# Quantum Computation for Quantum Chemistry and Statistical Mechanics 

Quantum Computation for Chemistry Applications

## Alán Aspuru-Guzik

${ }^{a}$ Department of Chemistry and Chemical Biology, Harvard University

Towler Insitute
Vallico Soto, Italy

## Outline

- What is quantum computation? Classical vs quantum computing.
- Quantum algorithms for finding protein low energy conformations
- Quantum algorithm for molecular energies


## Quantum Simulation vs. Quantum Emulation



## Quantum Simulation vs. Quantum Emulation

Why use quantum computers?

## Quantum Simulation

- Represent the system using a classical computer
- Exact algorithm (FCI) scales exponentially with the basis set size
- Approximate algorithms (HF, DFT, QMC, CI, CC) scale polynomially


## Quantum Emulation

- Map the wave function and Hamiltonian onto another quantum system (quantum computer)
- Exploit the quantum nature of the emulator to achieve polynomial-scaling exact algorithms


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$|\phi \phi \phi\rangle$


Classical Computer


Quantum Computer

## Stages of quantum computation



| $1000>$ |
| :--- |
| $1001>$ |
| $1010>$ |
| $1011>$ |
| $1100>$ |
| $1101>$ |
| $1110>$ |
| $1111>$ |



Quantum Algorithm

| 0 | 0 | 0 |
| :--- | :--- | :--- |
| 0 | 0 | 1 |
| 0 | 1 | 0 |
| 0 | 1 | 1 |
| 1 | 0 | 0 |
| 1 | 0 | 1 |
| 1 | 1 | 0 |
| 1 | 1 | 1 |

Measurement


## Classical bits

- Always has a value of 0 or 1
- A bit can be copied
- Doesn't change if read
- Reading a bit doesn't affect other unread bits.




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classical bit quantum bit (qubit)


0


## Quantum bits (qubits)

- All items on the left can fail.
- Superposition states
$\left(a_{0}|0\rangle+a_{1}|1\rangle\right)$
where $\sum_{i} a_{i}^{2}=1$
N -qubit state

$$
\begin{array}{lll}
a_{1}|0 \ldots 01\rangle & + & a_{2}|0 \ldots 10\rangle \\
a_{3}|0 \ldots 11\rangle & +\ldots+ & a_{n}|1 \ldots 11\rangle
\end{array}
$$

## Measuring qubits

Bloch sphere representation


$$
w=a_{0}|0\rangle+a_{1}|1\rangle \equiv \cos \frac{\theta}{2}|0\rangle+e^{i \varphi} \sin \frac{\theta}{2}|1\rangle
$$

## Properties

- Project system onto $|0\rangle$ or $|1\rangle$ : $\operatorname{Pr}(0)=\left|a_{0}\right|^{2}, \operatorname{Pr}(1)=\left|a_{1}\right|^{2}$
- Probabilistic result: may require multiple measurements.


## Classical gates

## Example circuit: adder



## Quantum gates



$$
-\mathrm{H}=1 / \sqrt{2}\left[\begin{array}{cc}
1 & 1 \\
1 & -1
\end{array}\right]
$$

## Quantum circuits

## Example circuit: quantum Fourier transform



## Quantum Emulation



## Feynman's Proposal

$$
\begin{aligned}
\left|\Psi^{m o l}\right\rangle & \rightarrow\left|\Psi^{Q C}\right\rangle \\
\hat{U}^{m o l}(t)=e^{-i \hat{H}^{m o l} t} & \rightarrow \hat{U}^{Q C}(t)=e^{-i \hat{H}^{Q C} t}
\end{aligned}
$$

## Jordan-Wigner Transformation

Mapping of fermionic systems to spin systems and vice versa
R. Somma et al, Phys. Rev. A 65042323 (2002)

## Quantum Emulation III

Jordan-Wigner transformations


## Multi-zone Ion Traps

- Linear 4-rod trap

- Planar 3 electrode trap

J. Chiaverini, et al., Quant. Inf. Comp. 5, 419 (2005)
S. Seidelin, et al., Phys. Rev. Lett. 96, 253003 (2006)
K. Brown, et al., Phys. Rev. A 75, 015401 (2007)

Slide courtesy of
Ken Brown, Georgia Tech

## Josephson-Junction superconducting qubits

Quantronics group, Saclay France


## D-Wave Systems's device



Oxidized Silicon wafer using a Niobium trilayer process The Economist, February 15th, 2007 (Others: Nature, Wired, etc.)

## D-Wave Qubit Coupler



## arXiv:cond-mat/0608253

## The physics

## The Hamiltonian

Two-dimensional Ising model in a magnetic field (2DIMM):

$$
E\left(\sigma_{1}, \ldots, \sigma_{N}\right)=\sum_{j=1}^{N} h_{j} \sigma_{z}^{j}+\sum_{i<j}^{N} J_{i j} \sigma_{z}^{i} \sigma_{z}^{j}+\sum_{j=1}^{N} a_{j} \sigma_{x}^{j}
$$

where $\sigma_{z}^{i}=+1,-1$

## Procedure

- Initialize in a highly quantum state ( $a_{j}$ large)
- Turn on couplings
- As you turn off $a_{j}$ slowly
- Read-out the answer


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## Adiabatic quantum computing

## Adiabatic evolution

$$
\begin{gathered}
i \frac{d}{d t}|\Psi(t)\rangle=H(t)|\Psi(t)\rangle \\
H(t)=\left(1-\frac{t}{T}\right) H(0)+\frac{t}{T} H_{\text {problem }}
\end{gathered}
$$

## Hilbert space

$$
\left|z_{1}\right\rangle \otimes\left|z_{2}\right\rangle \otimes \cdots \otimes\left|z_{n}\right\rangle
$$

The ground state of a given spin for the field in $\mathbf{x}$ is:


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$$

The ground state of a given spin for the field in $\mathbf{x}$ is:

$$
\begin{gathered}
\frac{1}{\sqrt{(2)}}\left(|0\rangle_{1}+|1\rangle_{1}\right) \\
|\Psi(0)\rangle=\frac{1}{2^{n / 2}}\left|z_{1} z_{2} z_{3} z_{4}\right\rangle>
\end{gathered}
$$

## Adiabatic evolution pictorially



## What can it do?

Maximum independent set


## Maximum Independent Set

What is it?


## MIS of a graph <br> A MIS is the largest subset of vertices of a graph for which there is no edge connecting the two. <br> Computational complexity class <br> This problem is NP-Hard (Nondeterministic <br> Polynomial-time hard)

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A MIS is the largest subset of vertices of a graph for which there is no edge connecting the two.

## Computational complexity class

This problem is NP-Hard (Nondeterministic Polynomial-time hard)

$$
\begin{aligned}
& \text { wikipedia.org/ } \\
& \text { Independent_set }
\end{aligned}
$$

## Exact Cover

- The problem Hamiltonian $H_{p}$ is a the sum of a series of constraints, $H_{p}=\sum_{j} h_{c}$.
- Each constraint involves three bits: One must have the value 1, and the other two must have 0 value.



## Farhi et al. Science 292 (2001) 472 and

## Exact Cover

- The problem Hamiltonian $H_{p}$ is a the sum of a series of constraints, $H_{p}=\sum_{j} h_{c}$.
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Farhi et al. Science 292 (2001) 472 and arxiv. org/ 000770

## Is there an advantage?

What could a device like this really do?

## Careful!

- A quantum device like this one might do better than a classical one in certain random instances of the problem. It might not necessarily do better in other instances.
- Farhi has evidence of quadratic scaling up to 20 qubits for the SAT problem.
- We need to gather evidence for larger systems!


## Simulation of classical systems

Somma et al. arxiv:quant-ph/0609216


- Adiabatic QC is very similar to Quantum Annealing (QA) (T=0). Introduce an external transverse magnetic field (e.g. in $\mathbf{x}$ ) that is lowered with simulation time.
- Simulated Annealing (SA). Introduce a simulation temperature $T$ that is lowered with simulation time.
Kirkpatrick et al. Science 22 (1983) 671, wikipedia.org/Quantum_annealing


## Lattice Protein Models

Mapping to 2D Ising Model in a Magnetic Field


Protein Lattice Model
Image: Prof. Backofen, Uni. Freiburg

## The hydrophobic-polar (HP) model

Mapping to 2D Ising Model in a Magnetic Field

## HP is Simplest Folding Code

h = \#HH contacts

OH
O P

h=0

$\mathrm{h}=4$

$\mathrm{h}=6$

## Lau \& Dill Macromol 223986 (1989)

Slide Credit: Ken Dill

## HP model Hamiltonian (structural constraints)

Primary structure


Energy $=0$


Energy $=100$

Hydrophobic interaction


Energy = 0


Energy =-2

Onsite repulsion


Energy = 0


Energy $=100$

- $2(N-2) \log _{2} N$ N -local variables are needed!
- But our Ising model is 2-local:
- We need to convert N-local hamiltonian to 2-local


## 2-local hamiltonian scaling

## Hamiltonian reduction recipe

Replace terms of the form $\sigma_{1} \sigma_{2} \sigma_{3}$ with new ancilla variables $\tau_{i}, \alpha_{i}$ :

$$
\sigma_{1} \sigma_{2} \sigma_{3} \rightarrow \tau_{1} \sigma_{3}
$$

## Additional complexity

This procedure adds extra terms to the Hamiltonian, such as:

$$
\sigma_{1} \sigma_{2}-\left(\sigma_{1}+\sigma_{2}\right) \tau_{1}-2 \alpha_{1}\left(\sigma_{1}+\sigma_{2}-\tau_{1}+1\right)+\sigma_{1}+\sigma_{2}-\tau_{1}
$$

Scaling: $2(N-2) \log _{2} N \rightarrow 2(N-2)\left(N^{2}-\log _{2} N-1\right)$

## 2-local Hamiltonian scaling plot



About 50,000 "cheap" qubits would be needed to do what a classical computer can do right now.

## Carrying out the experiment!

The simplest HP-model case system


## Mapping the HP loop

- 2-local network obtained.
- We need a 52-bit device: 8 core bits and 46 ancilla bits.


## Partitioning the problem

The simplest HP-model case system


## Divide and "conquer"

Partitioning schemes (local search) do not guarantee finding the global minimum but have been used with success in numerical (quantum annealing) protocols.

## Spin coupling network

Locally-optimized domains

## Low energy conformations on a quantum computer

 Present and future
## Currently

- Numerical simulation of 8192 8-qubit experiments was carried out.
- Colin Truncik at D-Wave is carrying out the experiments on their quantum device.


## Near future

- Extend to continuum force fields on a lattice.
- Carry out Experiment for $\mathrm{H}_{2} \mathrm{O}$


## Part II: Quantum Chemistry by Quantum Computation

A. Aspuru-Guzik, A. D. Dutoi, P. J. Love, M. Head-Gordon, Science 309 (2005) 3741

## The quantum chemistry problem



## Molecular Hamiltonian

$$
\hat{H}^{m o l}=\hat{T}_{e}+\hat{T}_{Z}+\hat{V}_{z Z}\left(L_{p q}\right)+\hat{V}_{e e}\left(r_{i j}\right)+\hat{V}_{e Z}\left(R_{p i}\right)
$$

## Full Configuration Interaction (FCI)

## Wavefunction representation

Expand wavefunction in all HF determinants:

$$
|\psi\rangle=\alpha_{0}\left|\psi^{H F}\right\rangle+\sum \alpha_{a}^{b}\left|\psi_{a}^{b}\right\rangle+\sum \alpha_{a b}^{c d}\left|\psi_{a b}^{c d}\right\rangle+\ldots
$$

## Hamiltonian: CI Matrix

Hamiltonian is given by all matrix elements between determinants Solving the matrix eigenvalue problem for this $\binom{2 K}{N} \times\binom{ 2 K}{N}$ matrix gives exact results within the given basis.

## Basis Functions

## Options

- Hydrogenic or Atomic (Slater Type Orbitals)
- Plane waves
- Wavelets
- Localized basis (e.g. Gaussians)


## Gaussian Basis Sets

- Give compact wavefunction representations
- The exact solution within a good basis set is usually chemically accurate.


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## Gaussian Basis Sets



## FCI by Phase Estimation

## Overview



## FCI by Phase Estimation

 Overview(1) Mapping between $\left|\Psi^{\mathrm{mol}}\right\rangle$ and $\left|\Psi^{Q C}\right\rangle$
(2) Preparation of $\left|\Psi_{0}^{Q C}\right\rangle$
(3) Construct $\hat{U}^{Q C}(t)$
(4) Energy Readout (recursive phase estimation algorithm)

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4 Energy Readout (recursive phase estimation algorithm)

# The Phase Estimation Algorithm 

R. Cleve et al, Proc. R. Soc. Lond. A 454313 (1998)
D. Abrams and S. Lloyd Phys. Rev. Lett. 835162 (1999)

## Goal

Assume an unitary operator $\hat{U}$, with eigenvector $|\Psi\rangle$ such that

$$
\hat{U}|\Psi\rangle=e^{i 2 \pi \phi}|\Psi\rangle,
$$

estimate $0<\phi<1$.

## Conditions

- Must be able to prepare a state with large overlap with the eigenstate
- Must be able to gate sequence $U^{2}$


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- Must be able to gate sequence $U^{2^{a}}$


## Phase Estimation: The Fourier State



## Choose $t ; E t=-2 \pi \phi$ $$
\hat{U}(t)|\Psi\rangle=e^{-i \hat{H} t}|\Psi\rangle=e^{-i E t}|\Psi\rangle
$$

## Phase Estimation: The Fourier State



Choose $t$; $E t=-2 \pi \phi$

$$
\hat{U}(t)|\Psi\rangle=e^{-i \hat{H} t}|\Psi\rangle=e^{-i E t}|\Psi\rangle
$$

## Phase Estimation: The Inverse Fourier Transform



## The Quantum Fourier Transform

If $\phi=m / 2^{b}$

$$
\frac{1}{\sqrt{2^{b}}} \sum_{n} e^{i(2 \pi \phi) n}|n\rangle=\frac{1}{\sqrt{2^{b}}} \sum_{n} e^{i\left(2 \pi m / 2^{b}\right) n}|n\rangle
$$

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$$
\frac{1}{\sqrt{2^{b}}} \sum_{n} e^{i(2 \pi \phi) n}|n\rangle=\frac{1}{\sqrt{2^{b}}} \sum_{n} e^{i\left(2 \pi m / 2^{b}\right) n}|n\rangle=Q F T|m\rangle
$$

## Wavefunction Mapping, $\mathrm{H}_{2}$

Compact Map
Direct Map


$$
\rightarrow q \& q|0111\rangle
$$

$$
\rightarrow f-R+|0110\rangle
$$

$$
\longleftarrow
$$

$$
\leftrightarrow P \leftrightarrow \uparrow P|0101\rangle \Leftarrow
$$

$$
\rightarrow \uparrow \rightarrow+|0100\rangle
$$

$$
\rightarrow \leftarrow \text { \&와 }|0011\rangle
$$

$$
\rightarrow \leftarrow R_{\leftarrow}|0010\rangle
$$

$$
\uparrow \leftarrow \rightarrow f|0001\rangle
$$

$$
\underbrace{\sim+\sim}_{|u\rangle} \underbrace{\sim}_{|g\rangle}|0000\rangle
$$

## The Non-eigenvector Case

## Algorithm Success Probability

- We must prepare the quantum computer in the analog of the molecular ground state.
- We may not be able to construct the ground state exactly.
- Given the trial function $\left|\Psi_{T}\right\rangle$, the algorithm succeeds with probability $\left|\left\langle\Psi_{0} \mid \Psi_{T}\right\rangle\right|^{2}$.


## Options

- Use the Hartree-Fock state (for some cases,
- Adiabatic state preparation
- Other chemically motivated Ansatzes


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## Options

- Use the Hartree-Fock state (for some cases, $\left|\left\langle\Psi_{0} \mid \Psi_{0}^{H F}\right\rangle\right|^{2} \approx 0.9$ )
- Adiabatic state preparation
- Other chemically motivated Ansatzes


## Adiabatic State Preparation

If HF is a bad guess, construct the FCI solution adiabatically.


## A Short Digression: The Adiabatic Theorem

M. Born et al, Zeit. f. Phys. 5165 (1928)
E. Farhi et al, quant-ph/0001106
W. van Dam et al, Proc. $42^{\text {nd }}$ IEEE Symp. (2002)

For

$$
\hat{H}(t)=\hat{H}^{H F}+\frac{t}{T}\left(\hat{H}^{F C I}-\hat{H}^{H F}\right)
$$

if

$$
\hat{H}(0)|\Psi(0)\rangle=E_{0}^{H F}|\Psi(0)\rangle
$$

and

$$
T \gg \max _{t}\left(\frac{\left.\left|\left\langle\Psi_{X}(t)\right| \hat{H}^{F C I}-\hat{H}^{H F}\right| \Psi_{0}(t)\right\rangle \mid}{\left(E_{X}(t)-E_{0}(t)\right)^{2}}\right)
$$

then

$$
\hat{H}(T)|\Psi(T)\rangle=E_{0}^{F C l}|\Psi(T)\rangle
$$

## Adiabatic State Preparation for Molecules?

## Arguments

- Molecules are insulators
- For a given system, we know a lot of properties of the eigenvalue spectrum from approximate classical methods.
- The gap is larger than the correlation energy
- At each stage in the Cl adiabatic state preparation the gap is large
- We conjecture that levels do not cross in between turning on $n$-tuple excitations and $n+1$ tuple excitations


## State Preparation Results

## $\mathrm{H}_{2}$, STO-3G singlet manifold




## Time Evolution

## Molecular Hamiltonian

$$
\hat{H}=\sum_{X} \hat{h}_{X}=\sum_{p, q}\langle p| \hat{T}+\hat{V}_{N}|q\rangle \hat{a}_{p}^{\dagger} \hat{a}_{q}-\frac{1}{2} \sum_{p, q, r, s}\langle p|\langle q| \hat{V}_{e}|r\rangle|s\rangle \hat{a}_{p}^{\dagger} \hat{a}_{q}^{\dagger} \hat{a}_{r} \hat{a}_{s}
$$

## Trotter Expansion and Jordan-Wigner Transformation



- Number of terms in $\hat{H}$ grows as the fourth power of the basis size
- Each term involves a controlled action on at most four qubits at a time
- Absolute bound of less than 400 gates required per term


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$$

## Trotter Expansion and Jordan-Wigner Transformation

$e^{-i \hat{H} t} \approx\left[\prod_{x} e^{-i \hat{h}_{x} t / M}\right]^{M}$

$$
\hat{a}_{p}^{\dagger} \hat{a}_{q} \rightarrow \hat{X}^{p} \hat{X}^{q}\left[\prod_{i=p+1}^{q-1} \hat{\sigma}_{z}^{i}\right] \hat{P}_{0}^{p} \hat{P}_{1}^{q}
$$

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## Precision Considerations

## Qubit Requirements

Need at least $b$ bits in readout register for $b$ bits of precision

## Chemical Accuracy Requirements

For 6 decimal digits of precision at least 20 logical control qubits are needed.

## Improvement: Recursive Implementation <br> - Allows readout register size to be independent of precision <br> - Fewer consecutive coherent gates

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## Phase Estimation: A Recursive Algorithm

Get a lower bound and measure the difference . . . repeatedly ... as much as you want.


## Qubit Requirements



## Qubit Requirements

Water molecule

| water | Basis set (number of functions) |  |  |
| :--- | :--- | ---: | ---: |
|  | STO-3G (7) | $6-31 G^{*}(19)$ | cc-pVTZ (58) |
| Mapping | 8 | 25 | 42 |
| compact (singlets) <br> compact <br> direct | 10 | 29 | 47 |
|  | 14 | 38 | 116 |

## One of the best classical results <br> Exact solution of the electronic Schrödinger equation for water, within a double-polarization (TZ) basis set G. Chan et al, J. Chem. Phys. 1188551 (2003)

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Water molecule

| water | Basis set (number of functions) |  |  |
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Exact solution of the electronic Schrödinger equation for water, within a double-polarization (TZ) basis set
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## Recursive Algorithm Results

$\mathrm{H}_{2} \mathrm{O}, 196$ determinants / LiH, $\approx 1200$ determinants

Electronic Energy
$\mathrm{H}_{2} \mathrm{O}$, STO-3G
-84.293663 vs.
-84.293665

LiH, 6-31G
-9.1228936 vs.
-9.1228934

## Can we do an experiment?

Proposed experimental $\mathrm{H}_{2}$ emulation

## Circuit for an actual calculation (1929 vintage)



The gate sequence for simulation of the $\mathrm{H}_{2}$ molecule in a minimal basis requires 5 quantum bits and under 40 elementary gates.

## Can we do an experiment?

Proposed experimental $\mathrm{H}_{2}$ emulation

## Circuit for an actual calculation (1929 vintage)



The gate sequence for simulation of the $\mathrm{H}_{2}$ molecule in a minimal basis requires 5 quantum bits and under 40 elementary gates. Within reach of NMR quantum computers!

## Thank you!

## Group

Sule Atahan Ivan Tubert-Brohman Ali Najmaie Masoud Mohseni<br>Ivan Kassal Alejandro Perdomo<br>Leslie Vogt James Whitfield

Carlos Amador-Bedolla Laura Dominguez

Michael Wan


## Collaborators

Colin Truncik (D-Wave)
Anthony Dutoi (Northwestern)
Martin Head-Gordon (Berkeley)
Peter Love (Haveford)
Sabre Kais (Purdue)
Hefeng Wang (Purdue)

## The Basics

## Electronic Structure Problem

Neglect $T_{Z}$, treat $V_{z z}$ classically

$$
\hat{H}^{\text {elec }}=-\frac{1}{2} \sum_{i=1}^{N} \vec{\nabla}_{i}^{2}-\sum_{i, L} \frac{Z_{L}}{r_{i L}}+\sum_{i>j}^{N} \frac{1}{r_{i j}}
$$

## Find the energy as a function of the Nuclear Coordinates

## Solve:



## Ab Initio: only inputs are $\left\{Z_{i}\right\}, N$

Output is $E$

## The Basics

## Electronic Structure Problem

Neglect $T_{Z}$, treat $V_{Z Z}$ classically

$$
\hat{H}^{\mathrm{elec}}=-\frac{1}{2} \sum_{i=1}^{N} \vec{\nabla}_{i}^{2}-\sum_{i, L} \frac{Z_{L}}{r_{i L}}+\sum_{i>j}^{N} \frac{1}{r_{i j}}
$$

## Find the energy as a function of the Nuclear Coordinates

Solve:

$$
E|\Psi\rangle=\hat{H}^{e l e c}|\Psi\rangle
$$

Ab Initio: only inputs are $\left\{Z_{i}\right\}, N$
Output is $E$

## The Basics



## So what?

Nuclei move on the electronic potential energy surfaces surface (PES) Knowledge of PES enables:

- Minima (equilibrum structures)
- Saddle points (Transition states)
- Reaction rates and mechanisms
- PES characterize most of physical chemistry


## Traditional Mexican ceramics

The tree of life


## The tree of life

Methods for the solution of Schrödinger's equation


Figure by Jim Anderson

## The tree of life



## Basis Set Methods



## Basis Set Methods



## Basis Set Methods



## Basis Set Methods



## Basis Set Methods



## Slater Determinants

(1) Approximate multi-electron w.f. using Hydrogenic orbitals
(2) Consider Hartree-Product w.f.: $\left|\chi_{O}^{1}(1)\right\rangle \otimes\left|\chi_{O}^{3}(2)\right\rangle \otimes\left|\chi_{O}^{4}(3)\right\rangle$
(3) Neglects interactions - also ignores indistinguishability
(9) Use a Slater Determinant: complete antisymmetrization of Hartree Products


## Slater Determinants

(1) Approximate multi-electron w.f. using Hydrogenic orbitals
(2) Consider Hartree-Product w.f.: $\left|\chi_{0}^{1}(1)\right\rangle \otimes\left|\chi_{0}^{3}(2)\right\rangle \otimes\left|\chi_{0}^{4}(3)\right\rangle$
(3) Neglects interactions - also ignores indistinguishability
(9) Use a Slater Determinant: complete antisymmetrization of Hartree Products


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(1) Use a Slater Determinant: complete antisymmetrization of Hartree Products

$$
\left|\chi_{0}^{1} \chi_{O}^{3} \chi_{0}^{4}\right\rangle=\frac{1}{\sqrt{3!}} \sum_{P \in \mathcal{S}_{3}}(-1)^{\operatorname{sign}(P)} P\left[\left|\chi_{O}^{1}(1)\right\rangle \otimes\left|\chi_{O}^{3}(2)\right\rangle \otimes\left|\chi_{O}^{4}(3)\right\rangle\right]
$$

## Hartree-Fock



## Molecular orbitals

First approximation - neglect e-e interactions Hartree- Fock - treat e-e electrons at mean field level

- Given a set of orbitals compute average potential felt by each electron
- Re-solve the non-interacting problem with this effective potential
- Iterate until convergence
- Result is a set of molecular orbitals


## HF Determinants



## HF Determinants


(1) HF GS: fill first $N$ orbitals and form Slater Determinant
(2) There are $\binom{2 K}{N}$
occupancy states
(configurations)
(3) These are organized into singles, doubles, triples, etc
(4) The determinants
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## HF Determinants

| Hartree Fock Ground stat | Hartree Fock Excited state |  | HF GS: fill first $N$ orbitals and form Slater Determinant |
| :---: | :---: | :---: | :---: |
| - | $\underbrace{\ldots-\substack{\text { 2K-N virtual } \\ \text { orbitals }}}_{\square}$ |  | There are $\binom{2 K}{N}$ occupancy states (configurations) |
| $\begin{aligned} & x_{\mathrm{N}}-\mathrm{O}- \\ & -\mathrm{O}- \\ & x_{4}-\mathrm{O}- \end{aligned}$ | $\underbrace{x^{-}-}_{x_{4}-\mathrm{O-}}$ | (3) | These are organized into singles, doubles, triples, etc |
| $\begin{aligned} & x_{3} \ldots-0- \\ & x_{2}-0- \\ & x_{1}=0- \end{aligned}$ | $\begin{aligned} & x_{3} \ldots-0- \\ & x_{2}-0- \\ & x_{1}=0- \end{aligned}$ | (4) | The determinants formed from these configurations form an N -electron basis |

## Somma's mapping

And how can we use it for quantum simulation?
Definition: Spin configurations: $[z] \equiv\left|z_{1} z_{2} z_{3} z_{4}\right\rangle$
Thermodynamic variables $A$ at $T$

$$
\langle A\rangle_{T}=\frac{1}{\mathcal{Z}(T)} \sum_{[z]} e^{-\beta E[z]} A_{[z]}
$$

Example: Ising model $E[z]=J_{i j} z^{i} z^{j}$

## Classical $\rightarrow$ quantum mapping

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[z] \rightarrow|[z]\rangle
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## Classical $\rightarrow$ quantum mapping

$$
\begin{aligned}
{[z] } & \rightarrow|[z]\rangle \\
z^{i} & \rightarrow \sigma_{z}^{i} \\
A & \rightarrow \hat{A}
\end{aligned}
$$

## Some goodies

## Quantum "Thermodynamic" averages

$$
\langle\hat{\boldsymbol{A}}\rangle=\operatorname{Tr}[\rho \hat{A}]=\frac{\langle\psi(T)| \hat{\boldsymbol{A}}|\psi(T)\rangle}{\langle\psi(T) \mid \psi(T)\rangle} \equiv\langle\boldsymbol{A}\rangle_{T}
$$

But, does the Hamiltonian $[A, H]=0$ that gives the thermodynamic states exist?

## It exictol See-Henley J. of Phys. Cond. Mat 16 (2004) S891

For any classical statistical-mechanics model with a discrete state space, and endowed with a dynamics satisfying detailed balance (...) a quantum Hamiltonian can be constructed (on the same state space) such that the ground state wavefunction coincides with the classical equilibrium distribution. Furthermore the excited eigenstates correspond to classical relaxation modes (...) Quantum and classical correlation functions are related by analytic continuation to the imaginary time axis.

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## How to get the magic $C \rightarrow Q$ Hamiltonian?

## Classical master equation

$$
\frac{d p_{i}}{d \tau}=\sum_{j \neq i}\left(W_{i j} p_{j}(\tau)-W_{j i} p_{i}(\tau)\right)
$$

with $W_{i i}=-\sum_{j \neq i} W_{j i}$

## Similarity-transformed transition matrix

$$
\hat{W}(T)=e^{-\beta H / 2} W(T) e^{\beta H / 2}
$$

- Shares eigenvalues with $W(T)$


## Here it is!

$$
H_{q}(T)=I-\hat{W}(T)
$$

With this Hamiltonian_one can show that for $T>0 .|\Psi(T)\rangle$ is the

## Properties and examples

## Important results of these papers

- Thermodynamics of classical spin $1 / 2$ can be obtained from the ground state of a quantum system with classical interactions (determined by T and H ) and an external homogeneous transverse field.
- Quantum fluctuations $\Longleftrightarrow$ Classical fluctuations
- $\Psi(T \rightarrow \infty)\rangle \approx \frac{1}{2^{n / 2}}|[z]\rangle>$


## 1D Ising model

Frustrated Hamiltonian, except for $T=0$.

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## 1D Ising model

$$
H_{q}^{j}(T)=\sigma_{x}^{j}-\cosh (\beta J)-\cosh (\beta J) \sinh (\beta J)\left(\sigma_{z}^{j-1} \sigma_{z}^{j}+\sigma_{z}^{j} \sigma_{z}^{j+1}\right)-\sinh (\beta J)^{2} \sigma_{z}^{(j-1)} \sigma_{z}^{(j+1)}
$$

Frustrated Hamiltonian, except for $T=0$.

## Why do chemists care?

## Plan of attack

- An adiabatic QC like the one described above could yield quantum states that are analogous to thermodynamic states.
- One can obtain statistics for lattice models of interest to chemists at finite temperature

> Specific example of interest to us: Protein lattice models
> - We have found a mapping of the Hydrophobic-Polar model to a 2DIMM
> - Working with D-Wave for experimental realization
> - We plan to use Somma's method to study $T>0$ states of this model experimentally using their quantum device.

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## HP model

Ivan Tubert-Brohman and Colin Truncik (D-Wave) and AAG


## HP model mapping to 52 quantum bits

Ivan Tubert-Brohman and Colin Truncik (D-Wave) and AAG


## Interview with David Deutsch, Wired Magazine

## David Deutsch

I think the field doesn't need acceptability. The idea will either be valid, or not. The claim will either be true, or not. I think that the normal processes of scientific criticism, peer review and just general discussion in the scientific community is going to test this idea provided enough information is given of what this idea is. That will be quite independent of what kind of access they provide to the public. However, I think the idea of providing an interface such as you describe is a very good one. I think it's a wonderful idea....

## TeQuiLA: A High-Performance QC Simulator



## Excited states: Multiconfigurational Self-Consistent Field (MCSCF)

Work in progress: In collaboration with Sabre Kais, Purdue University

## MCSCF in a nutshell

- Choose a subspace $\mathcal{H}_{\text {MCSCF }} \subset \mathcal{H}$
- Find the optimal coefficents $C_{\mu i}$ and orbitals $\phi_{i}$ self-consistently
- Note: The orbitals will be different to the Cl orbitals (natural orbitals)


## MCSCF Equations

$$
\psi_{M C S C F}=\sum_{K} A_{K} \Phi_{K}, \quad \Phi_{K}=A \prod_{i \subset K} \phi_{i}, \quad \phi_{i}=\sum_{\mu} \chi_{\mu} C_{\mu i}
$$

## MCSCF advantages

- $\left|\left\langle\Psi_{\text {MCSCF }} \mid \Psi_{0}\right\rangle\right|^{2}>\left|\left\langle\Psi_{H F} \mid \Psi_{0}\right\rangle\right|^{2}$
- Can be prepared classically in polynomial time
- Reproduces better potential energy surfaces and excited states.
- We conjecture that it has a significative overlap with a polynomial number of states.


## State Preparation

- Use Natural orbital occupation coefficients as a guess, or
(2) Prepare the MCSCF state efficiently


## Valence active space

Capturing the important correlations


- Use near-optimal orbitals (e.g. coming out from imperfect pairing method)
- Only consider excitations of the valence electrons
- Able to treat more exciting chemical problems


## Other things we will work on next semster

 When the students join the group!
## Phase estimation

- Effect of Trotter discretization
- Finish work on effects of noise
- Excited states
- Molecular properties (polarizability, dipole moments)
- Precise gate counts and sequences for series of molecules


## Other quantum algorithms

- Finding protein low-energy conformations (Ivan Tubert-Brohman)
- Chemical reaction dynamics (Masoud Mohseni)
- Density Functional theory and correlation (Ali Najmaie)


## Conclusions and Outlook <br> "We want to use this machine in the same sense ... as a cyclotron is used in a physics laboratory" - John Von Neumann

- Quantum chemistry includes a well-defined set of problems which are optimal candidates for small quantum computers.
- Much chemical intuition available: should enable proof of conjectures about, e.g. adiabatic state preparation
- Experimental realizations - yes, please
- Use Tequila to design further small realizable examples
- Further algorithmic improvements, other eigenfunction Ansatzes, active space methods, lattice gas methods, ...


## Thank you!



Anthony Dutoi, Peter Love, Martin Head-Gordon


Kinga Partyka, James Whitfield

## Also thanks to:

- Mikko Möttönen (Factorization)
- The David Cory group (Jonathan Hodges, Troy Borneman)
- The Martin Head-Gordon group
- D-Wave Systems (funding)

Reference:
Aspuru-Guzik, Dutoi, Love and Head-Gordon Science 3095741 (2005)

## But where are we?

Active control of qubits


Steffen et al. Science 313 (2006) 1423

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## Adiabatic State Preparation

If HF is a bad guess, construct the FCI solution adiabatically.

## Open question

## Discretization effects?



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## Adiabatic State Preparation for Molecules?

## Arguments

- Molecules are insulators and they often have color (even most polymers).
- For a given system, we know a lot of properties of the eigenvalue spectrum from approximate classical methods.
- Kohn's argument against wave function theories does not lead to an exponential increase in preparation time.



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For an group of $K$ non-interacting subsystems call $S_{1}=\left|\left\langle\Psi_{0}^{1} \mid \Psi_{T}^{1}\right\rangle\right|$, then the overall overlap $S$ will decrease as $S_{1}^{K}$,

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$$
\lim _{K \rightarrow \infty}\left[1-S_{1}\right]=\frac{\ln S}{K}
$$

## The Aspuru-Guzik Group

Department of Chemistry, Harvard University

## Renewable Energy Materials

- Polymer Fuel Cell Membranes
- Nanoparticle/Organic photovoltaic materials


## Density Functional Theory development <br> - Non-local density functional theory <br> - Connections with quantum information theory

## Quantum simulation

- Quantum devices (computers and simulators) and their application to chemistry.
- Connections between quantum algorithms and physical systems.


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