Quantum chemistry on quantum computers

Quantum computational simulations

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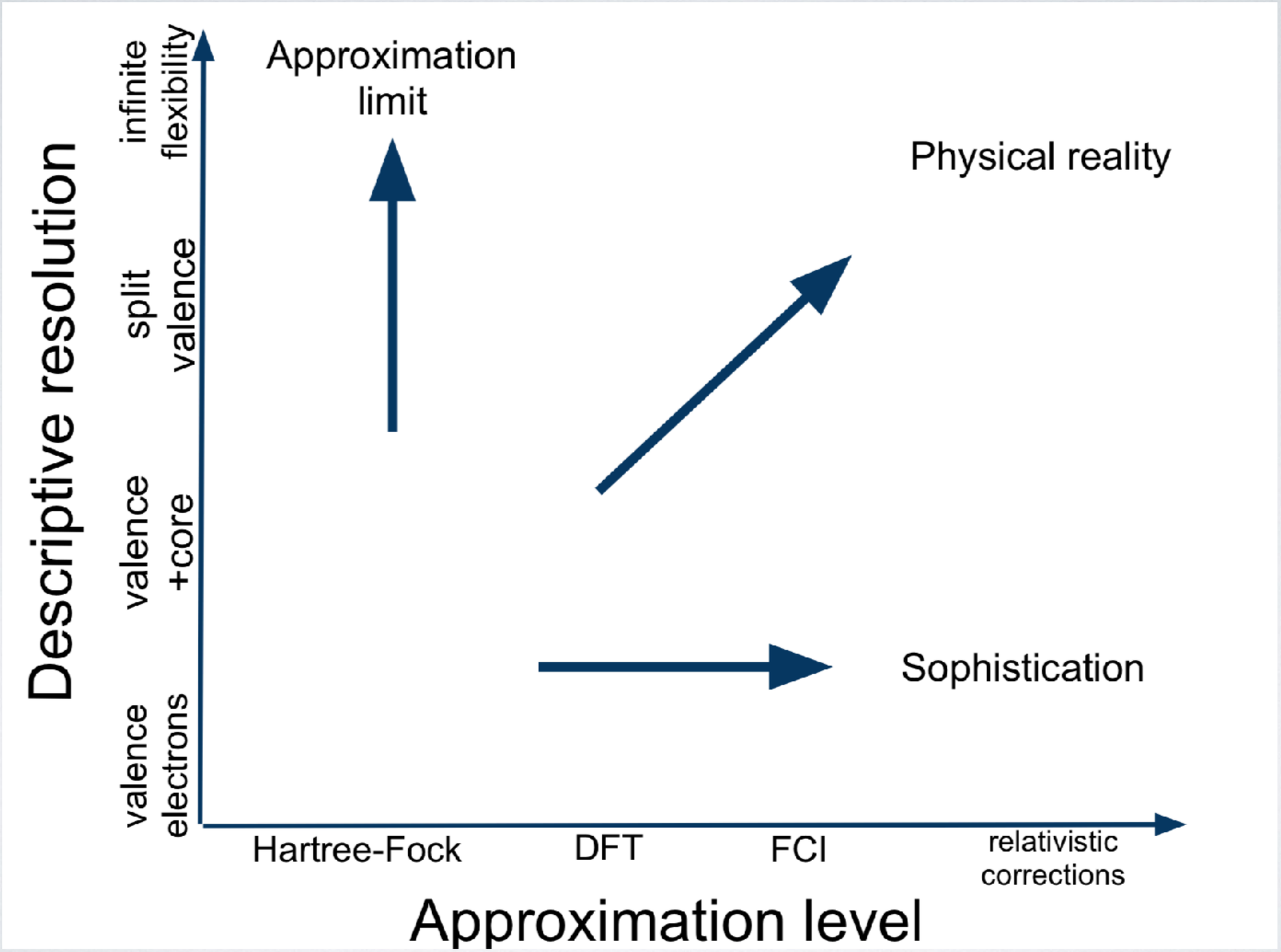
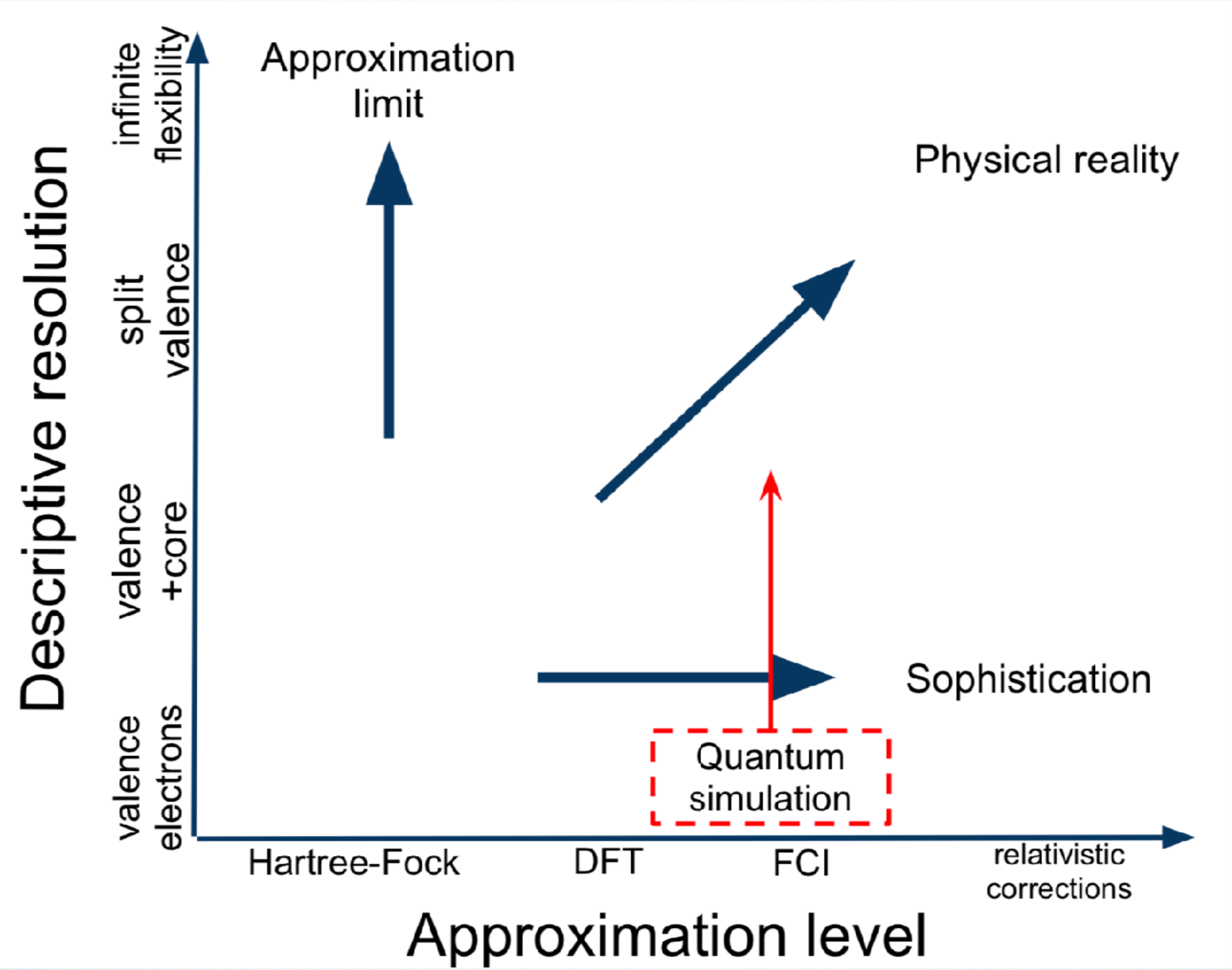
Course overview

Lecture 1: QCQC (slides)
Lecture 2: Technical introduction (board)
Lecture 3: Quantum for simulation (slides/board)

Objectives

1. Understand how quantum mechanics intersects chemistry
2. Connect quantum computation to quantum chemistry
3. Background knowledge to get start in the literature


Descriptive resolution
infinite flexibility
split valence
valence +core
valence electrons
Approximation limit
Physical reality
Sophistication
Hartree-Fock
DFT
FCI
relativistic corrections
Approximation level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ALPHABET SOUP

- DFT = Density functional theory (GGA, LDA, B3LYP are all abbreviations for names of commonly DFT functionals)
- DMRG = density matrix renormalization group
- CCSD = Coupled Cluster, singles doubles
- CI = Configuration interaction, FCI = Full configuration interaction, CISD = CI single and double excitations
- SCF = Self Consistent Field, the algorithm behind Hartree-Fock and practical implementations of DFT
- MCSCF, CASSCF, RASSCF, = Multi-configuration; Complete active space; Restricted active space
- MP2 = Second order Møller-Plesset perturbation theory
- cc-pVTZ = correlation consistent polarized valence triple zeta basis set
- MO = molecular orbitals, the orbitals obtained via SCF
- AO = atomic orbitals, the initial atom centered orbitals of the basis set

$$\Psi(x_1, x_2, \ldots, x_{\mathbf{i}}, \ldots, x_{\mathbf{j}}, \ldots, x_N)$$
$$= - \quad \Psi(x_1, x_2, \ldots, x_{\mathbf{j}}, \ldots, x_{\mathbf{i}}, \ldots, x_N)$$

Explicit action of permutation (first quantization)

$$P_{jk}\left(|\phi_m\rangle \otimes \ldots |\phi_{\mathbf{i}}\rangle \otimes \ldots |\phi_{\mathbf{j}}\rangle\right) = \left(|\phi_m\rangle \otimes \ldots |\phi_{\mathbf{j}}\rangle \otimes \ldots |\phi_{\mathbf{i}}\rangle\right)$$

- No canonical ordering, build and apply antisymmetrizer

Implicit action of permutation (second quantization)

$$P_{ij}\left(a_m^\dagger \ldots a_{\mathbf{i}}^\dagger a_{\mathbf{j}}^\dagger \ldots\right)|vacuum\rangle = -\left(a_m^\dagger \ldots a_{\mathbf{i}}^\dagger a_{\mathbf{j}}^\dagger \ldots\right)|vacuum\rangle$$

- Fix ordering; compute action of permutation as needed (± 1)

- N_f registers of lattice points for each electron
  - $\left| \underline{*} \_ \_ \_ \right\rangle \ \left| \_ \_ \underline{*} \_ \right\rangle$

- Explicit action of permutation

$$P_{jk}|\phi_i ... \phi_k \phi_j\rangle = P_{jk}|\phi_i\rangle \otimes ... |\phi_j\rangle \otimes |\phi_k\rangle = |\phi_i\rangle \otimes ... |\phi_k\rangle \otimes |\phi_j\rangle$$

- No canonical ordering, build and apply antisymmetrizer
- Higher efficiency for a single particle sector
  - $O(N_f^2)$ interaction terms rather than $O(M_{basis}^4)$ interactions

Second quantization		
Creation operator	$a_i^\dagger \lvert j_1, ..., 0_i, ..., j_n\rangle$ $= \Gamma_i^{\mathbf{j}} \lvert j_1, ..., 1_i, ..., j_n\rangle$ $a_i^\dagger \lvert j_1, ..., 1_i, ..., j_n\rangle = 0$	with $\Gamma_i^{\mathbf{j}} = \prod_{k=1}^{i-1}(-1)^{j_k}$
Annihilation operator	$a_i \lvert j_1, ..., 1_i, ..., j_n\rangle$ $= \Gamma_i^{\mathbf{j}} \lvert j_1, ..., 0_i, ..., j_n\rangle$ $a_i \lvert j_1, ..., 0_i, ..., j_n\rangle = 0$	
Commutation relations	$a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}\mathbf{1}$ $a_i a_j + a_i a_j = 0$	

Fock space		
Fock states	$\lvert\mathbf{j}\rangle = \lvert j_1, j_2, ..., j_n\rangle$ $= \prod_{p=1}^{N} \left(a_p^\dagger\right)^{j_p} \lvert\Omega\rangle$	where $j_i = 0, 1$
Inner product	$\langle\mathbf{j}\lvert\mathbf{k}\rangle = \prod_{p=1}^{n} \delta_{j_p,k_p}$	
Vacuum state	$\langle\Omega\lvert\Omega\rangle = 1$ $a_i\lvert\Omega\rangle = 0$	
Single electron operator, $\hat{A}(x_1)$	$A_{ij} a_i^\dagger a_j$	$A_{ij} = \int \phi_i^*(x_1)\hat{A}(x_1)\phi_j(x_1)dx_1$
Two electron operator, $\hat{A}(x_1, x_2)$	$A_{ijkl} a_i^\dagger a_j^\dagger a_k a_l$	$A_{ijkl} = \int dx_1 dx_2$ $\phi_i^*(x_1)\phi_j^*(x_2)\hat{A}(x_1, x_2)\phi_k(x_2)\phi_l(x_1)$ is a two electron operator

Full Hamiltonian

$$H = -\sum_i^N \left(\frac{1}{2}\nabla_i^2 + \sum_A^M \frac{Z_A}{r_{iA}} \right) + \sum_i^N \sum_{j<i}^N \frac{1}{r_{ij}} + \sum_{\substack{A \\ B>A}} \frac{Z_A Z_B}{R_{AB}} - \frac{1}{2M_A} \sum_A \nabla_A^2$$

Second quantized Electronic Hamiltonian

$$\begin{aligned} H &= \sum_{pq} \left[\int \mathrm{d}\mathbf{x}\, \chi_p^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{r_{A\mathbf{x}}} \right) \chi_q(\mathbf{x}) \right] a_p^\dagger a_q \\ &\quad + \frac{1}{2} \sum_{pqrs} \left[\int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{\chi_p^*(\mathbf{x}_1)\chi_q^*(\mathbf{x}_2)\chi_r(\mathbf{x}_2)\chi_s(\mathbf{x}_1)}{r_{1\,2}} \right] a_p^\dagger a_q^\dagger a_r a_s \end{aligned}$$

Jordan-Wigner transform from $\{X_k, Y_k, Z_k\} \mapsto \{a_j, a_j^\dagger\}$

$$a_k = \bigotimes_{j=1}^{k-1} Z_j \otimes |0\rangle\langle 1|$$

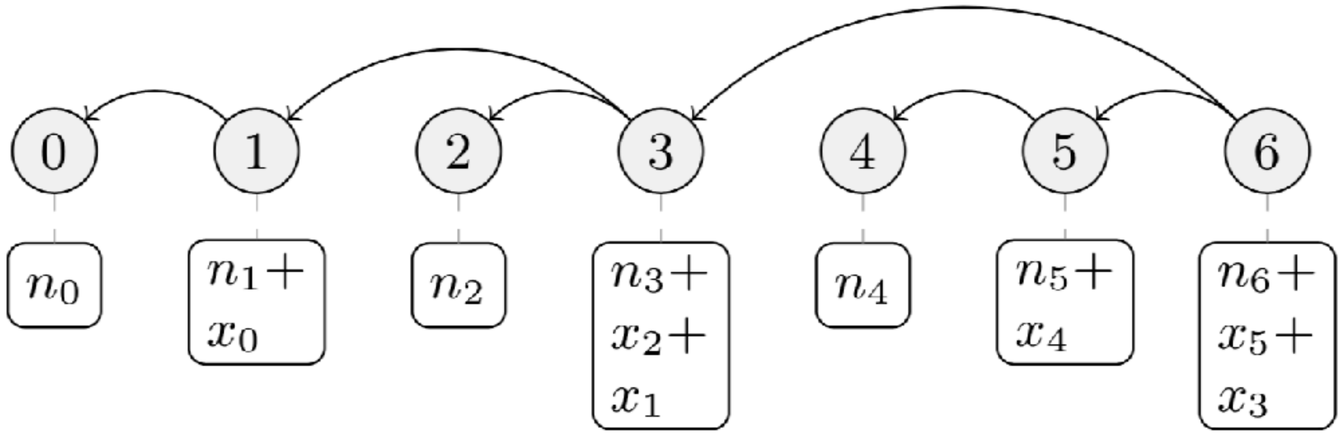
$$\begin{aligned} a_4^\dagger &= Z \otimes Z \otimes Z \otimes |1\rangle\langle 0| \\ \times\, a_2 &= Z \otimes |0\rangle\langle 1| \otimes \mathbf{1} \otimes \mathbf{1} \\ \hline a_4^\dagger a_2 &= \mathbf{1} \otimes (+|0\rangle\langle 1|) \otimes Z \otimes |1\rangle\langle 0| \end{aligned}$$

Outline

- Spin to fermion mappings
- Qubit Hamiltonian propagation methods
- Measurement
- State Preparation

Fenwick trees (binary index trees)

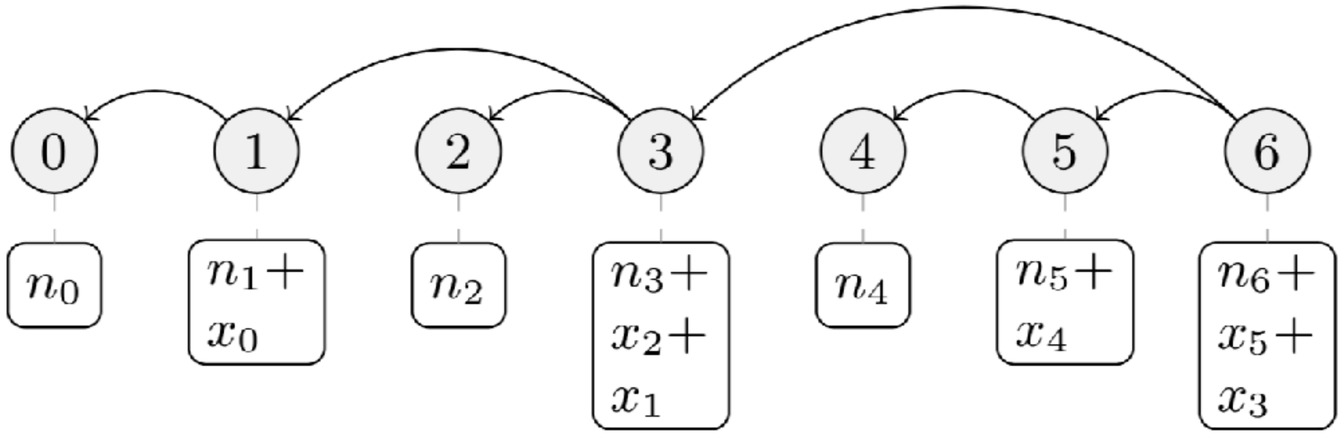
Fenwick, "A new data structure for cumulative frequency tables" 1994



- Fenwick node x_i contains sum of fermion occupancy n_i and all progeny occupancies

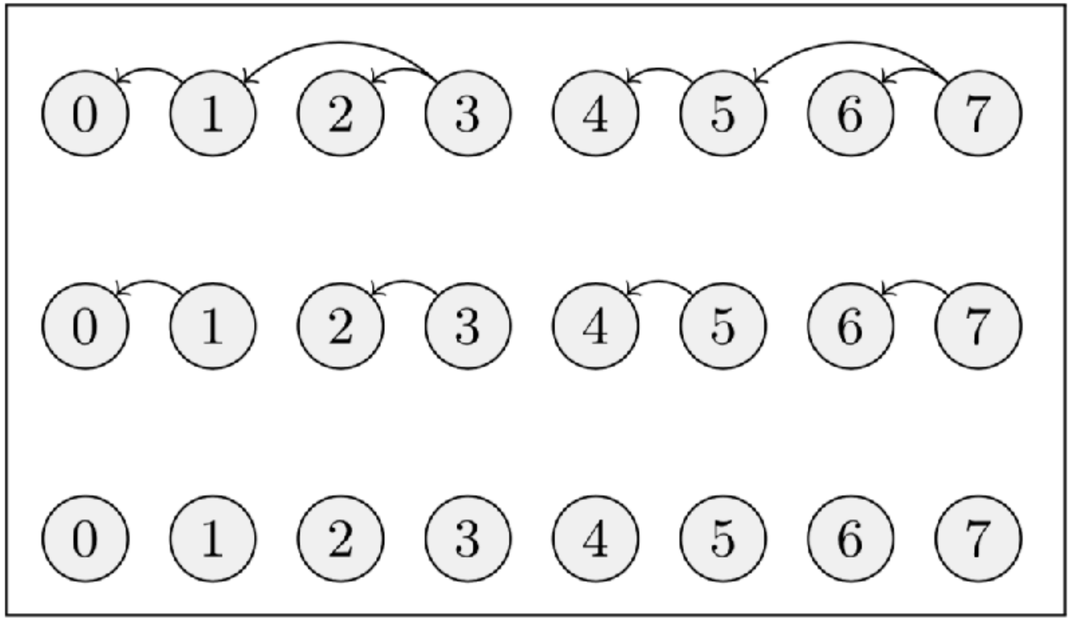
Fenwick trees (binary index trees)

Fenwick, "A new data structure for cumulative frequency tables" 1994



- Fenwick node x_i contains sum of fermion occupancy n_i and all progeny occupancies

NOTEBOOK I



JW - depth 0 Fenwick trees

⋮

BK - depth log N Fenwick tree

Codebase available

Fermion-to-spin parity trees in Julia Language

Outline

- Spin to fermion mappings
- **Qubit Hamiltonian propagation methods**
- Measurement
- State Preparation

Block encoding, LCU methods

$$W = \begin{pmatrix} \sqrt{p}U & * & * \\ * & * & * \\ * & * & * \end{pmatrix}$$

$$W|0\rangle|\psi\rangle = \sqrt{p}\,|0\rangle U|\psi\rangle + \sqrt{1-p}\,|\perp\rangle$$

Want to boost probability of implementing U

Block encoding, LCU methods

$$W|0\rangle|\psi\rangle = \sqrt{p}\,|0\rangle U|\psi\rangle + \sqrt{1-p}\,|\perp\rangle$$

If $U = \sum \beta_j V_j$ with Vj unitary then LCU

PREPARE

$$PrepB|0\rangle = \frac{1}{\sqrt{\sum \beta_k}} \sum_j \sqrt{\beta_j}\,|j\rangle$$

SELECT

$$SelV = |j\rangle\langle j| \otimes V_j$$

Want to boost probability

$$W|0\rangle|\psi\rangle = \sqrt{p}\,|0\rangle U|\psi\rangle + \sqrt{1-p}\,|\perp\rangle$$

$$W = (PrepB^{\dagger} \otimes 1) \times (SelV) \times (PrepB \otimes 1)$$

$$PrepB|0\rangle = \frac{1}{\sqrt{\sum \beta_k}} \sum_j \sqrt{\beta_j}\,|j\rangle$$

$$SelV = |j\rangle\langle j| \otimes V_j$$

$$p = 1/\sum \beta_j$$

Reflections in Hilbert Space

involutions: (Mathematics) a function, transformation, or operator that is equal to its inverse, i.e., which gives the identity when applied to itself.

Velazquez, *Las Meninas*

Reflections

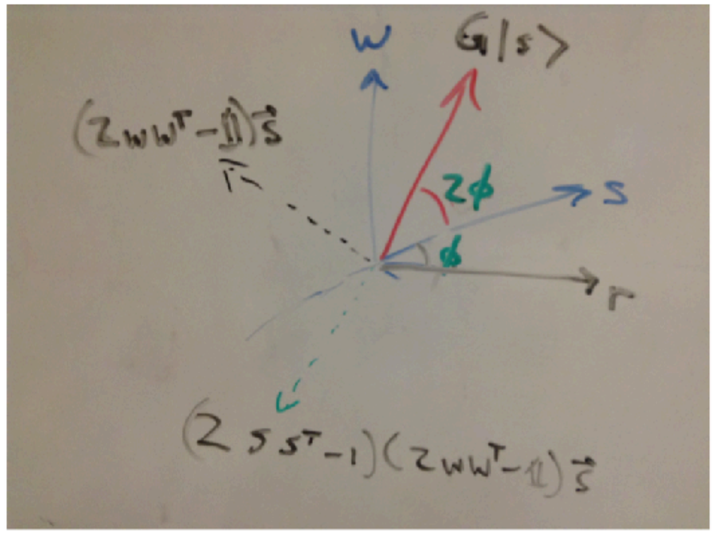
$R = 2\mathbf{P} - \mathbf{1} = \sqrt{\mathbf{1}}$

- $\mathbf{P} = \mathbf{P}^2$
- $R^2 = \mathbf{1}$
- Matrix decompositions
- Quantum algorithms

Exercise: Given any $\vec{x} \neq \vec{y}$ both with norm r show a reflection operator connects them. *Hint: try* $\vec{x} - \vec{y}$

Reflections in Hilbert Space

involutions: (Mathematics) a function, transformation, or operator that is equal to its inverse, i.e., which gives the identity when applied to itself.



- The optimal algorithm devised in 1996
  - $R_1 = 2\vec{w}\vec{w}^T - \mathbf{1}$ is the *oracle* for the winner state, $\vec{w}$
  - $R_2 = 2\vec{s}\,\vec{s}^T - \mathbf{1}$ with $\vec{s} = \frac{1}{\sqrt{N}} \sum_{\sigma}^{\text{possible states}} \vec{\sigma}$
  - $G = -R_2 R_1$ With high probability $G^{O(\sqrt{N})}\,\vec{s} = \vec{w}$

Extensions of Grover search

- Amplitude amplification
- Oblivious amplitude amplification

Block encoding, LCU methods $U = \sum \beta_j V_j$

$$W = (PrepB^\dagger \otimes 1) \times (SelV) \times (PrepB \otimes 1)$$

$$R = (1 - 2|0\rangle\langle 0|) \otimes 1$$

$$p = 1/\sum \beta_j$$

Oblivious Amplitude Amplification

$$(-WRW^\dagger R)^l W|0\rangle|\psi\rangle \approx |0\rangle U|\psi\rangle$$

$$\sqrt{p} = \sin\theta \mapsto \sqrt{p_{(l)}} = \sin((2l+1)\theta)$$

First order Trotter

$$e^{-iHt} = \left(e^{-ih_1 t/n} e^{-ih_2 t/n} \cdots e^{-ih_N t/n}\right)^n + O(t^2/n)$$

Second order Suzuki-Trotter

$$e^{-iHt} = \left(\prod_{m=1}^{M} e^{-iH_m t/2n} \prod_{m'=M}^{1} e^{-iH_{m'} t/2n}\right)^n + O(t^3/n^2)$$

Optimal Suzuki-Trotter

Approximately linear scaling with t [Berry et al '06]

$$H = \sum_k \alpha_k W_k$$

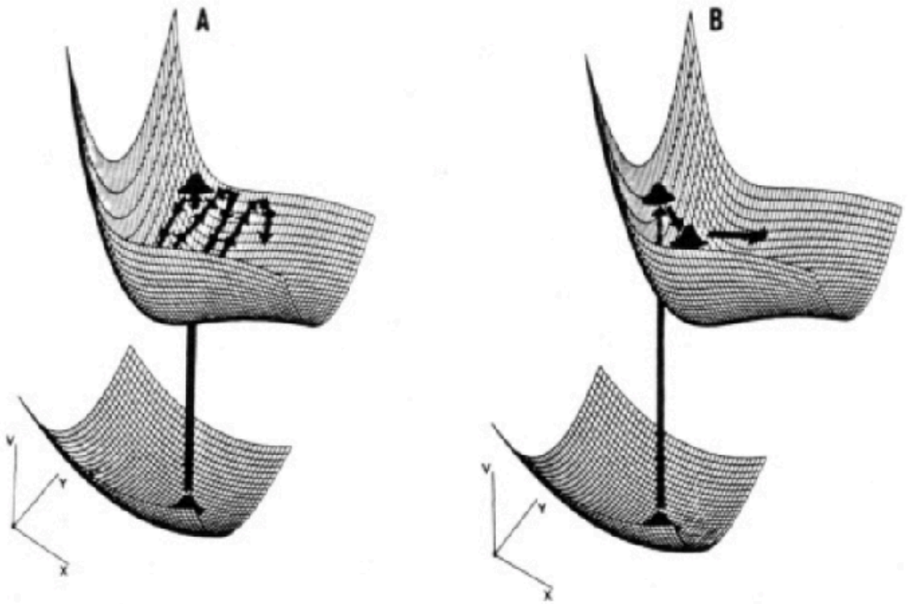
$$\exp(-iHt) = \sum_{n=0}^{\infty} (-i[\sum_k \alpha_k W_k]t)^n / n! = \sum \beta V_j$$

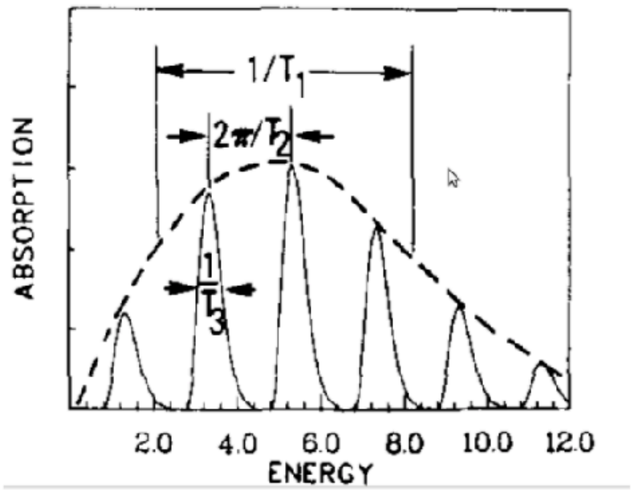
NOTEBOOK

Python notebook

Outline

- Spin to fermion mappings
- Qubit Hamiltonian propagation methods
- **Measurement**
- State Preparation





Heller. *Accounts of Chemical Research* (1981)

Absorption spectroscopy

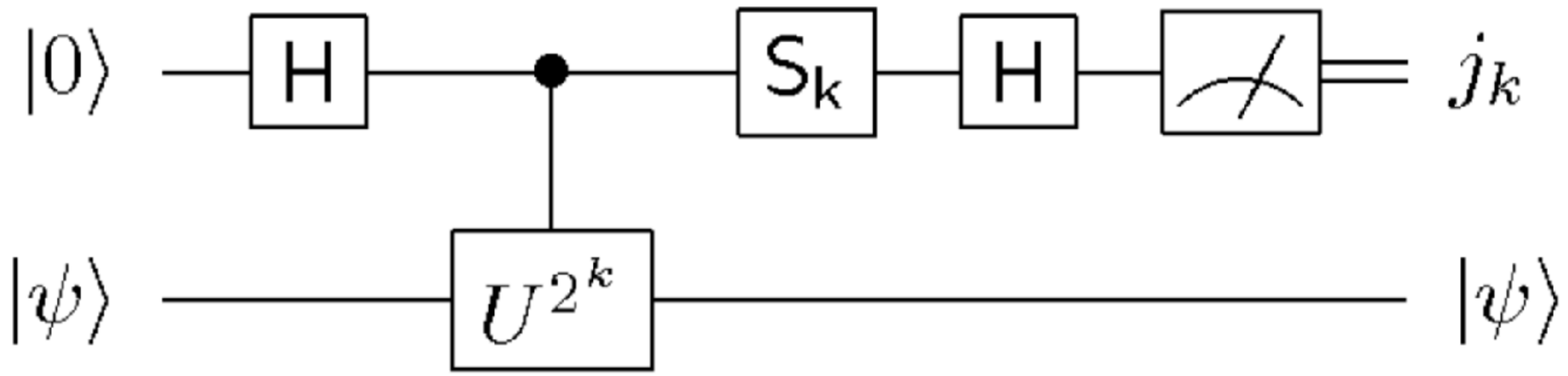
$$\epsilon(\omega) = C\omega \int_{-\infty}^{\infty} e^{i(\omega+E_0)t} \langle \psi(t)|\psi(0)\rangle \, dt = \mathcal{F}[\langle \psi | e^{-iHt} | \psi \rangle](\omega)$$

Exponential quantum improvements (BQP)

- Simulating quantum time evolution with full r_{ij}^{-1} operator
- Quantum factoring algorithm

Simulated quantum evolution scales linearly with target time (Feynman 82, Lloyd 96)

- Propagate then measure properties of final state
- Fourier transform for frequency (energy) information
  - von Neumann 55, Ramsey 63, Shor 94, Kitaev 95, Cleve+ 97



Fourier method of energy measurement

Fourier transform approach

- $U|\psi_n\rangle = e^{-iE_n t}|\psi_n\rangle = e^{2\pi i\phi}|\psi_n\rangle$
- Fourier transform phase factor
- $\phi = 0.j_0 j_1 j_2 \ldots = \left(\frac{j_0}{2}\right) + \left(\frac{j_1}{4}\right) + \left(\frac{j_2}{8}\right) + \ldots$

For each bit of ϕ, $U^{2^j}|\psi_n\rangle = e^{2\pi i(2^j\phi)}|\psi_n\rangle$

- If N bits of precision are needed U must be applied $2^N - 1$
- With $t = \frac{2\pi}{E_{HF}}$ used for the propagation time $\phi = E_{HF}/2E_{exact}$

MEASUREMENT PROTOCOL

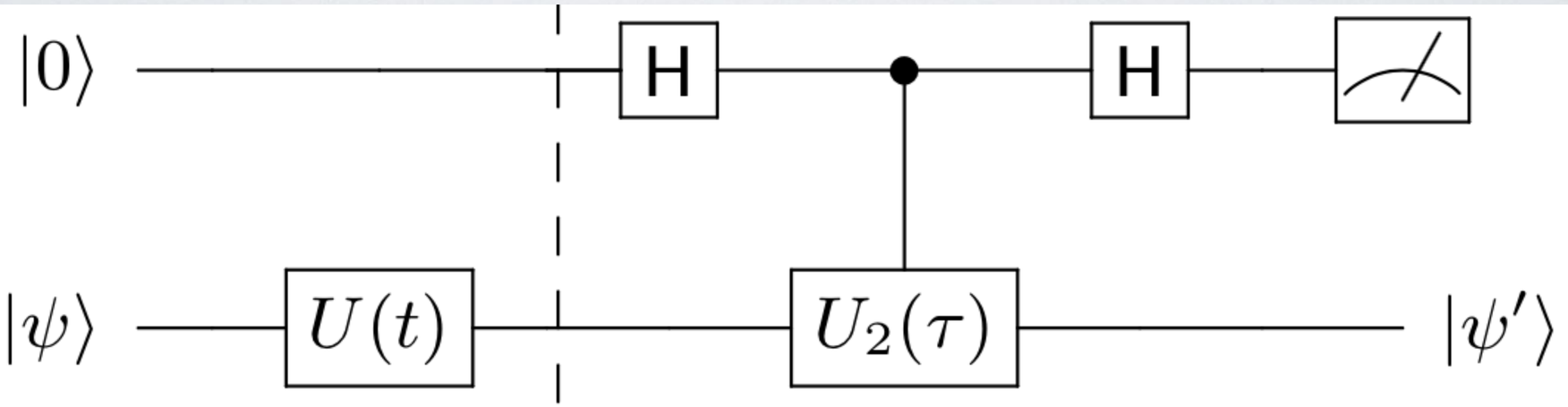
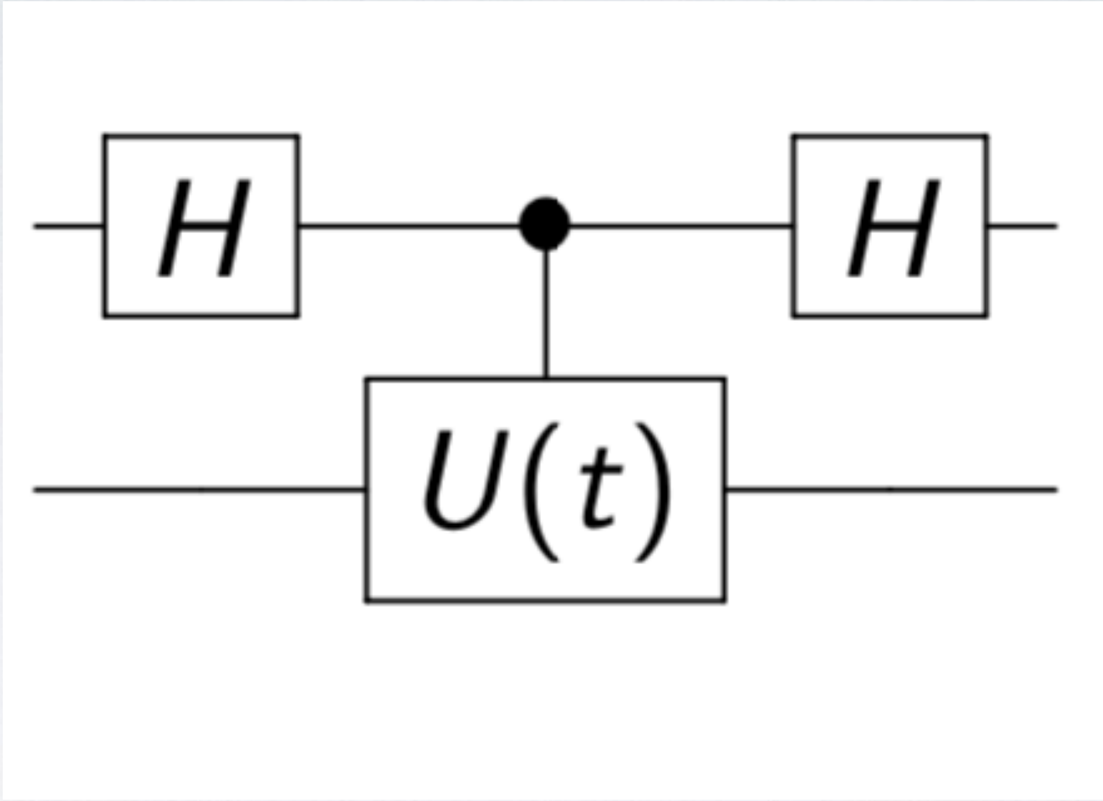


Figure 1. The circuit for measuring the density matrix. The half before the dashed line is used for evolving the state to time t, the half after is used for doing the measurement of an observable at time t via phase estimation.

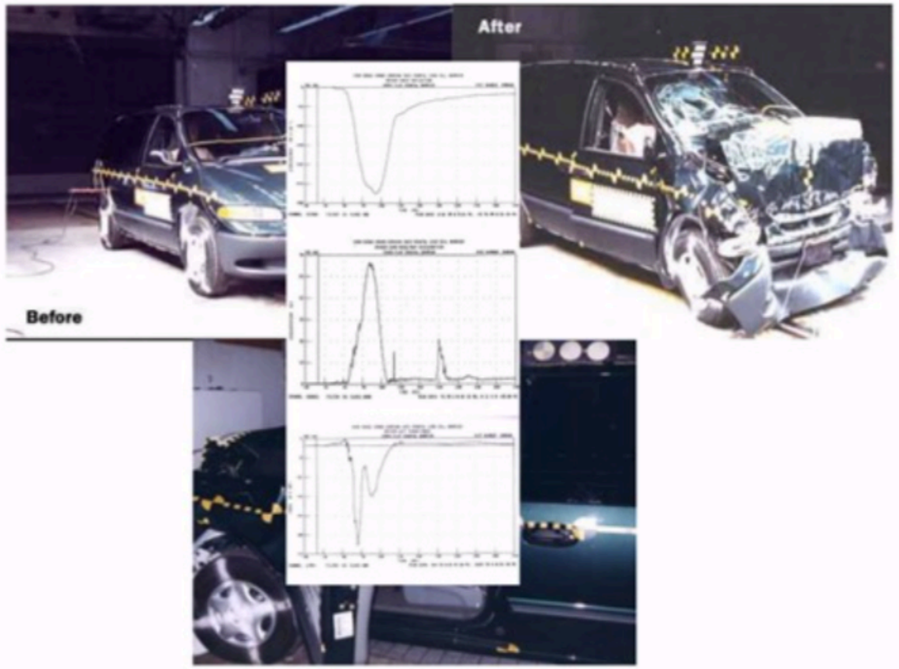


NOTEBOOK 3

Phase estimation

Outline

- Spin to fermion mappings
- Qubit Hamiltonian propagation methods
- Measurement
- **State Preparation**



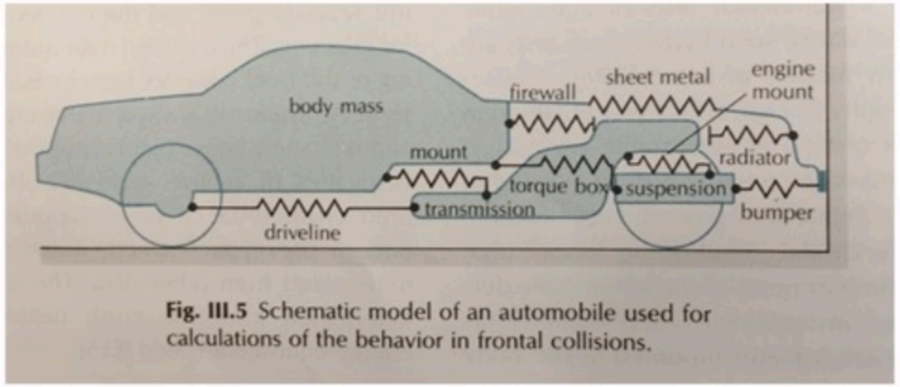


Fig. III.5 Schematic model of an automobile used for calculations of the behavior in frontal collisions.

- A random state of n qubits has expected overlap 2^{-n} with the groundstate
- Preparing arbitrary states is in quantum version NP-hard

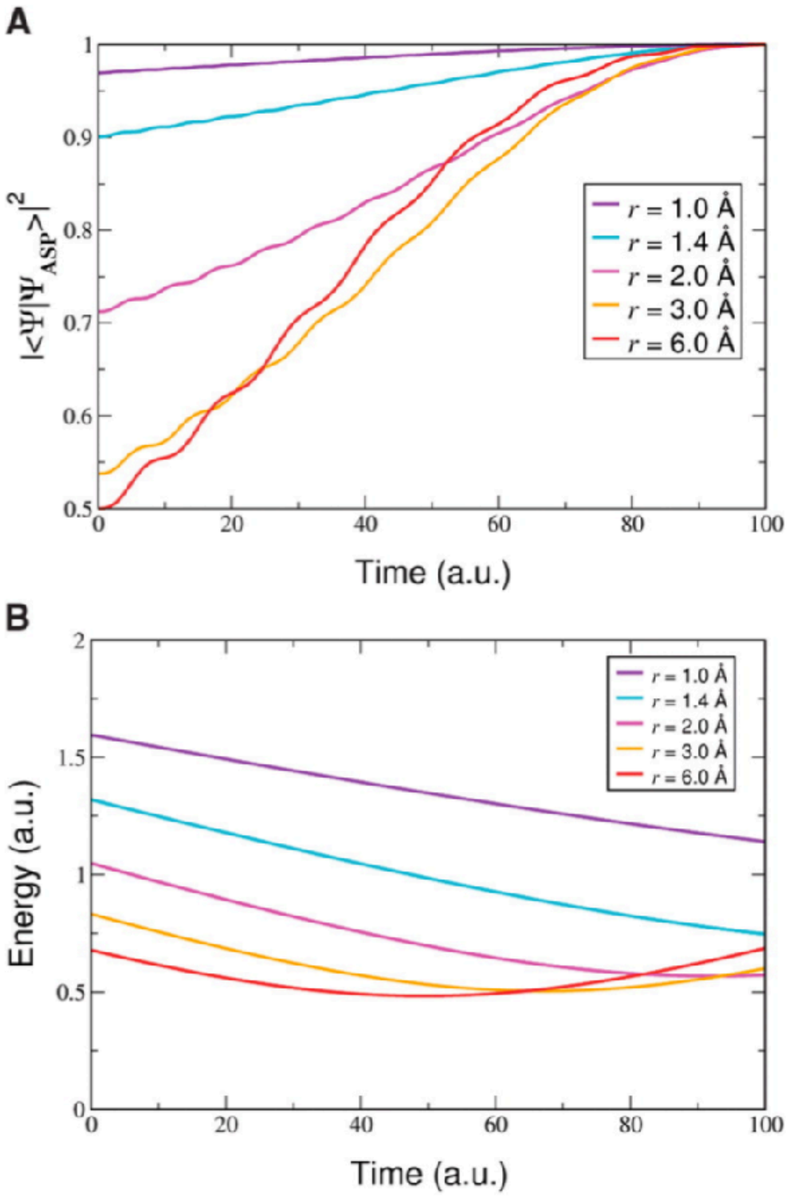
Generic state preparation can be expensive

Molecular orbital approach

- Identify qubits with molecular orbitals
- $|HF\rangle = |1 \cdots 100 \cdots 0\rangle$

Adiabatic approach

- $H_{HF} \xrightarrow{slowly} H_{FCI}$
  $|HF_0\rangle \rightarrow |FCI_0\rangle$
- Speed limited by the spectral gap along the adiabatic path



EXPONENTIAL ANSATZ

Coupled cluster

- Exponential ansatz, $|CC\rangle = exp\left[\sum \mathbf{c}_j \mathbf{T}_j\right] |\psi_{HF}\rangle$
- $\mathbf{T}_j$ are the excitations that change j orbitals at a time
- $\mathbf{c}_j$ are variational parameters
- Current gold standard: CCSD(T)
  CC with singles ($\mathbf{c}_1\mathbf{T}_1$) and doubles ($\mathbf{c}_2\mathbf{T}_2$) plus perturbative triples,

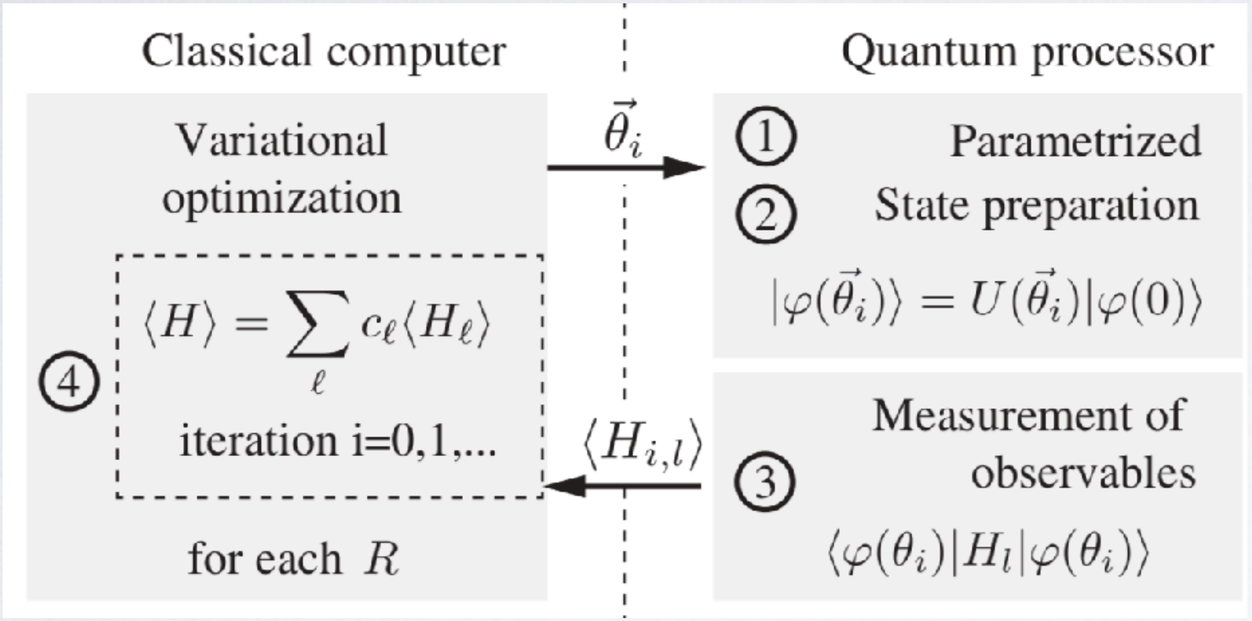
$$\mathbf{T}_1 = \sum_m^{occ} \sum_p^{virt} t_m^p \, a_p^\dagger a_m = \sum_m^{occ} \sum_p^{virt} t_m^p T_m^p$$

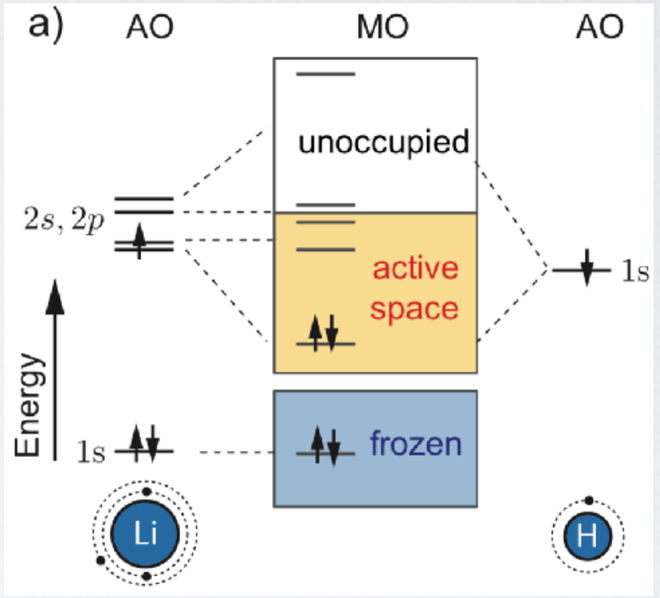
$$\mathbf{T}_2 = \sum t_{mn}^{pq} a_p^\dagger a_m a_q^\dagger a_n = \sum t_{mn}^{pq} T_{mn}^{pq}$$

Quantum Chemistry Calculations on a Trapped-Ion Quantum Simulator

Cornelius Hempel, Christine Maier, Jonathan Romero, Jarrod McClean, Thomas Monz, Heng Shen, Petar Jurcevic, Ben P. Lanyon, Peter Love, Ryan Babbush, Alán Aspuru-Guzik, Rainer Blatt, and Christian F. Roos

Phys. Rev. X **8**, 031022 – Published 24 July 2018





$$U_{\mathrm{UCC}}(\vec{\theta}) = \mathrm{e}^{\sum_\gamma \theta_\gamma (T_\gamma - T_\gamma^\dagger)}$$

LAYERED ANSÄTZE

Letter | Published: 13 September 2017

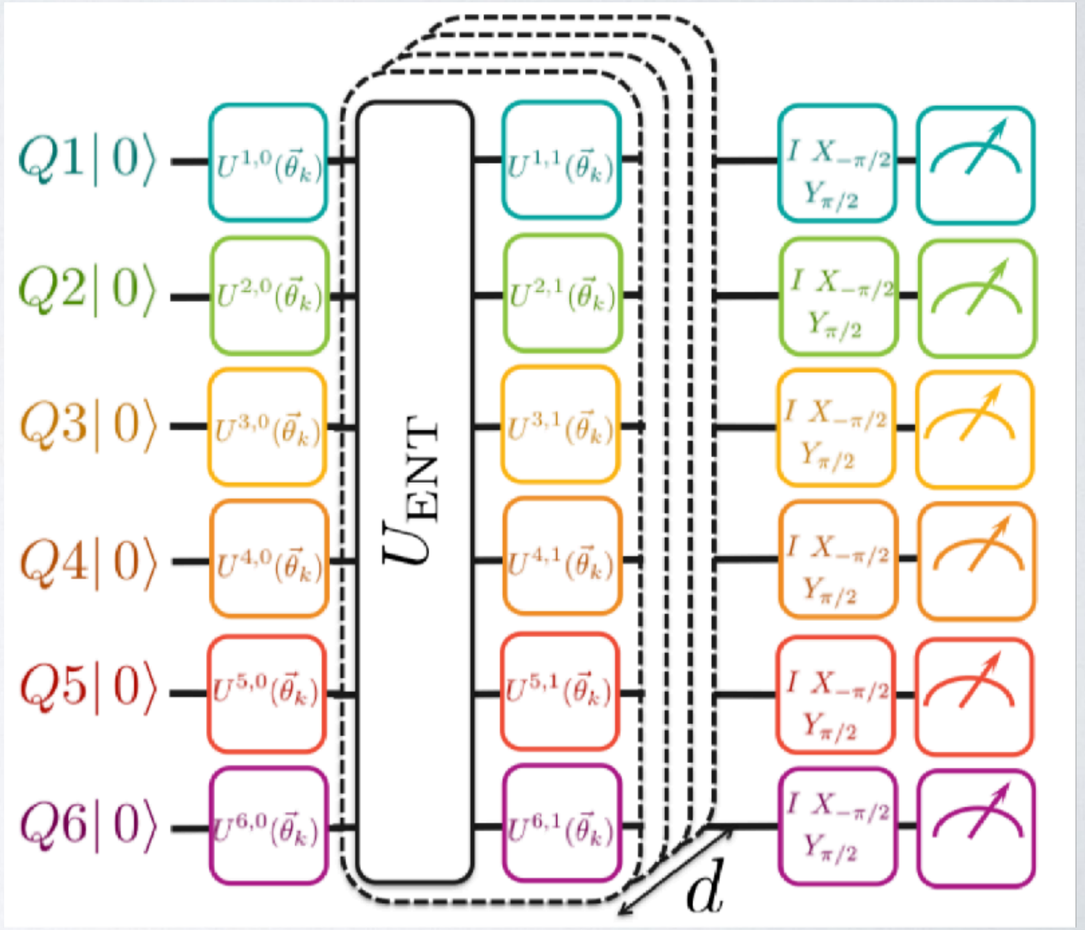
Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets

Abhinav Kandala, Antonio Mezzacapo, Kristan Temme, Maika Takita, Markus Brink, Jerry M. Chow & Jay M. Gambetta

Nature **549**, 242–246 (14 September 2017) | Download Citation

$$|\Phi(\vec{\theta})\rangle = \prod_{q=1}^{N}\left[U^{q,d}(\vec{\theta})\right] \times U_{\mathrm{ENT}} \times \prod_{q=1}^{N}\left[U^{q,d-1}(\vec{\theta})\right]$$

$$\cdots \times U_{\mathrm{ENT}} \times \prod_{q=1}^{N}\left[U^{q,0}(\vec{\theta})\right]|00\ldots0\rangle.$$



NOTEBOOK 3

State Preparation

FIN

Key ideas

- Quantum computing isn't going to solve the ground state problem
- Quantum computing can propagate your system
- Propagation leveraged to obtain eigenenergies

Quantum Information Science
at Dartmouth