a_i a_j$$

$$e^{T - T^\dagger} = \left(\prod_{i,a} e^{\frac{t_a^i}{n}(a_a^\dagger a_i - h.c.)} \prod_{\substack{i,j \\ a,b}} e^{\frac{t_{ab}^{ij}}{n} a_a^\dagger a_b^\dagger a_i a_j} \right)^{n} + O\left(\frac{t^2}{n}\right)$$

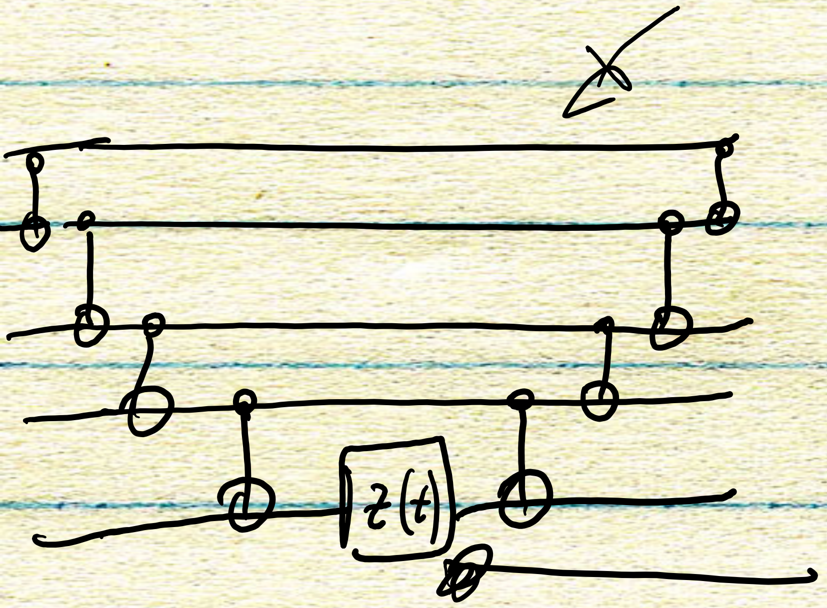
Suzuki - Trotter decomposition

Variational circuits

$t(a_i^\dagger a_j - a_j^\dagger a_i)$ Quantum circuit?

ℓ

$$t(a_i^\dagger a_j - a_j^\dagger a_i) \overset{JW}{\underset{i<j}{=}} t\,i\left(\sigma_i^x \sigma_{i+1}^z \cdots \sigma_{j-1}^z \sigma_j^x + \sigma_i^y \sigma_{i+1}^z \cdots \sigma_{j-1}^z \sigma_j^y\right)$$



$\Rightarrow e^{it\sigma_1^z \cdots \sigma_5^z}$

1-body

Variational circuits

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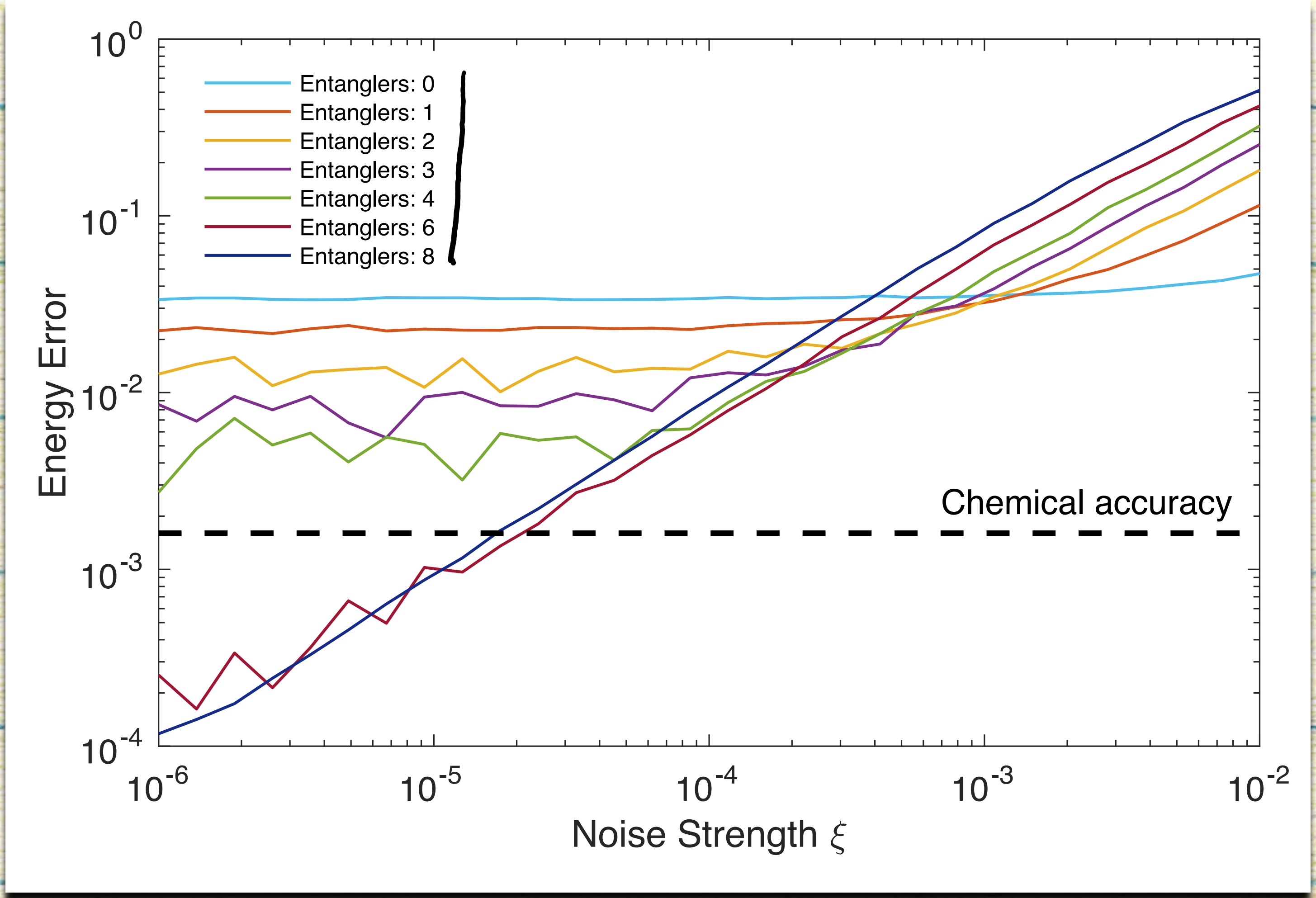

Problem with UCCSD: high depts required

Variational circuits

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QAOA on fixed
Qubit architectures

Hardware Efficient:
Entanglers + Euler Rotations

UCCSD

QAOA

Easier to realize
on quantum hardware

Guided by physical/chemical
intuition

QMA - COMPLETE
PROBLEM

Convergence to the exact ground state is never guaranteed in general

Optimization

Optimization

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Fermionic Hamiltonian problem

Map the problem to qubits

Trial State prepared on quantum chip

Energy measurement on quantum chip

Optimization

Solution

Optimization

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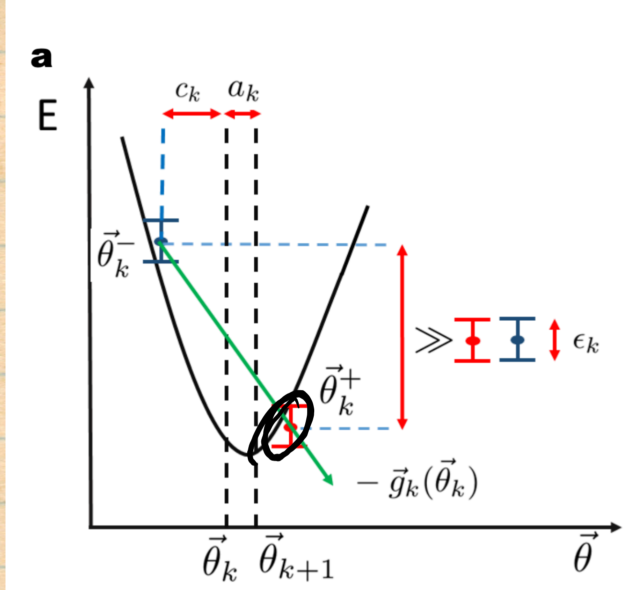

SPSA optimization: same level of accuracy with 1/p less function calls, with stochastic fluctuations

VQE on hardware

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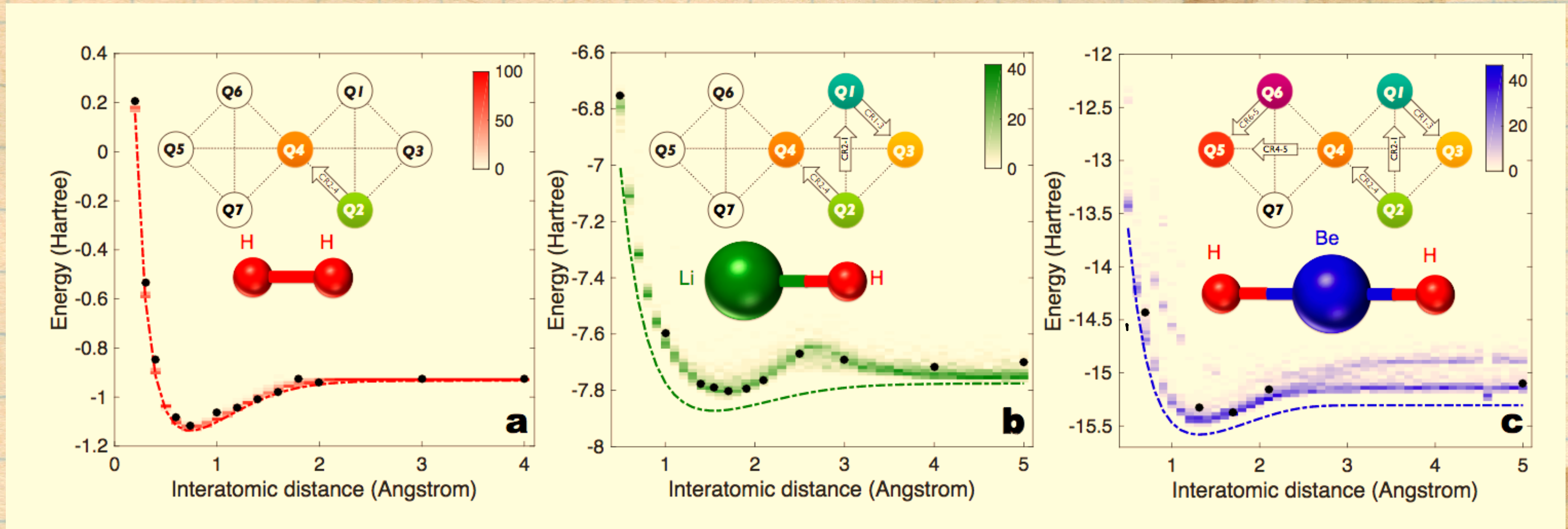
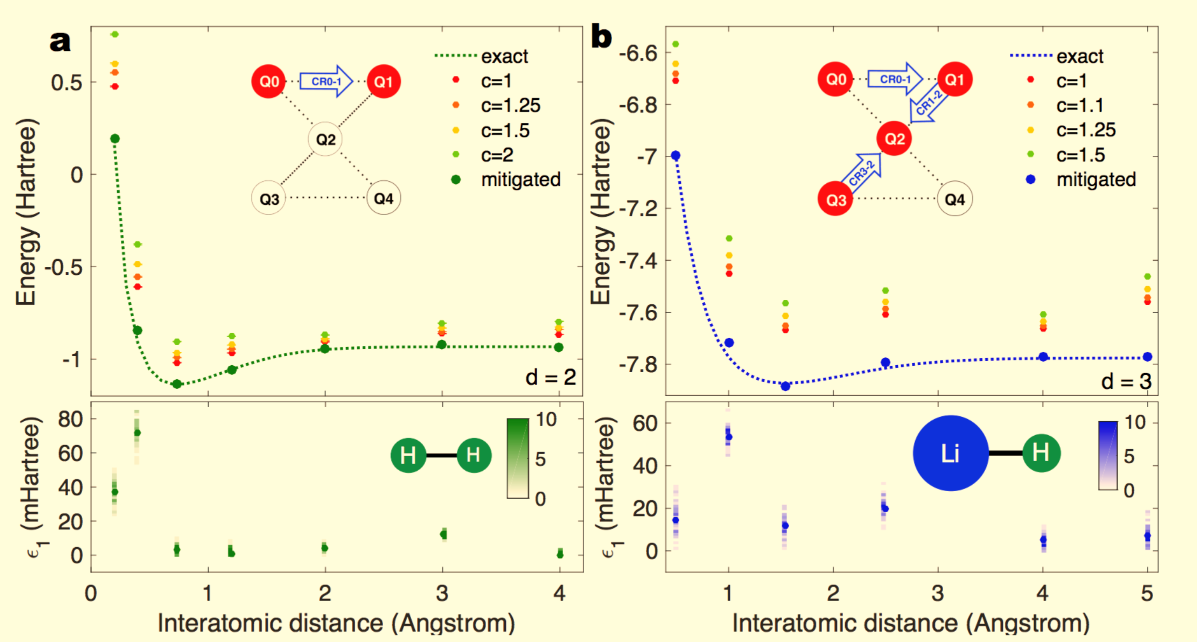


2017



2019

Current challenges for using quantum computers to target chemistry applications

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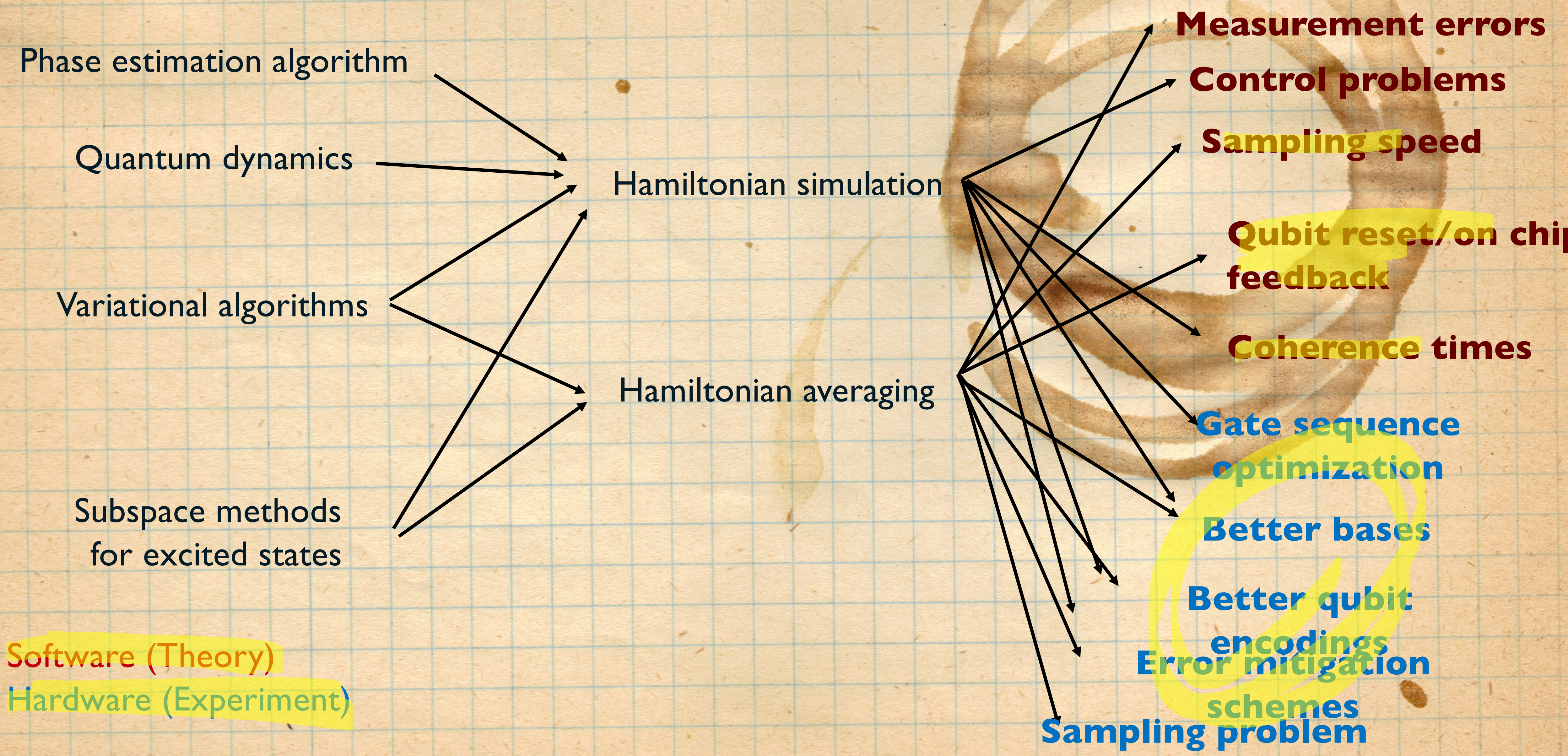

Topics covered

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Construct Qubit Hamiltonians for molecules

- Second quantization notation
- Basics of fermion to qubit mappings

Variational Quantum Algorithms

- Why they work
- Popular Variational Wavefunctions
- Open challenges

THANK YOU!!

ANTONIO.MEZZACAPO@IBM.COM

Notes

IBM **Quantum**

Molecular Electronic-Structure Theory
Author(s): Trygve Helgaker Poul Jørgensen Jeppe Olsen

Advanced Quantum Mechanics
Authors: Schwabl, Franz

Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory
Authors : Szabo, Ostlund

Math Compact

$a^{+}, a \rightarrow$ bosons (oscillators)
Zlatko's talk

$c^{+}, c \rightarrow$ fermions

Notes

Notes

Notes

IBM **Quantum**

Notes

IBM **Quantum**

Notes

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