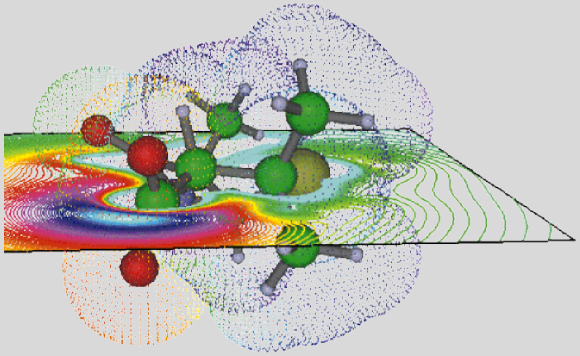

Quantum Chemistry

on

Quantum Computers

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Outline

Why to simulate chemistry on quantum devices?

- The size of the Hilbert space needed for the description of a studied system grows *exponentially* with the system size - **curse of dimensionality**.
- For example, the *exact* N-electron k-orbital wave function expansion:

$$\Psi_{\mathrm{el}} = \sum_{n_1 n_2 \ldots n_k} \psi^{n_1 n_2 \ldots n_k} \left| n_1 n_2 \cdots n_k \right\rangle \qquad \begin{aligned} |n_i\rangle &\in \{|\mathrm{empty}\rangle, |\downarrow\rangle, |\uparrow\rangle, |\downarrow\uparrow\rangle\}, \\ \sum_i n_i &= N \end{aligned}$$

  Dimension of the Hilbert space increases *exponentially* with a system size: $\mathcal{O}(4^k)$

- in PVDZ basis set:

  100 dets $\Rightarrow$ $\approx 10^7$ dets $\Rightarrow$ $\approx 10^{46}$ dets

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Two questions which naturally pop up:

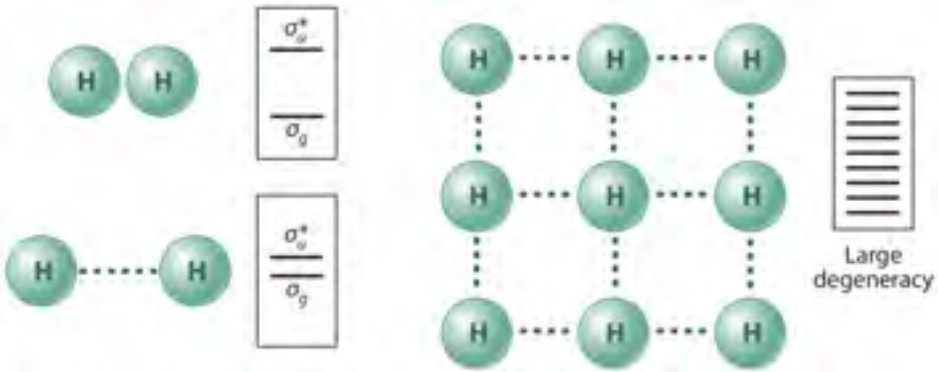
1. Do we really need the *exact* solution?

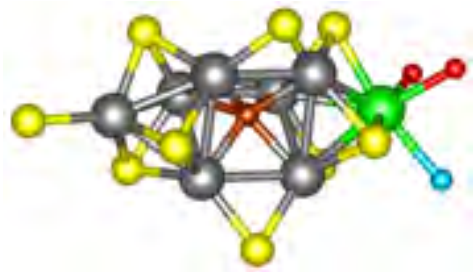
2. Do not most of the relevant wave functions lie in some low-entangled corner of the Hilbert space which would allow efficent parametrization (e.g. tensor networks)?

Weak versus strong correlation

$$\Psi_{\mathrm{el}} = \Psi_{\mathrm{HF}} + \Psi_{\mathrm{corr}}$$

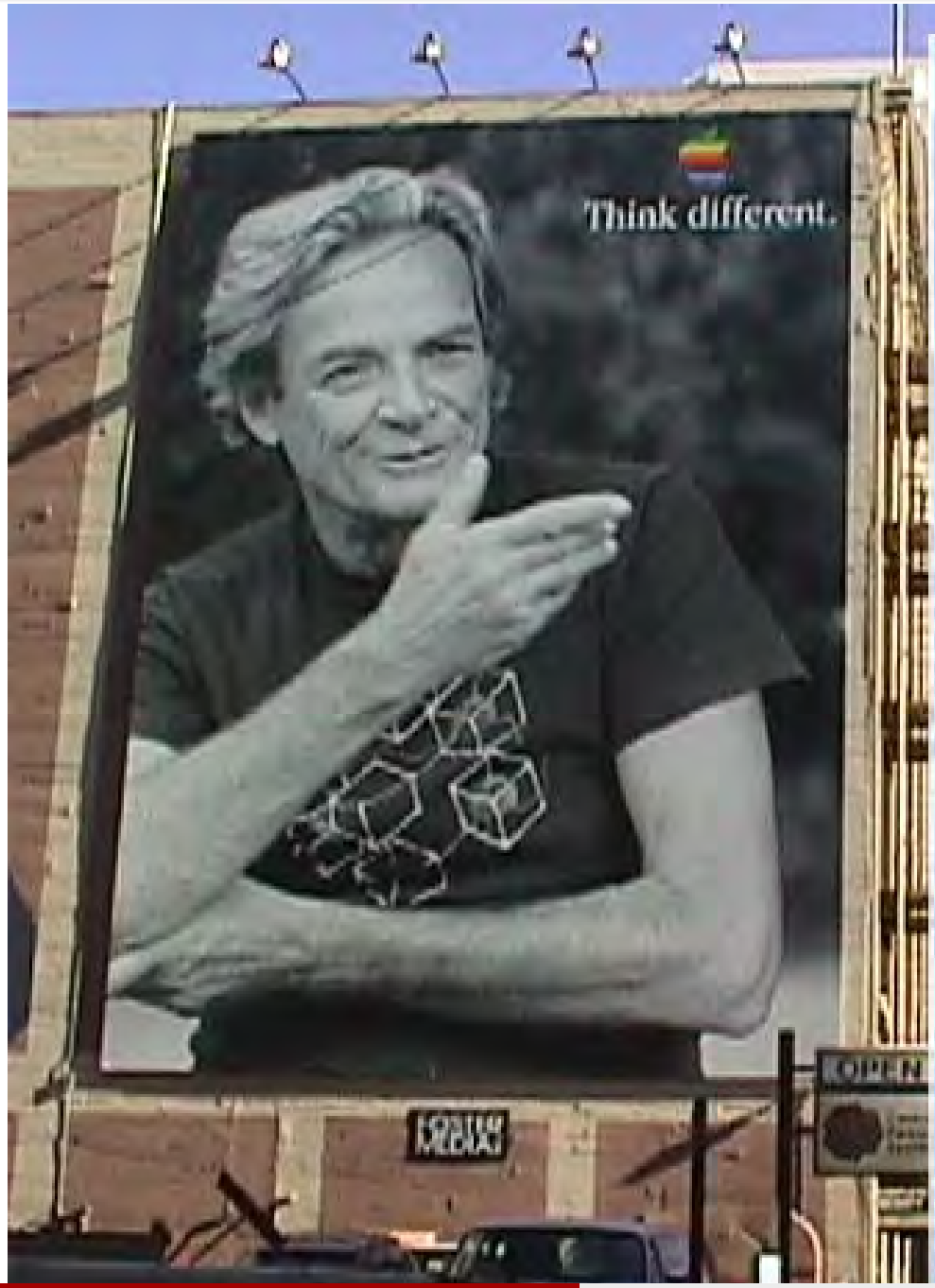
- Weakly correlated (or single reference) regime:
  - Ψ_{HF} - good approximation to Ψ_{el}, Ψ_{corr} is supposed to be small
  - DFT can accurately treat hundreds of atoms, CCSD(T) with spectroscopic accuracy
- Strongly correlated (or multireference) regime:
  - Coefficients in determinant expansion of Ψ_{corr} are large, the mean field approach fails!
  - Strongly correlated states arise when there is near degeneracy in underlying orbitals





- For near degenerate orbitals, we *generally* need the exact solution.
- Moreover, there are probably no *efficient* classical parametrizations, we need FCI!

Solution: Quantum Chemistry on Quantum Computers



Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy. (1982)

Quantum computing in a nutshell

- Quantum unit = qubit

$$|\psi\rangle = \alpha\,|0\rangle\ + \beta\,|1\rangle\ , \qquad |\alpha|^2 + |\beta|^2 = 1,$$

computational basis

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{therefore} \quad |\psi\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

- When going to n qubits, we work with 2^n dimensional Hilbert space, e.g.

$$|00\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |01\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$|10\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |11\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

- A general two qubit's state has the form

$$|\psi\rangle = \alpha|00\rangle + \beta|01\rangle + \gamma|10\rangle + \delta|11\rangle.$$

- Multi-qubit states can be

Product states

$$\frac{1}{\sqrt{2}}\big(|00\rangle + |01\rangle\big) = |0\rangle \otimes \frac{1}{\sqrt{2}}\big(|0\rangle + |1\rangle\big)$$

- can be written as tensor products of subsystem wave functions

Entangled states

$$\frac{1}{\sqrt{2}}\big(|00\rangle + |11\rangle\big)$$

- "spooky action at a distance"
- key ingredients in quantum computing

- Qubits are usually initialized in a $|\text{zero}\rangle$ state $= |0\ldots0\rangle$.
- Computational basis states encode decimal numbers in their binary form:

$$|4\rangle = \big|\ 1\ \ 0\ \ 0\ \big\rangle$$

convention: *third qubit* *second qubit* *first qubit*

Basics of quantum computing: gates

- Since time evolution of quantum systems must be unitary $\Rightarrow$ quantum gates are unitary operators.
- Every multi-qubit operation can be decomposed into single and entangling two-qubit gates.
  - Pauli gates:

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

$$Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

  - Rotations about x, y, z axes:

$$R_x(\theta) = e^{-i\theta X/2}, R_y(\theta) = e^{-i\theta Y/2}, R_z(\theta) = e^{-i\theta Z/2}$$

  - Controlled NOT (CNOT):

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

$$\begin{aligned} |00\rangle &\rightarrow |00\rangle \\ |01\rangle &\rightarrow |01\rangle \\ |10\rangle &\rightarrow |11\rangle \\ |11\rangle &\rightarrow |10\rangle \end{aligned}$$

  - Bloch sphere representation:

$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$

  - Hadamard gate: $|0\rangle \rightarrow \frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right)$

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

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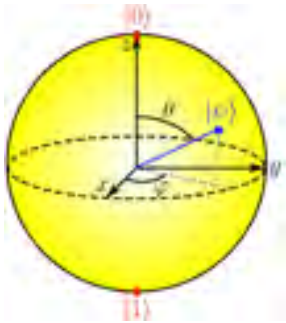

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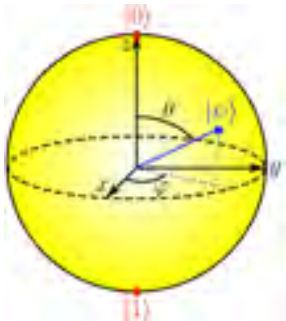

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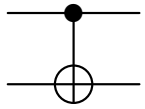
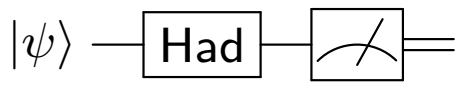


$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\begin{aligned} |00\rangle &\rightarrow |00\rangle \\ |01\rangle &\rightarrow |01\rangle \\ |10\rangle &\rightarrow |11\rangle \\ |11\rangle &\rightarrow |10\rangle \end{aligned}$$

- Final element of quantum circuits is a measurement.
- Measurement is destructive.
- Observables O are represented by Hermitian matrices, we can measure the expectation value of O, i.e. $\langle O \rangle = \langle \psi | O | \psi \rangle$ by averaging over many measurements.
- Measuring in the *computational basis* of i^{th} qubit: $\langle \psi | Z_i | \psi \rangle$.
- Strings of fermionic second quantized operators can be represented as strings of Pauli operators (we will see later) - we need to measure also in X and Y bases $\Rightarrow$ bases transformations, e.g.

Measuring in X basis:



$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

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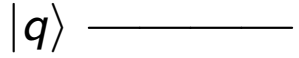
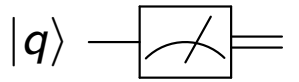
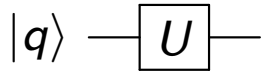
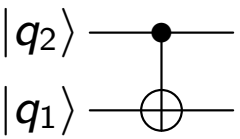
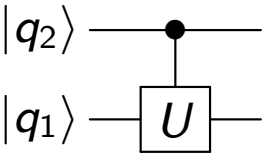
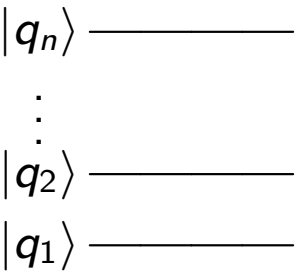
Basics of quantum computing: graphical notation

wire carrying a qubit	
measurement: projection onto $\|0\rangle$ and $\|1\rangle$	
single qubit unitary gate U	
controlled-NOT operation	
controlled-U operation	
qubits ordering convention: $\|q_n \dots q_2 q_1\rangle$	

- Analog quantum simulation: mapping of a Hamiltonian onto a tunable purpose specific quantum device (not discussed here).
- Digital quantum simulation: quantum algorithm decomposed to single and two-qubit gates and implemented on a *universal quantum computer*.

1. System to qubits mapping:

$$|\psi(t=0)\rangle \to |\psi_q\rangle \qquad H \to H_q$$

2. Time evolution via e^{-itH_q}

$$H_q = \sum_j^{\text{polynomial}} h_j, \quad \text{however} \quad [h_j, h_k] \neq 0$$

$$e^{-itH_q} = e^{-it\sum_j h_j} = \left(\prod_j e^{-ih_j t/N}\right)^N + \mathcal{O}(t^2/N) \qquad \text{Trotter approx.}$$

3. Measurement of desired quantities (e.g. spin correlation functions)

$$H_{\text{Ising}} = \sum_{\langle i,j \rangle} J_{ij} Z_i Z_j + \sum_i B_i X_i \qquad \langle i,j \rangle \ldots \text{nearest-neighbor}$$

- Simple system to qubits mapping: $|\alpha\rangle \equiv |0\rangle$, $|\beta\rangle \equiv |1\rangle$, $H_{\text{Ising}} \equiv H_q$.
- After Trotterization: $e^{-iB_i X_i \delta t}$ and $e^{-iJ_{ij} Z_i Z_j \delta t}$, where $\delta t = t/N$.

$$R_X^i(2B_i\delta t)$$

$$Z \otimes Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} =$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{matrix} |00\rangle \\ |01\rangle \\ |10\rangle \\ |11\rangle \end{matrix}$$

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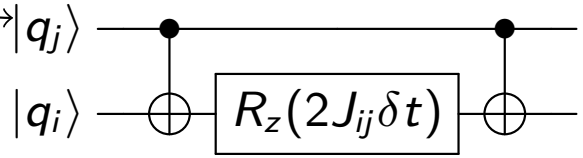
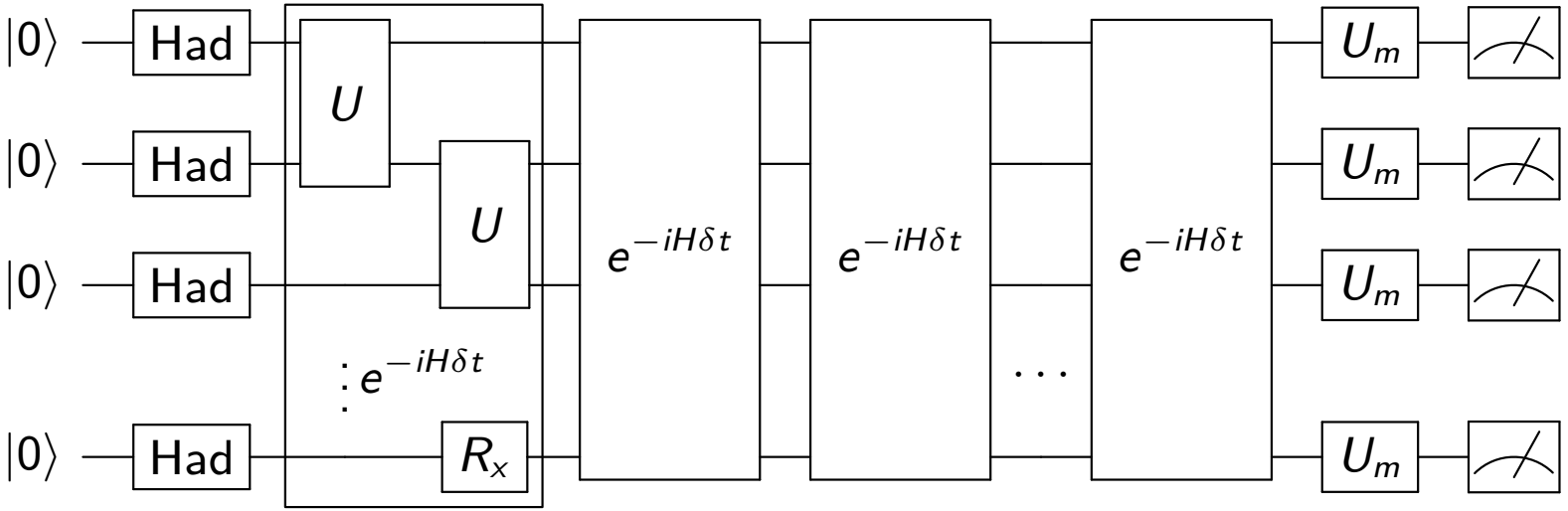
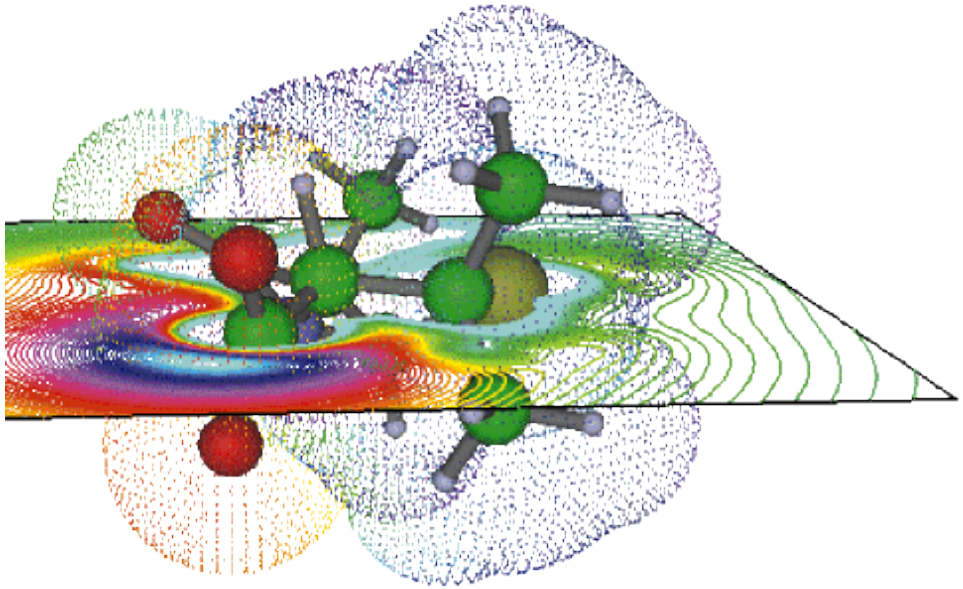




- Initial Hadamard gates align the spins along the x axis.

$$U_{ij} = \mathrm{CNOT}^{i,j} R_z^j(2J_{ij}\delta t)\mathrm{CNOT}^{i,j} R_x^i(2B_i\delta t)$$

Quantum chemistry in a nutshell



- The electronic structure Hamiltonian (employing the Born-Oppenheimer approximation):

$$H_{\text{el.}} = -\sum_i \frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}.$$

- The first step: Hartree-Fock (HF, mean-field) approximation:

- N-electron problem $\Rightarrow$ one-electron problem:

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \epsilon_i\chi_i(\mathbf{x}_1)$$

$$f(\mathbf{x}_1) = -\frac{\nabla_1^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} + v^{\text{HF}}(\mathbf{x}_1)$$

$$v^{\text{HF}}(\mathbf{x}_1) = \sum_i \int \chi_i^*(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}(1 - P_{12})\chi_i(\mathbf{x}_2)\mathrm{d}\mathbf{x}_2,$$

Slater determinant:

$$|\chi_1\chi_2\ldots\chi_N\rangle \equiv \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_1(\mathbf{x}_2) & \ldots & \chi_1(\mathbf{x}_N) \\ \chi_2(\mathbf{x}_1) & \chi_2(\mathbf{x}_2) & \ldots & \chi_2(\mathbf{x}_N) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_N(\mathbf{x}_1) & \chi_N(\mathbf{x}_2) & \ldots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- Analytic solution of HF equations is generally not possible $\Rightarrow$ solved numerically:

$$\chi_i(\mathbf{x}) \xrightarrow[\text{integrated out}]{\text{spin}} \psi_i(\mathbf{r}) = \sum_\mu C_{\mu i}\ \phi_\mu(\mathbf{r})$$

$C_{\mu i}$: optimized during HF-SCF

- Natural step: expand in H-atom one-electron wave functions

$$\phi(\mathbf{r}) = R_{nl}(r)\, Y_{lm}(\theta, \phi)$$

Slater type orbitals (STOs):

$$R^{\text{STO}}(r) \propto e^{-\zeta r}$$

difficult for integration

Gaussian type orbitals (GTOs):

$$R^{\text{GTO}}(r) \propto e^{-\alpha r^2}$$

$\mathcal{O}(M^4)$ Hamiltonian terms

- Recently there has been some interest in the plane wave basis

$$\phi^{\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k}\mathbf{r}}$$

  and its dual form (Fourier transform), which leads to diagonal two-electron interaction and thus less Hamiltonian terms $\mathcal{O}(M^2)$
- However for molecules, about 100 times more plane waves than GTOs is necessary (for a given accuracy).
- Since the number of Hamiltonian terms directly influences the cost of quantum algorithms, the goal is to have the most compact basis with the minimum number of Hamiltonian terms.
- Alternative to basis set methods: grid based methods (basis of δ functions at given positions $\{|r\rangle\}$):

$$|\Psi\rangle = \sum_{\mathbf{x}_1 \ldots \mathbf{x}_N} \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)\mathcal{A}(|\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\rangle), \qquad |\mathbf{x}_i\rangle = |\mathbf{r}_i\rangle|\sigma_i\rangle$$

Classical scaling: $P^{3N} \times 2^N$

- Electrons are not properly correlated at the Hartree-Fock level.
- The Hartree-Fock solution in a complete basis is certainly not exact!
- The exact wave function - full configuration interaction (FCI):

$$|\Psi\rangle_{\mathrm{FCI}} = c|\Phi\rangle + \sum_{ia} c_i^a |\Phi_i^a\rangle + \sum_{\substack{a<b \\ i<j}} c_{ij}^{ab} \left|\Phi_{ij}^{ab}\right\rangle + \cdots$$

- Correlation energy:

$$\Delta E_{\mathrm{corr}} = E^{\text{FCI-lim.}} - E^{\text{HF-lim.}}.$$

  about 1% of the Hartree-Fock energy, but in absolute values huge effect!
- Concept of "chemical accuracy" $\sim$ 1 kcal/mol ($1.6 \cdot 10^{-3}$ Hartree), reaction rates within on order of magnitude (at room temperature)

$$v \propto e^{-\Delta E^{\dagger}/k_B T}$$

- Calculated by post-HF methods:

$$|\Psi\rangle = \Omega|\Phi_{\mathrm{HF}}\rangle$$

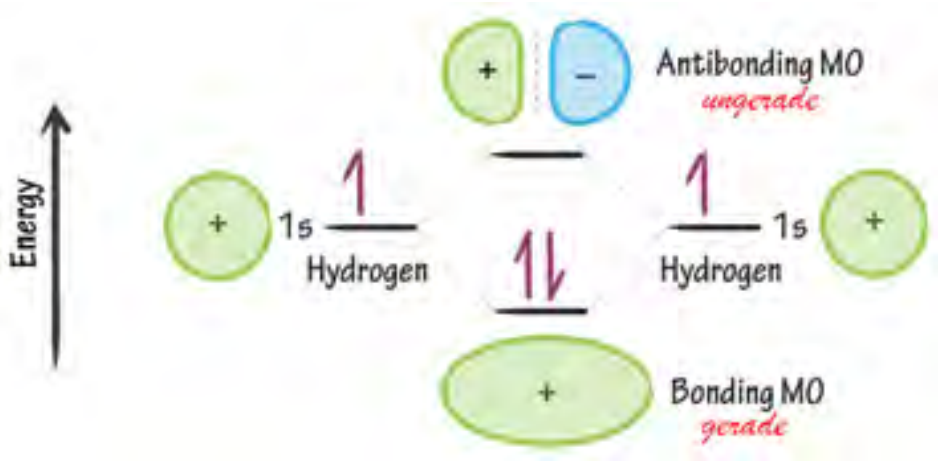
- Properties of determinants $\rightarrow$ algebraic properties of creation and annihilation operators.
- $a_p^\dagger$ creates an electron in p^{th} spin orbital, a_q destroys an electron in q^{th} spin orbital
- Fermionic anti-commutation rules:

$$\begin{aligned} \{a_p, a_q^\dagger\} &= a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}, \\ \{a_p, a_q\} &= \{a_p^\dagger, a_q^\dagger\} = 0 \end{aligned}$$

Notice Pauli exclusion principle satisfaction: $a_p^\dagger a_p^\dagger = 0$

- Slater determinants are represented in the occupation basis:

$$|\chi_1 \chi_2 \dots \chi_N\rangle = |o_1, \dots, o_p, \dots, o_M\rangle \qquad o_p = \{0, 1\}$$



H_2 in a minimal basis: $|o_{g\uparrow} o_{g\downarrow} o_{u\uparrow} o_{u\downarrow}\rangle$

- $\Phi_{\text{HF}} = |1100\rangle = a_{g\uparrow}^\dagger a_{g\downarrow}^\dagger |\rangle$

$$\begin{aligned} a_{g\downarrow}|1100\rangle &= a_{g\downarrow} a_{g\uparrow}^\dagger a_{g\downarrow}^\dagger |\rangle = -a_{g\uparrow}^\dagger a_{g\downarrow} a_{g\downarrow}^\dagger |\rangle = \\ &= -a_{g\uparrow}^\dagger (1 - a_{g\downarrow}^\dagger a_{g\downarrow}) |\rangle = -a_{g\uparrow}^\dagger |\rangle = \\ &= -|1000\rangle \end{aligned}$$

- Action of creation and annihilation operators on general determinants:

$$\begin{aligned} a_p|o_1,\ldots,o_p,\ldots,o_M\rangle &= \delta_{o_p,1}(-1)^{\sum_{i=1}^{p-1} o_i}|o_1,\ldots,o_p\oplus 1,\ldots,o_M\rangle, \\ a_p^\dagger|o_1,\ldots,o_p,\ldots,o_M\rangle &= \delta_{o_p,0}(-1)^{\sum_{i=1}^{p-1} o_i}|o_1,\ldots,o_p\oplus 1,\ldots,o_M\rangle, \end{aligned}$$

- Second quantization: proper anti-symmetry of a wave function is maintained by properties of creation and annihilation operators applied on it.
- First quantization: operators applied on a wave function retain its anti-symmetry, which must be explicitelly created during initialization.
- Electronic Hamiltonian in second quantization:

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$h_{pq} = \int \chi_p(\mathbf{x}_1)^* \left(-\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r}_1-\mathbf{R}_I|}\right)\chi_q(\mathbf{x}_1)d\mathbf{x}_1 \qquad \langle pq|rs\rangle = \int \frac{\chi_p(\mathbf{x}_1)^*\chi_q(\mathbf{x}_2)^*\chi_r(\mathbf{x}_1)\chi_s(\mathbf{x}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{x}_1 d\mathbf{x}_2$$

- The configuration interaction (CI) is a *variational* method, which unlike HF is not restricted to a single Slater determinant

$$\Omega_{\mathrm{CI}} = c + \sum_{\alpha} C_{\alpha} \quad \ldots \text{linear form}$$

$$\begin{aligned} C_1 &= \sum_{ia} c_i^a \; a_a^\dagger a_i, \\ C_2 &= \sum_{\substack{a<b \\ i<j}} c_{ij}^{ab} \; a_a^\dagger a_b^\dagger a_j a_i, \\ &\vdots \end{aligned}$$

variational params.

- Recall that FCI is exact within a given orbital basis, however only up to 20 orbitals are feasible.
- Restricted CI: CIS (singles), CISD (singles, doubles).
- The consequences of linear wave operator: slow convergence with excitation rank and size-nonextensivity.

- The coupled cluster (CC) wave operator has an exponential form

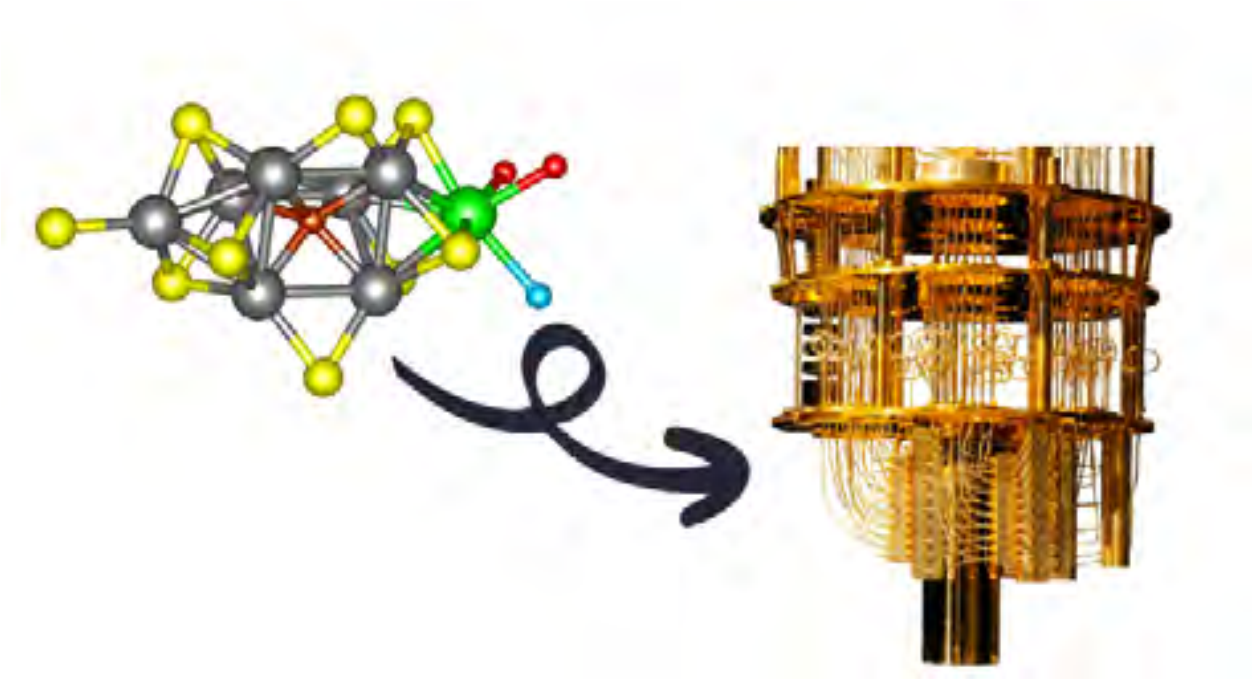
$$\Omega_{\mathrm{CC}} = e^{T} \qquad T = \sum_{\alpha} T_{\alpha}$$

$$\begin{aligned} T_1 &= \sum_{ia} t_i^a \, a_a^\dagger a_i, \\ T_2 &= \sum_{\substack{a<b \\ i<j}} t_{ij}^{ab} \, a_a^\dagger a_b^\dagger a_j a_i, \\ &\vdots \end{aligned}$$

CC amplitudes

- Exponential ansatz: faster convergence with excitation rank, size-extensivity
- Not variational, because $\langle \Psi | H | \Psi \rangle = \langle \Phi_{\mathrm{HF}} | e^{T^\dagger} H e^{T} | \Phi_{\mathrm{HF}} \rangle$ would lead to ∞ commutator series
- Instead: $H|\Psi\rangle = E|\Psi\rangle = E e^{T}|\Phi_{\mathrm{HF}}\rangle \xrightarrow[\langle \Phi_{\mathrm{HF}}| \cdot]{\cdot e^{-T}} \langle \Phi_{\mathrm{HF}} | e^{-T} H e^{T} | \Phi_{\mathrm{HF}} \rangle = E$
- Amplitude equations: $\langle \Phi^* | e^{-T} H e^{T} | \Phi_{\mathrm{HF}} \rangle = E \langle \Phi^* | \Phi_{\mathrm{HF}} \rangle = 0$, where $\Phi^* = \Phi_i^a, \Phi_{ij}^{ab}$, etc.

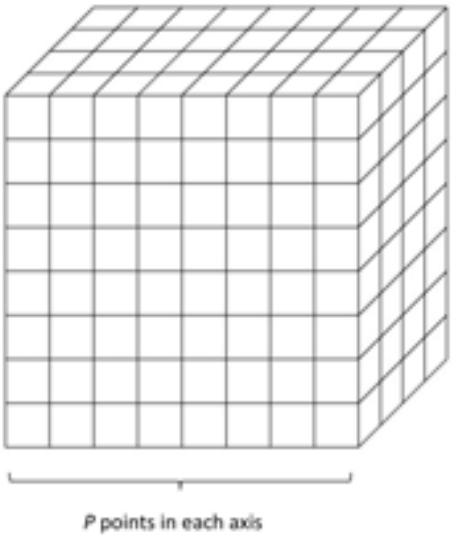
Quantum chemistry to quantum computing mappings



- The task is to encode fermionic Hamiltonians and wave functions onto register of qubits (say distingushible spins).

First quantized mappings for grid based approaches

$$|\Psi\rangle = \sum_{\mathbf{x}_1 \ldots \mathbf{x}_N} \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N) \mathcal{A}(|\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\rangle), \qquad |\mathbf{x}_i\rangle = |\mathbf{r}_i\rangle |\sigma_i\rangle$$



- State of a single particle: $2 \cdot P^3$ amplitudes (spin: 2; spatial: P^3)
- State of N particles: $(2P^3)^N = P^{3N} \times 2^N$
- Let's have $P = 2^m \Rightarrow 2^{(3m+1)N}$ amplitudes
- $(3m+1)N$ qubits can store the wave function

- Simple example: 2 *spinless* fermions on a four-point 1D grid
- 4 points can be represented by 2 qubits: $|0\rangle \equiv |00\rangle$, $|1\rangle \equiv |01\rangle$, $|2\rangle \equiv |10\rangle$, $|3\rangle \equiv |11\rangle$.

S. McArdle, S. Endo, A. Aspuru-Guzik, S. C. Benjamin, X. Yuan, *Rev. Mod. Phys.* **92**, 015003 (2020)

First quantized mappings for grid based approaches

- We distinguish two wave functions: 'n' and 'u'

$$
\begin{aligned}
|\phi_n\rangle &= \frac{1}{\sqrt{6}}|0\rangle + \frac{1}{\sqrt{3}}|1\rangle + \frac{1}{\sqrt{3}}|2\rangle + \frac{1}{\sqrt{6}}|3\rangle \\
|\phi_u\rangle &= \frac{1}{\sqrt{3}}|0\rangle + \frac{1}{\sqrt{6}}|1\rangle + \frac{1}{\sqrt{6}}|2\rangle + \frac{1}{\sqrt{3}}|3\rangle
\end{aligned}
$$

- We need to initialize the anti-symmetric wave function

$$
\begin{aligned}
|\Phi\rangle &= \frac{1}{\sqrt{2}}\left(|\phi_n\rangle_1|\phi_u\rangle_2 - |\phi_u\rangle_1|\phi_n\rangle_2\right) = \\
&= \frac{1}{6\sqrt{2}}\Big(|1\rangle_1|0\rangle_2 - |0\rangle_1|1\rangle_2 + |1\rangle_1|3\rangle_2 - |3\rangle_1|1\rangle_2 + \\
&+ \quad |2\rangle_1|0\rangle_2 - |0\rangle_1|2\rangle_2 + |2\rangle_1|3\rangle_2 - |3\rangle_1|2\rangle_2\Big)
\end{aligned}
$$

- Then the time evolution, i.e. $e^{-iH\delta t}$ can follow (discussed a bit later)
- Favourable scaling (quadratic potential), easy to generalize for equal treatment of nuclei and electrons (beyon Born-Oppenheimer).
- High number of qubits required (to represent a grid).

- We need $N\lceil \log_2 M \rceil$ qubits to represent N electrons in M basis functions (ordered from $|0\ldots00\rangle$ to $|1\ldots11\rangle$).
- Let's recall H_2 minimal basis example:

  $|g_\uparrow\rangle = |00\rangle = |0\rangle$, $|g_\downarrow\rangle = |01\rangle = |1\rangle$, $|u_\uparrow\rangle = |10\rangle = |2\rangle$, and $|u_\downarrow\rangle = |11\rangle = |3\rangle$
- Again anti-symmetrization is necessary:

$$|\Phi_{\mathrm{HF}}\rangle = \frac{1}{\sqrt{2}}\left(|0\rangle_1|1\rangle_2 - |1\rangle_1|0\rangle_2\right)$$

$$|\Psi\rangle = \alpha|g_\uparrow g_\downarrow\rangle + \beta|u_\uparrow u_\downarrow\rangle = \frac{\alpha}{\sqrt{2}}\left(|0\rangle_1|1\rangle_2 - |1\rangle_1|0\rangle_2\right) + \frac{\beta}{\sqrt{2}}\left(|2\rangle_1|3\rangle_2 - |3\rangle_1|2\rangle_2\right)$$

  The Hamiltonian obtained by projection onto the single-particle basis:

$$H = \sum_{i=1}^{N}\sum_{p,q=1}^{M} h_{pq}|\chi_p\rangle_i\langle\chi_q|_i + \frac{1}{2}\sum_{i\neq j}^{N}\sum_{p,q,r,s}^{M}\langle pq|rs\rangle|\chi_p\rangle_i|\chi_q\rangle_j\langle\chi_s|_j\langle\chi_r|_i,$$

- Each term can be expressed as a string of Pauli operators, $\mathcal{O}(N^2M^6)$ terms

- Goal: express second-quantized operators of indistinguishable electrons in terms of Pauli operators acting on distiguishable qubits.
- **Jordan-Wigner (JW) mapping:**
  - Qubits encode occupation

$$|o_1 \dots o_M\rangle \to |q_M \dots q_1\rangle, \qquad q_p \in \{0, 1\}$$

  - Representation of second-quantized operators:

$$a_p^\dagger = \left(\bigotimes_{j=1}^{p-1} Z_{j'} \right) \otimes Q_{p'}^\dagger, \quad a_p = \left(\bigotimes_{j=1}^{p-1} Z_{j'} \right) \otimes Q_{p'}$$

ensure proper phase / "parity of the state"

  - $Q = |0\rangle\langle 1| = (X + iY)/2$ and $Q^\dagger = |1\rangle\langle 0| = (X - iY)/2$ decrease and increase occupation of a given spin orbital

$$H = \sum_j h_j P_j = \sum_j h_j \prod_i \sigma_{i'}^j \qquad \sigma_i^j \in (I, X, Y, Z)$$

$$\Rightarrow e^{-iH\delta t}$$

- Example of one-electron part of $H_{\text{el.}}$

$$H_1 = \sum_{pq} h_{pq} a_p^\dagger a_q = \sum_p h_{pp} a_p^\dagger a_p + \sum_{p<q} \left(h_{pq} a_p^\dagger a_q + h_{qp} a_q^\dagger a_p \right)$$

- Diagonal terms after JW:

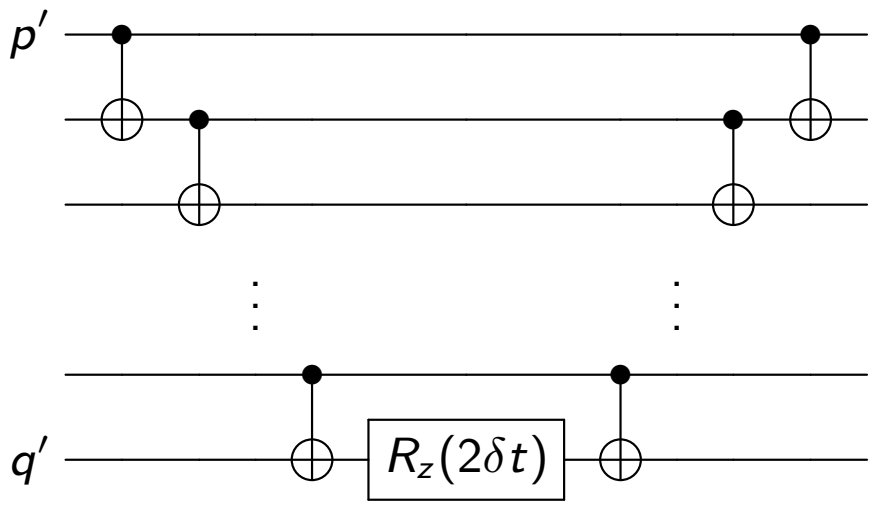
$$h_{pp} a_p^\dagger a_p = h_{pp} Q_{p'}^\dagger Q_{p'} = h_{pp} |1\rangle_{p'} \langle 0|_{p'} |0\rangle_{p'} \langle 1|_{p'} = h_{pp} |1\rangle_{p'} \langle 1|_{p'} = \frac{h_{pp}}{2} \left(I_{p'} - Z_{p'} \right)$$

$$\Rightarrow e^{-i h_{pp} a_p^\dagger a_p \delta t} = e^{\frac{-i h_{pp} \delta t}{2}} R_z(-h_{pp} \delta t)_{p'}$$

- Off-diagonal terms after JW:

$$h_{pq} a_p^\dagger a_q + h_{qp} a_q^\dagger a_p = \frac{h_{pq}}{2} \left[X_{p'} \otimes Z_{p' \to q'} \otimes X_{q'} + Y_{p'} \otimes Z_{p' \to q'} \otimes Y_{q'} \right]$$

- $\exp[-i\delta t(Z \otimes \ldots \otimes Z)]$ is diagonal in the computational basis with the phase shift $e^{\pm i\delta t}$ on the diagonal.
- The sign of this phase shift depends on the parity of the corresponding basis state ("+" if the number of ones in the binary representation is odd, "-" otherwise).



- The X and Y gates action on p' and q' qubits realized by change of the basis (e.g. Hadamard).
- The quantum gates overhead: $\mathcal{O}(M)$. Parity is not stored locally.

- **Patity mapping:**

$$|o_1 \dots o_M\rangle \to |q_M \dots q_1\rangle, \qquad q_{p'} = \left[\sum_{i=1}^{p} o_i\right] (\text{mod } 2)$$

- Now the parity is stored locally and the occupation of spin-orbitals non-locally.
- If the occupation of the first spin orbital is changed $\Rightarrow$ parities of all have to be updated. No gain, $\mathcal{O}(M)$ overhead!

- **Bravyi-Kitaev (BK) mapping:**
- Combines locality of occupation and parity information.
- The qubits store partial sums of occupation numbers:

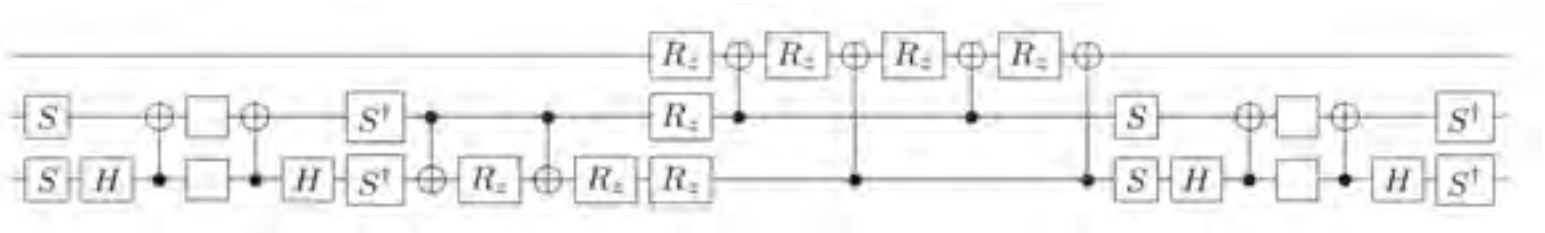
$$|o_1 \dots o_M\rangle \to |q_M \dots q_1\rangle, \qquad q_{p'} = \left[\sum_{q=1}^{p} \beta_{pq} o_q\right] (\text{mod } 2)$$

$$\begin{aligned} \beta_1 &= [1], \\ \beta_{2^{i+1}} &= \begin{pmatrix} \beta_{2^i} & \mathbf{0} \\ \mathbf{A} & \beta_{2^i} \end{pmatrix} \end{aligned}$$

$$\beta_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

- By this approach, the overhead is $\mathcal{O}(\log_2 M)$.

Quantum algorithms for chemical problems



1. Quantum phase estimation algorithm
2. Variational quantum-classical algorithms

- Important subroutine of quantum phase estimation is the *efficient* Quantum Fourier Transform (QFT).
- Classical discrete Fourier transform: $(x_0, \ldots, x_{N-1}) \to (y_0, \ldots, y_{N-1})$

$$y_k = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} x_j e^{2\pi ijk/N}$$

$$|k\rangle \xrightarrow{QFT} \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} e^{2\pi ijk/N} |j\rangle, \qquad N = 2^n, \qquad |j\rangle \equiv |j_n j_{n-1} \cdots j_1\rangle$$

- Alternatively: $U_{\mathrm{QFT}} \left(\sum_{j=0}^{N-1} x_j |j\rangle \right) = \sum_{k=0}^{N-1} y_k |k\rangle$
- QFT can be performed with $\mathcal{O}(n^2)$ number of gates $\Rightarrow$ exponential speedup, since classical FFT: $\mathcal{O}(N \log_2 N = n 2^n)$
- QFT cannot be used as an *efficient* replacement of FFT, only as a subroutine.

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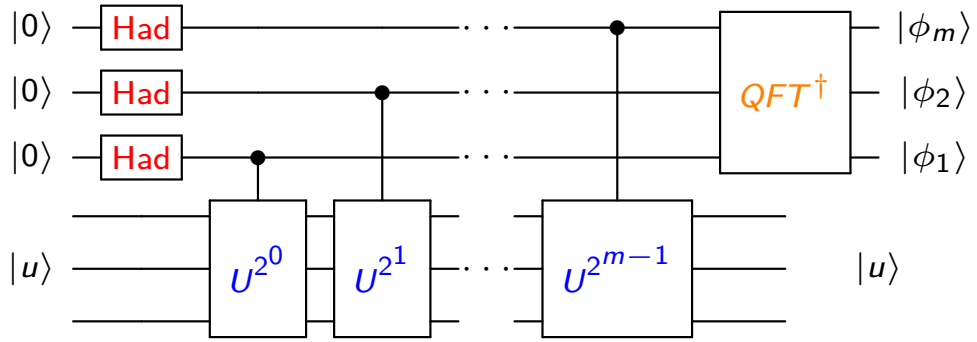
Phase estimation algorithm (PEA)

- Let's have the eigen-problem of a unitary operator U

$$U|u\rangle = e^{2\pi i\phi}|u\rangle, \qquad \phi \in \langle 0,1)\ldots \text{phase}$$

- For simplicity: $\phi = 0.\phi_1\phi_2\ldots\phi_m = \frac{\phi_1}{2} + \frac{\phi_2}{2^2} + \ldots + \frac{\phi_m}{2^m} \qquad \phi_i \in \{0,1\}$

- Quantum register: $\underbrace{|0\rangle^{\otimes m}}_{\text{read-out}} \otimes \underbrace{|u\rangle}_{\text{system}}$



$$|\text{reg}\rangle = \frac{1}{\sqrt{2^m}}\Big(|0\rangle + |1\rangle\Big)\Big(|0\rangle + |1\rangle\Big)\ldots\Big(|0\rangle + |1\rangle\Big)|u\rangle$$

$$= \frac{1}{\sqrt{2^m}}\Big(|0\rangle + e^{2\pi i 2^{m-1}\phi}|1\rangle\Big)\Big(|0\rangle + e^{2\pi i 2^{m-2}\phi}|1\rangle\Big)\ldots\Big(|0\rangle + e^{2\pi i 2^{0}\phi}|1\rangle\Big)|u\rangle = \frac{1}{\sqrt{2^m}}\sum_{j=0}^{2^m-1} e^{2\pi i j\phi}|j\rangle|u\rangle$$

$$= |2^m\phi\rangle|u\rangle$$

- We certainly do not know the *exact* eigenstate

$$|\psi_{\text{init}}\rangle = \sum_i c_i |u_i\rangle$$

- Due to the linearity of QM, the success probability is proportional to $|c_i|^2$
- PEA can be used for ground as well as excited states, but needs some reasonable approximation to the target state (QMA-complexity of a general problem).

1. Adiabatic state preparation
   - Starting with trivial H_{init} (e.g. Hartree-Fock) and register in the ground state and slowly varying to H_{exact}:

$$H = (1 - t/T)H_{\text{init}} + (t/T)H_{\text{exact}} \qquad t : 0 \longrightarrow T$$

2. Initial states provided by conventional polynomially scaling computational methods: CI, CASSCF, DMRG, etc.

- In case of Hamiltonian diagonalization, we take

$$U = e^{-iH\tau}$$

$\tau \ldots$ time-like parameter assuring $\phi \in \langle 0, 1)$

$$|\psi_{\text{init}}\rangle \xrightarrow[\text{"time evolution"}]{e^{-i\tau \mathbf{H}}} |\tilde{\psi}_{\text{init}}\rangle \xrightarrow[\tau \to E]{\text{Fourier transform}} \text{energy}$$

- Trotterization is not the only approach for approximating time evolution, more sophisticated algorithms exist.
- The overall scaling is low polynomial in M (depends on many aspects and still improving).
- PEA-based approaches require long quantum circuits $\Rightarrow$ quantum error correction, not a near-term goal.

- We explicitely do not have the Pauli operator structure of the Hamiltonian as in previous examples.
- We have the grid-based (i.e. position) representation of the wave function.

$$H = T(p) + V(r)$$

- Again the split-operator approach:

$$e^{-iH\delta t} = e^{-iT\delta t}\ e^{-iV\delta t} + \mathcal{O}(\delta t^2)$$

diagonal in a momentum repr. ← → diagonal in a position repr.

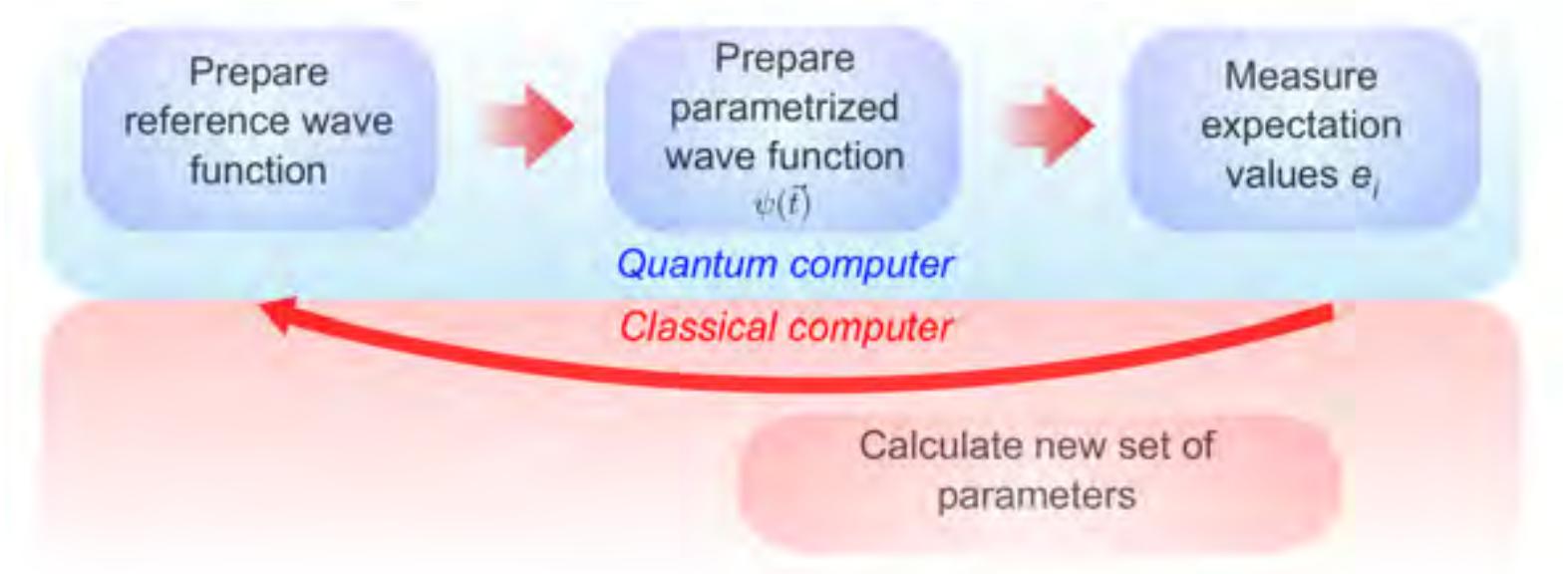
$$|\psi(\delta t)\rangle = e^{-iH\delta t}|\psi(0)\rangle \approx \mathrm{QFT}\, e^{-iT(p)\delta t}\, \mathrm{QFT}^\dagger\, e^{-iV(r)\delta t}|\psi(0)\rangle$$

Variational quantum-classical algorithms

- VQE - variational quantum eigensolver
- Promising alternative to PEA for NISQ (Noisy Intermediate-Scale Quantum) devices
- Variational energy minimization:

$$E = \min_{\vec{\theta}} \left\langle \Psi(\vec{\theta}) \middle| H \middle| \Psi(\vec{\theta}) \right\rangle$$

  - state preparation, measurement of $\left\langle \Psi(\vec{\theta}) \middle| H \middle| \Psi(\vec{\theta}) \right\rangle$ on a quantum computer
  - optimization of $\vec{\theta}$ on a classical computer
  - employes the exponential capacity of quantum registers, however, the number of $\vec{\theta}$ must be *polynomial*



- Second-quantized reprezentation of H $\xrightarrow{\text{JW or BW mapping}}$ linear combination of products of Pauli operators

$$E(\vec{\theta}) = \sum_j h_j \left\langle \Psi(\vec{\theta}) \right| \prod_i \sigma_i^j \left| \Psi(\vec{\theta}) \right\rangle \qquad \sigma_i^j \in \{I, X, Y, Z\}$$

$h_j \rightarrow$ 1-el. and 2-el. integrals

- Each measurement requires fresh $\Psi(\vec{\theta})$.
- Classical gradient or gradient-free optimization of $\vec{\theta}$
- VQE trades long coherent circuits of PEA for short circuits and loads of measurements.
- The overall scaling is again low polynomial in M (advanced methods for number of measurements reduction, still improving)

Possible parametrizations $\Psi(\vec{\theta})$ (ansatze):

1. Unitary coupled clusters

$$U(\vec{\theta}) = e^{T - T^\dagger}$$

   - Clasically intractable
   - State preparation like time evolution
   - Not exact!

2. Hardware-efficient ansatz
   - Parametrized gate set optimal for a given device
   - For first experiments

Take home messages

- Advanced computational methods for quantum computers with exponential speed-up exist!
- Most of them have been also experimentally realized.
- *Efficient* exact diagonalization via phase estimation - long term goal.
- Variational quantum-classical approaches for near term devices.