Quantum computing & chemistry

Quantum computer: solves quantum problems!

$H = H^\dagger$ "Hamiltonian"

Eigenvalues E_k & Eigenvectors $|\psi_k\rangle$

energies $E_0 \leq E_1 \leq \dots$

① At zero temperature → state $|\psi_0\rangle$, ground state energy E_0

② At non-zero temperature T & equilibrium

→ state $\rho = \dfrac{e^{-\beta H}}{\mathrm{tr}[e^{-\beta H}]}$ $\beta = 1/k_B T$ thermal state

③ Dynamics: initial state $|\psi\rangle$, after time t we have $e^{-iHt}|\psi\rangle = |\psi(t)\rangle$

Plan for today

① Basic quantum chemistry

② Models & methods

③ Quantum algorithms

① Basic quantum chemistry

$\in \mathbb{R}^3$

nuclei with positions $\underset{\vec{R}}{R_1, \dots, R_{n_n}}$

electrons with positions $\underset{\vec{r}}{r_1, \dots, r_{n_e}}$ $\qquad r_i = (x_i, y_i, z_i)$

quantum state: superposition over all possible positions

$\Psi(\vec{R}, \vec{r}) \qquad \Psi \in L^2(\mathbb{R}^{3(n_n + n_e)})$ — one subtlety: spin, discuss later

$\hookrightarrow \alpha_0 |0\rangle + \alpha_1 |1\rangle \rightarrow \int dr \, \psi_r \, |r\rangle$

Hamiltonian = kinetic energy + electromagnetic interactions

$\uparrow$ laplacian $\qquad \uparrow \sim \frac{1}{|r_i - r_j|}$

$m_p / m_e \approx 1800$

↖ electrons move much faster!

Born-Oppenheimer approximation

- fix classical positions nuclei
- keep electrons quantum

$\Longrightarrow \Psi = \Psi(\vec{r})$

Hamiltonian depends on $\vec{R}$

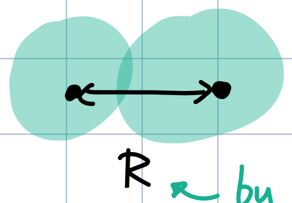
Two layer strategy:

Ⓐ given nuclear positions, find $E_0(\vec{R})$ ground state energy of $H_{\vec{R}}$

Ⓑ nuclear positions known (experiment), or minimize energy over choice of $\vec{R}$, ...

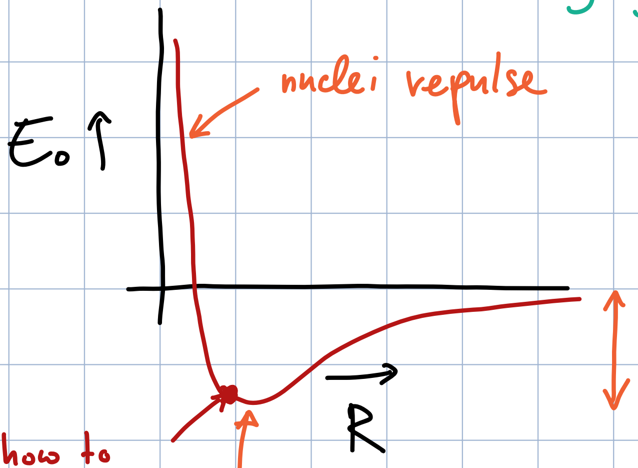
$E_0(\vec{R})$ = energy surface

Example:



(e.g. H_2)

← by symmetry, only 1D here



nuclei repulse

energy needed to break bond

how to compute 1 point here?

minimal energy configuration → stable molecule

More generally: some landscape, determines stable molecules & reaction rates

Hamiltonian:

kinetic

electron-electron

$$H\Psi(\vec{r}) = \Big[-\sum_i \left(\partial^2_{x_i} + \partial^2_{y_i} + \partial^2_{z_i}\right) + \sum_{i\neq j} \frac{1}{\|r_i - r_j\|} - \sum_{i,k} \frac{Z_k}{\|r_i - R_k\|}\Big]\Psi(\vec{r})$$

electron-nucleus

(atomic units: $\hbar = m_e = e = 1$
& ignore constant n-n interactions)

Example $n_e = n_n = 1$ hydrogen atom

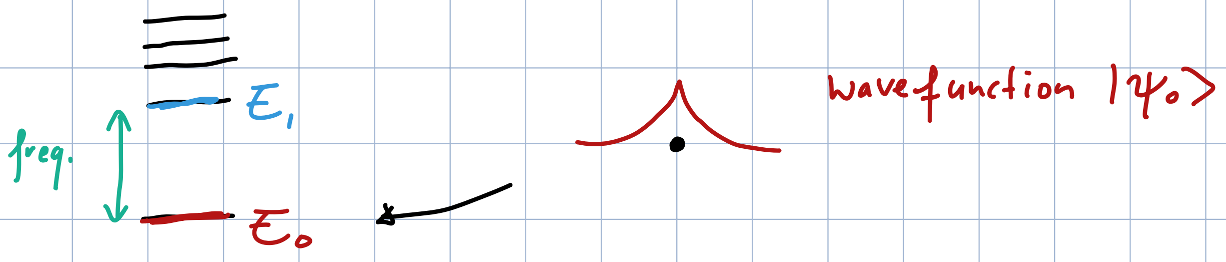
$$\Psi(x,y,z) \to \Psi(r,\theta,\phi)$$

explicit solutions ψ_k with energies E_k

orbitals are a basis for $L^2(\mathbb{R}^3)$

- electron can be in different orbital states, ground state (= lowest energy): electron is close to nucleus

- electron can jump between different states & emit photons with that energy (= frequency)



Special example: only a single particle!

electrons are fermions: antisymmetry

$$\Psi(r_1, r_2) = -\Psi(r_2, r_1)$$ for two particles

misnomer: just formalism

Second quantization & fermions

Forget about continuous degrees of freedom for a moment, consider a finite dimensional single-particle space

called 'orbitals' or 'modes'

$$\mathcal{H} = \mathbb{C}^N = \operatorname{span}\{|1\rangle, \dots, |N\rangle\}$$

think of N lowest orbitals of atom

2 particles: $\mathbb{C}^N \otimes \mathbb{C}^N$ e.g. $|p\rangle \otimes |q\rangle$ - particle 1 in state p
particle 2 in state q

$(\mathbb{C}^N)^{\otimes n}$ F_{ij} : operator swapping copies i & j

$$\Lambda^n(\mathcal{H}) = \{ |\psi\rangle \in (\mathcal{H})^{\otimes n} : F_{ij}|\psi\rangle = -|\psi\rangle \ \forall i \neq j \}$$

e.g. $\Lambda^2(\mathcal{H}) = \operatorname{span}\{|p\rangle \otimes |q\rangle - |q\rangle \otimes |p\rangle\}$

$$\mathcal{F}(\mathcal{H}) = \bigoplus_{n=0}^{N} \Lambda^n(\mathcal{H})$$

↙ vacuum, no particles

$$\Lambda^0(\mathcal{H}) := \mathbb{C} = \mathrm{span}\{|\Omega\rangle\}$$

antisymmetric projection onto $\Lambda^n(\mathbb{C}^N)$

$$\Pi_n = \frac{1}{n!}\sum_{\pi\in S_n} \mathrm{sgn}(\pi)\,\pi \qquad (\text{e.g. } \Pi_2 = I - F_{12})$$

basis $|p_1\rangle\wedge\dots\wedge|p_n\rangle := \sqrt{n!}\,\Pi_n\,|p_1\rangle\otimes\dots\otimes|p_n\rangle$ ↙ we say "orbitals $p_1,\dots,p_n$ are occupied"

↰ 0 if $p_k = p_\ell$ $k\neq\ell$

can reorder $p_1<\dots<p_n$ with only ± sign

for $p_1<\dots<p_n$

"Slater determinant"

$$\longrightarrow \begin{cases} \Lambda^n(\mathbb{C}^N) = 0 \text{ for } n>N \\ \dim(\Lambda^n(\mathbb{C}^N)) = \binom{N}{n} \\ \dim(\mathcal{F}(\mathbb{C}^N)) = \sum_{n=0}^{N}\binom{N}{n} = 2^N \end{cases}$$

if $|p\rangle$ = function $\phi_p(r)$

$$|p_1\rangle\wedge..\wedge|p_n\rangle \Rightarrow \Psi(\vec{r}) = \det\begin{bmatrix} \phi_{p_1}(r_1) & \dots & \phi_{p_1}(r_n) \\ \vdots & & \vdots \\ \phi_{p_n}(r_1) & \dots & \phi_{p_n}(r_n) \end{bmatrix}$$

e.g.
$$\det\begin{bmatrix} \phi_1(r_1) & \phi_1(r_2) \\ \phi_2(r_1) & \phi_2(r_2) \end{bmatrix} = \phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)$$

antisymmetrized wave function

Linear map $\Lambda^n(\mathcal{H}) \to \Lambda^{n+1}(\mathcal{H})$

$$a_q^\dagger : \quad |p_1\rangle \wedge \dots \wedge |p_n\rangle \mapsto \underbrace{|q\rangle}_{\text{add particle in orbital } q} \wedge |p_1\rangle \wedge \dots \wedge |p_n\rangle$$

$a_q^\dagger |p_1\rangle \wedge \dots \wedge |p_n\rangle = 0$ if $p_k = q$

Adjoint a_q removes particle from orbital q
(and $=0$ if no particle present)

Properties: $a_p^2 = 0 = (a_p^\dagger)^2$ $\quad \{a_p, a_q\} = a_p a_q + a_q a_p$

$$\overset{\Vert}{0} = \{a_p^\dagger, a_q^\dagger\}$$

$\{a_p^\dagger, a_q\} = \delta_{pq}$

i.e. $a_p^\dagger a_p + a_p a_p^\dagger = \mathbb{1}$

We can write $|p_1\rangle \wedge \dots \wedge |p_n\rangle = a_{p_1}^\dagger \dots a_{p_n}^\dagger |\Omega\rangle$

vacuum

with n particles

Number operator $n_p = a_p^\dagger a_p$

on basis : n_p acts as 0 or 1 depending on whether p is occupied

note: n_p, n_q commute

Fermions vs qubits

Idea: "occupation string" $\vec{x} = (x_1, \dots, x_N)$

$$x_p = \begin{cases} 1 & p \text{ occupied} \\ 0 & p \text{ unoccupied} \end{cases}$$

map $(\mathbb{C}^2)^{\otimes N} \longleftrightarrow \mathcal{F}(\mathbb{C}^N) \leftarrow$ recall: $\dim(\mathcal{F}(\mathbb{C}^N)) = 2^N$

$$|x_1 \dots x_N\rangle \longrightarrow (a_1^\dagger)^{x_1} \dots (a_N^\dagger)^{x_N} |\Omega\rangle$$

$N=1$: $|\Omega\rangle = |0\rangle$, $a^\dagger|\Omega\rangle = |1\rangle$

$$a^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad n = a^\dagger a = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

generally, need to be careful with signs!

$$a_p^\dagger \to \underbrace{Z \otimes \dots \otimes Z}_{p-1} \otimes \underset{p}{\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}} \otimes I \otimes \dots \otimes I \qquad Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$a_p \to \overbrace{Z \otimes \dots \otimes Z} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes I \otimes \dots \otimes I$$

This fixes $\{a_p, a_q\} = 0 = \{a_p^\dagger, a_q^\dagger\}$
& $\{a_p^\dagger, a_q\} = \delta_{pq} I$

Jordan-Wigner transformation (there are other options)

Back to electrons:

$$\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 = \mathcal{H}$$

spin (not in H, but fermionic nature makes it relevant!)

$$\phi(r) \otimes |\uparrow\rangle$$
$$\phi(r) \otimes |\downarrow\rangle$$

Hilbert space $\Lambda^n(L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$

What does the Hamiltonian look like?

Note: $$H = \sum_i I \otimes \dots \otimes h \otimes \dots I$$

position i

$$+ \sum_{i \neq j} I \otimes \dots \otimes V \otimes \dots \otimes I$$

position i & j

$$h = -(\partial_{x_i}^2 + \partial_{y_i}^2 + \partial_{z_i}^2) + \sum_k \frac{Z_k}{\|r_i - R_k\|}$$

single-particle term

$$V = -\frac{1}{\|r_i - r_j\|}$$

two-particle term

Easy calculation: restricted to $\mathcal{F}(\mathcal{H})$

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum v_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$h_{pq} = \langle p | h | q \rangle \qquad v_{pqrs} = \langle p | \langle q | V | r \rangle | s \rangle$$

Choose a basis $\phi_1, \phi_2, \dots$ of $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 = \mathcal{H}$

- Hydrogen orbitals
- Plane waves

typical: $\phi(r) \otimes |\uparrow\rangle$
$\phi(r) \otimes |\downarrow\rangle$

basis $\phi_{i_1} \wedge \phi_{i_2} \wedge \dots \wedge \phi_{i_n} = a^\dagger_{i_1} \dots a^\dagger_{i_n} |\Omega\rangle$
of $\Lambda^n(L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$

$$|p\rangle = \phi_p \otimes |\uparrow\rangle$$

$$V_{pqrs} = \int\limits_{\mathbb{R}^3}\int\limits_{\mathbb{R}^3} dr_1\, dr_2\; \overline{\phi}_p(r_1)\, \overline{\phi}_q(r_2)\, \frac{1}{\|r_1 - r_2\|}\, \phi_r(r_1)\, \phi_s(r_2)$$

Note: H does not depend on spin, but still important because of fermions & Pauli exclusion!

Mapping this to qubits:

$X = a^\dagger + a = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $Y = i(a - a^\dagger) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

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

$$\{ P_1 \otimes P_2 \otimes \dots \otimes P_N ,\ P_i \in \{I, X, Y, Z\} \}$$

form a basis for all operators on $(\mathbb{C}^2)^{\otimes N}$

$$H = \sum_{p,q} h_{pq} \, a_p^\dagger a_q + \sum_{pqrs} v_{pqrs} \, a_p^\dagger a_q^\dagger a_r a_s$$

N-qubit Pauli operators

is mapped to $H = \sum_\ell \alpha_\ell P_\ell$

sparse: # terms is $O(N^4)$
while total number of Pauli operators 4^N

so difficulty comes from electron interactions

One-body Hamiltonians are easy to solve!

$H = \sum_p \epsilon_p \underbrace{a_p^\dagger a_p}_{n_p}$ has $a_{p_n}^\dagger \dots a_{p_1}^\dagger |\Omega\rangle$

as eigenstates & energies $\epsilon_{p_1} + \dots + \epsilon_{p_n}$

Ground state: occupy all p with $\epsilon_p < 0$

$H = \sum_{pq} h_{pq} \, a_p^\dagger a_q$ $\quad h = [h_{pq}]_{p,q=1}^N$ = Herm. $N \times N$ matrix

→ choose new basis of orbitals on $\mathbb{C}^N$ which makes h diagonal!

↳ diagonalize $N \times N$ matrix h instead of $2^N \times 2^N$ matrix H

② Models & methods

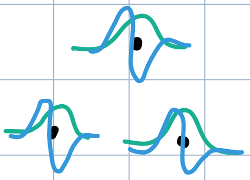
Discretize: choose finite dimensional

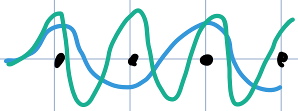
$$\mathcal{H} \subseteq L^2(\mathbb{R}^3)\otimes\mathbb{C}^2$$

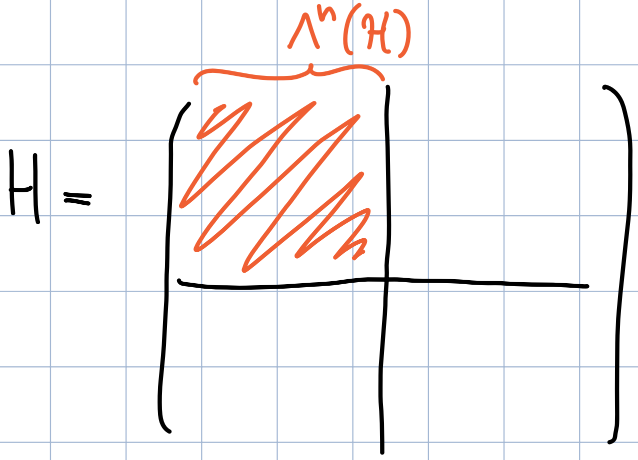
← idea: ignore orbitals which are (almost) unoccupied in ground state
also easy to ignore core electrons which are always occupied, only keep valence electrons

$$\mathcal{H} = \mathrm{span}\{\phi_1,\dots,\phi_N\} \cong \mathbb{C}^N$$

e.g. low energy atomic orbitals or plane waves

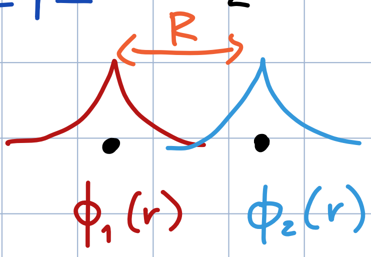






project Hamiltonian to finite subspace

Example H_2 with minimal basis



↖ take orthonormal

$$\phi_i \otimes |\uparrow\rangle, \quad \phi_i \otimes |\downarrow\rangle$$

$$\Lambda^2(\mathbb{C}^4) \quad \text{dimension} \quad \binom{4}{2} = 6$$

one-body: $\sigma, \tau \in \{\uparrow, \downarrow\}$

$$\langle 1\sigma | h | 1\tau \rangle = \langle 2\sigma | h | 2\tau \rangle = E_0 \, \delta_{\sigma\tau}$$

ignore, const. shift

$$\langle 1\sigma | h | 2\tau \rangle = \langle 2\tau | h | 1\sigma \rangle = -t \, \delta_{\sigma\tau}$$

two-body:

$$\langle 1\uparrow | \langle 1\downarrow | \, V \, | 1\uparrow \rangle | 1\downarrow \rangle = (1 \leftrightarrow 2) = U$$

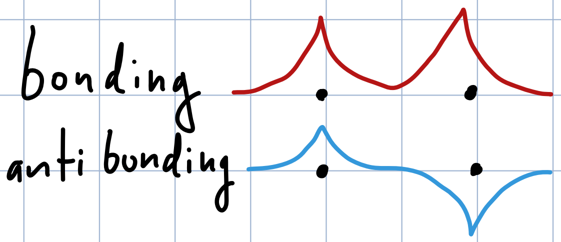
terms with 1 & 2 : smaller by ~ $1/R$ dependence

so we ignore!

$$H = \underbrace{-t \sum_{\sigma=\uparrow,\downarrow} a^\dagger_{1\sigma} a_{2\sigma} + a^\dagger_{2\sigma} a_{1\sigma}}_{h = -t\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \text{ for } \sigma = \uparrow, \downarrow} + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow})$$

if R large, t small & this term is dominant

ground state: fill $|+\rangle = \phi_1 + \phi_2$ for ↑ & ↓



$\phi_1 + \phi_2 = |+\rangle$ $\qquad |+\uparrow\rangle, |+\downarrow\rangle$

$\phi_1 - \phi_2 = |-\rangle$ $\qquad |-\uparrow\rangle, |-\downarrow\rangle$

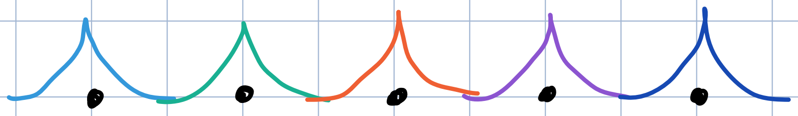
$$a^\dagger_{+\uparrow} a^\dagger_{+\downarrow} |\Omega\rangle =$$

$$\underbrace{(\phi_1(r_1) + \phi_2(r_2))(\phi_1(r_2) + \phi_2(r_2))}_{\text{symmetric}} \otimes \underbrace{(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)}_{\text{anti-symmetric}}$$

this state is close to the ground state in this example!

"covalent bonding"

Example lattice, each atom has 1 free electron



$$H = \sum_{n,\sigma} -t\left(a^\dagger_{n,\sigma} a_{n+1,\sigma} + a^\dagger_{n+1,\sigma} a_{n,\sigma}\right) + m a^\dagger_{n,\sigma} a_{n,\sigma}$$
$$+ \sum_n U n_{n,\uparrow} n_{n,\downarrow}$$

(keeping only nearest-neighbour 1-body & on-site 2-body terms!)

"Hubbard model"

& similar for 2D or 3D

this models a material
if $U=0$ → easy to solve by Fourier analysis on single-particle space
"band theory", which (in more sophisticated versions) works well in many cases.

Example suppose U is very strong, and #electrons equals #sites
$n_{n\uparrow} n_{n\downarrow}$ enforces 1 electron per site, only the spin degree of freedom remains
→ non-fermionic effective model with spins (= qubits) at each site

$(\mathbb{C}^2)^{\otimes n}$ $\qquad$ $H = \underset{\overset{\uparrow}{\text{i,j nearest neighbours}}}{\sum_{\langle i,j\rangle}} \overset{\text{term acting on qubits i,j}}{h_{ij}}$

Brief overview of classical computational methods

Variational principle: $E_0 = \min_{\| |\psi\rangle \| = 1} \langle \psi | H | \psi \rangle$

① **Hartree-Fock** (HF)

minimize over $|\psi\rangle =$ Slater determinant

↖ also optimize over choice of basis

baseline approach, cheap but not so accurate

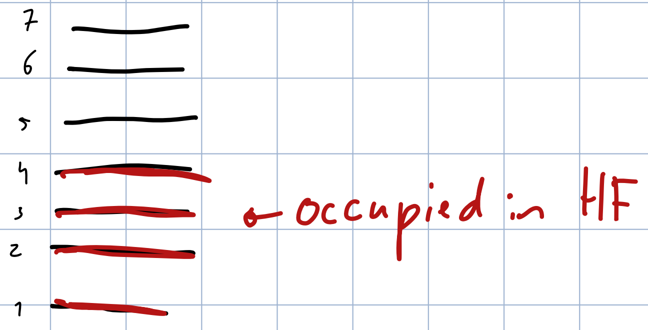
often starting point for choice of orbitals & reference state

② Solve in some subspace

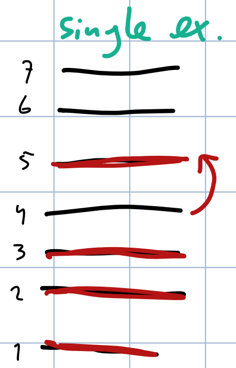
- the **full space** (given orbitals) (FCI) "full configuration interaction"
  ↳ very large!
- start from HF state $|\Phi\rangle$ & consider
  $\text{span}\{ a_p^\dagger a_q |\Phi\rangle \}$ (CIS "singles")
  $\text{span}\{ a_p^\dagger a_q^\dagger a_r a_s |\Phi\rangle \}$ (CISD "singles, doubles")
- **tensor network** states (DMRG) states with limited entanglement
- **coupled cluster**:

$$\exp\Big(\sum \underset{\overset{\uparrow}{\text{singles}}}{t_{pq}} a_p^\dagger a_q + \underset{\overset{\uparrow}{\text{doubles}}}{\ldots}\Big) |\Phi\rangle$$

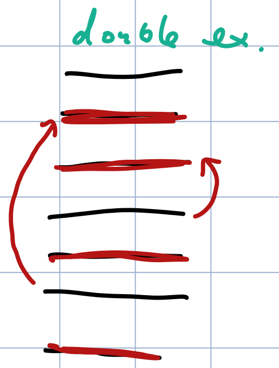
(CCSD)



$|\Psi\rangle = a_4^\dagger a_3^\dagger a_2^\dagger a_1^\dagger |\Omega\rangle$



$a_5^\dagger a_4 |\Psi\rangle$



$a_6^\dagger a_5^\dagger a_4 a_2 |\Psi\rangle$

③ Perturbation theory (PT)

HF = solution to effective one-body H, treat the remainder as "small perturbation"

④ Density functional theory (DFT)

$\Psi(r_1, \dots, r_n)$ = wave function

$\rho(r)$ = electron density = probability density you measure an electron at position r

much lower dimensional object!

Fact: $E_0 = \min_{|\psi\rangle} \langle \psi | H | \psi \rangle = \min_{\rho} F(\rho)$

but F is unknown! One can use approximations to F to good effect.

(and many more: quantum Monte Carlo, dynamical mean field theory, ...)

Why computational quantum chemistry?

Qualitative understanding

like Hubbard model

→ for characteristic models, mechanisms for reactions or properties like magnetism, superconductivity etc.

Quantitative understanding

→ given molecule/material, predict its properties correctly
  - potentially replace experiments
  - search for new molecules/materials } need accuracy + speed...
  - understand physics where experiments difficult/impossible such as outer space / earth core

→ this requires accurate model (sufficiently many orbitals) + precise solution of the model

③ Quantum algorithms

$$H = \sum_{pq} h_{pq} \, a_p^\dagger a_q + \sum_{pqrs} V_{pqrs} \, a_p^\dagger a_q^\dagger a_r a_s$$

on N orbitals

$\Rightarrow$ qubit Hamiltonian on N qubits

Goal: compute E_0 = ground state energy

There is a broad class of variational approaches, which we will ignore!

Key idea: e^{iH} = unitary & E_0 encoded as one of its phases!

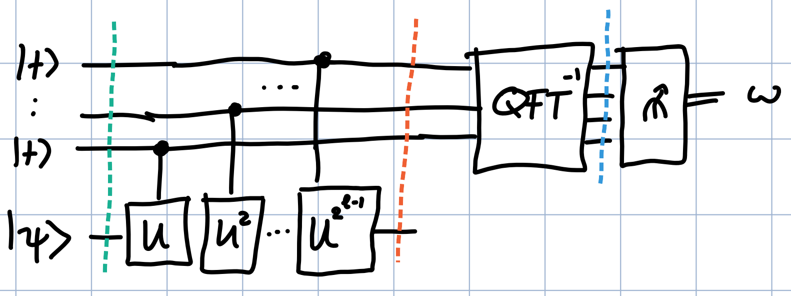
Suppose H has energies/eigenstates $\{E_k, |\psi_k\rangle\}$

& $|\psi\rangle$ is an arbitrary state, we can write

$$|\psi\rangle = \sum_k \alpha_k |\psi_k\rangle$$

Perform quantum phase estimation (QPE)

$L = 2^{\ell}$



① $$\sum_{t=0}^{L-1} |t\rangle|\psi\rangle = \sum_{t=0}^{L-1} \sum_k \alpha_k |t\rangle|\psi_k\rangle$$

② $$\sum_{t=0}^{L-1} |t\rangle e^{itH} |\psi\rangle = \sum_k \alpha_k \sum_{t=0}^{L-1} e^{itE_k} |t\rangle|\psi_k\rangle$$

③ For the sake of simplicity, assume $E_k = \frac{2\pi\omega(k)}{L}$ for integers $\omega(k)$

$$\sum_k \alpha_k |\omega(k)\rangle|\psi_k\rangle$$

So, measure $\omega(k)$ with prob $|\alpha_k|^2$

→ get ℓ bits of E_k using e^{itH} $t = 2^{\ell}$

↳ precision $\sim 2^{-\ell}$

need to repeat $\sim \frac{1}{|\alpha_0|^2}$ times to get E_0

Conclusion: E_0 to precision ε

needs e^{itH} for $\underbrace{t = O(\varepsilon^{-1})}_{\text{this is optimal}}$ & $\underbrace{|\alpha_0|^{-2} \text{ repetitions}}_{\text{this can be improved with amplitude amplification}}$

Need two things!

① A guiding state $|\psi\rangle$ with $|\langle\psi|\psi_0\rangle|^2 = |\alpha_0|^2$ not too small

② Implement e^{itH} on quantum computer

① Guiding state

A random state will have $|\langle\psi|\psi_0\rangle|^2 \sim \exp(-N)$ on N qubits so this gives exponential cost...

Local Hamiltonian ground state energy

$$\underbrace{\text{given } H = \sum_n h_n \text{, compute } E_0}_{\text{this problem is QMA-hard}}$$

lecture Tony: quantum version of NP, strongly believed to be hard for quantum computers

This remains true when restricted to electronic structure type problems: e.g. Hubbard model with tunable interactions

$\Rightarrow$ QMA-hard to find guiding states with

$$|\langle\psi|\psi_0\rangle| = 1/\text{poly}(N)$$

(since QPE is efficient, gives a poly(N) algo)

Conclusion: no black-box solution to find $|\psi\rangle$, depends on the problem at hand!

Some reasons for optimism:

- the 'hard cases' constructed in the proof of QMA-hardness are very artificial, with strong interactions
- classical Hartree-Fock is NP-hard, but works well in practice
- wealth of classical methods that give potential guiding states, numerical evidence seems positive for molecules, harder to judge for materials
- molecules & materials that occur naturally: if Nature can prepare them, it should be efficient to simulate
- in many cases, adiabatic preparation works well: H_t is a path of Hamiltonians, with H_0 easy to solve and $H_1 = H$ the target Hamiltonian. Start with $|\psi_0\rangle$, ground state for H_0, and evolve along slowly changing H_t. If you go slow enough, you end with a state close to the ground state of $H = H_1$.

  Note: in general, it is possible you need to go exponentially slow... but in practice this often works well.

Power of quantum computer vs classical methods:

once you have a good guiding state, you can reach guaranteed precision with QPE in polynomial time

② Hamiltonian simulation

The key subroutine is Hamiltonian simulation:
simulate the unitary $U = e^{iHt}$ as a quantum circuit

↳ note: this is of interest not just as subroutine for QPE, but also to directly simulate time evolution of quantum systems.

$H = \sum_{\ell=1}^{L} h_\ell$, h_ℓ is simple but e^{itH} need not be...

In general, if f is a function, define $f(H)$
by $f(H) = \sum_k f(E_k) |\psi_k\rangle\langle\psi_k|$ (i.e. apply to eigenvalues)
or by Taylor expansion, e.g. $e^{itH} = \sum_{n=0}^{\infty} \frac{(itH)^n}{n!}$

Trotterization

$$e^{i\delta\sum_\ell h_\ell} = \prod_\ell e^{i\delta h_\ell}$$

← assume $e^{i\delta h_\ell}$ has exact quantum circuit

false if the h_ℓ do not commute!

However, consider a short time δ, then

$$e^{i\delta\sum_\ell h_\ell} = I + i\sum_\ell h_\ell \delta + O(\delta^2)$$

$$\prod_\ell e^{i\delta h_\ell} = \prod_\ell \left(I + i h_\ell \delta + O(\delta^2)\right)$$

$$= I + i \sum_\ell h_\ell \delta + O(\delta^2)$$

So, $$e^{i\delta \sum_\ell h_\ell} = \prod_\ell e^{i\delta h_\ell} + O(\delta^2)$$

$$\left\| e^{i\delta \sum_\ell h_\ell} - \prod_\ell e^{i\delta h_\ell} \right\|_\infty = O(\delta^2)$$

For large t, break into r small time steps

$$e^{itH} = \left(e^{i\frac{t}{r}H}\right)^r$$

$$= \left(\prod_\ell e^{i\frac{t}{r}h_\ell} + O\left(\left(\frac{t}{r}\right)^2\right)\right)^r$$

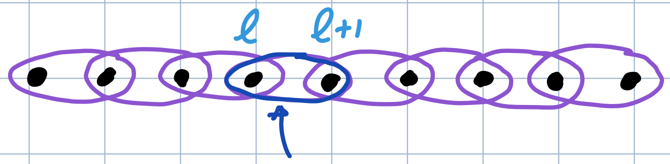
$$= \left(\prod_\ell e^{i\frac{t}{r}h_\ell}\right)^r + O\Big(\underbrace{r\cdot\left(\frac{t}{r}\right)^2}_{\frac{t^2}{r}}\Big)$$

error $= \varepsilon \rightarrow$ choose $r \sim \frac{t^2}{\varepsilon}$

note: "$O(\frac{t^2}{r})$" hides dependence on $H = \sum_\ell h_\ell$

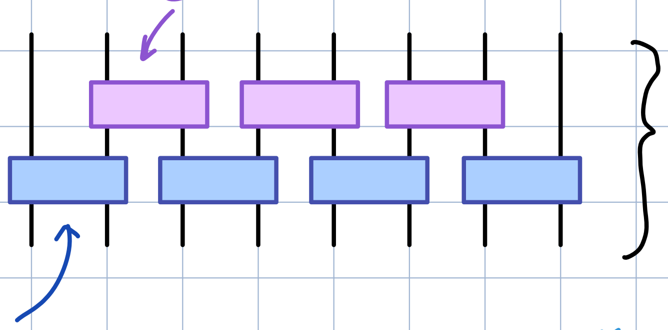
Conclude: simulate e^{itH} to error ε using $O(L t^2 \varepsilon^{-1})$ uses of $e^{i\delta h_\ell}$

Typical example: $H = \sum_{\ell=1}^{L} h_{\ell,\ell+1}$



$$h_{\ell,\ell+1} = \underbrace{I \otimes \dots \otimes I}_{\ell-1} \otimes \underbrace{h_{\ell,\ell+1}}_{\ell,\ell+1} \otimes \underbrace{I \otimes \dots}_{>\ell+1}$$

$e^{i\delta h_{2,3}}$



$\Bigg\} \prod_{\ell} e^{i\delta h_{\ell,\ell+1}}$

$e^{i\delta h_{1,2}}$ = 2-qubit gate

repeat many of these layers!

Can also have higher-order variants, e.g.

$$\prod_{\ell=1}^{L} e^{i\frac{\delta}{2}h_\ell} \prod_{\ell=L}^{1} e^{i\frac{\delta}{2}h_\ell}$$ also gets $O(\delta^2)$ term right

$$\to r = O(t^{3/2}\varepsilon^{-1/2})$$

Pro:

- shows e^{itH} can be simulated
- conceptually easy
- works well in practice for lattices with local interactions

Con:

- scaling $t^2\varepsilon^{-1}$ suboptimal (also higher orders suboptimal)
- chemistry: as many as $L \approx N^4$ terms
- "$O(Lt^2\varepsilon^{-1})$" hides some dependence on H

Qubitization

Actually, in QPE can replace e^{iH} by $e^{if(H)}$ for some function f, get $f(E_0) \to$ deduce E_0

it turns out that $e^{i\arcsin(H)}$ is convenient!

Different model for $H=\sum_\ell h_\ell$ with h_ℓ simple

$$H=\sum_{\ell=0}^{L-1} c_\ell U_\ell$$

linear combination of unitaries (LCU)

U_ℓ unitary on N qubits

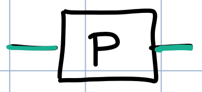
$c_\ell \geq 0$

Consider two operations, acting on

— log(L) qubits
basis $|0\rangle, \dots, |L-1\rangle$

— N qubits

① P



"prepare"

$$P|0\rangle = \sum_{\ell=0}^{L-1} \sqrt{\frac{c_\ell}{\lambda}}\,|\ell\rangle$$

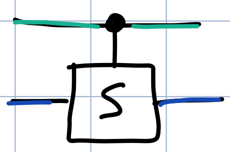
$$\lambda = \sum_\ell c_\ell$$

makes sure the state is normalized

for now, set $\lambda = 1$

and $P|\ell\rangle$ is anything you like for $\ell \neq 0$

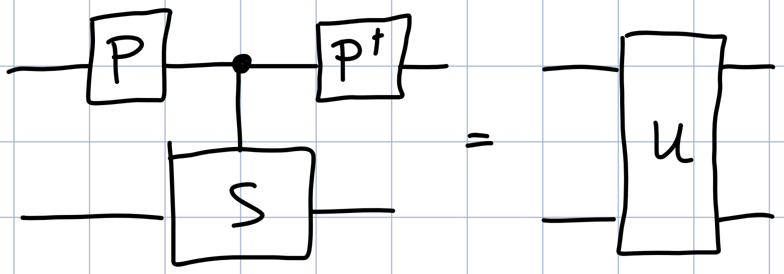
② S



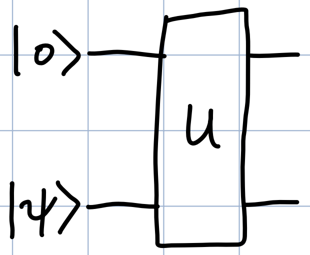
"select"

controlled on ℓ, apply U_ℓ

$$= \sum_{\ell=0}^{L-1} |\ell\rangle\langle\ell| \otimes U_\ell$$



is such that



$$|0\rangle|\psi\rangle \xrightarrow{P} \sum_\ell \sqrt{c_\ell}\,|\ell\rangle|\psi\rangle$$

$$\xrightarrow{S} \sum_\ell \sqrt{c_\ell}\,|\ell\rangle\, U_\ell|\psi\rangle$$

$$\xrightarrow{P^\dagger} |0\rangle \underbrace{\sum_\ell c_\ell U_\ell}_{H}|\psi\rangle + |\psi^\perp\rangle$$

orthogonal to $|0\rangle$ in first register (not normalized)

Known as a block encoding: $(\langle 0|\otimes I)\,U\,(|0\rangle\otimes I) = H$

$$U = \left(\begin{array}{c|c} H & * \\ \hline * & * \end{array}\right)$$

Let $R = 2|0\rangle\langle 0| - I$ on the auxilliary system

reflection

$$\hookrightarrow \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix}$$

$|0\rangle \to |0\rangle$

$|\ell\rangle \to -|\ell\rangle \quad \ell \neq 0$

& assume each U_ℓ is s.t. $U_\ell^2 = I$

(for example true for Pauli matrices)

$$R^2 = I, \quad U^2 = PS\underbrace{P^\dagger P}_{=I}SP^\dagger = P\underset{\overset{\|}{I}}{S^2}P^\dagger = PP^\dagger = I$$

energy E_k eigenstate

now normalized

$$U|0\rangle|\psi_k\rangle = E_k|0\rangle|\psi_k\rangle + \sqrt{1-E_k^2}\,|\psi_k^\perp\rangle$$

$R|\psi_k^\perp\rangle = -|\psi_k^\perp\rangle$

RU maps $|0\rangle|\psi_k\rangle \to E_k|0\rangle|\psi_k\rangle - \sqrt{1-E_k^2}\,|\psi_k^\perp\rangle$

$$RU|\psi_k^\perp\rangle = RU\left(\frac{1}{\sqrt{1-E_k^2}}\left(U|0\rangle|\psi_k\rangle - E_k|0\rangle|\psi_k\rangle\right)\right)$$

$$= \frac{1}{\sqrt{1-E_k^2}}\left[|0\rangle|\psi_k\rangle - E_k R\left(E_k|0\rangle|\psi_k\rangle + \sqrt{1-E_k^2}\,|\psi_k^\perp\rangle\right)\right]$$

$$= \frac{1-E_k^2}{\sqrt{1-E_k^2}}|0\rangle|\psi_k\rangle + E_k|\psi_k^\perp\rangle$$

$$= \sqrt{1-E_k^2}\,|0\rangle|\psi_k\rangle + E_k|\psi_k^\perp\rangle$$

Conclusion: on span$\{|0\rangle|\psi_k\rangle, |\psi_k^\perp\rangle\}$

$W = RU$ acts as $W = \begin{pmatrix} E_k & \sqrt{1-E_k^2} \\ -\sqrt{1-E_k^2} & E_k \end{pmatrix}$

rotation

$\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$

$\theta = \arccos(E_k)$

has eigenvalues $e^{\pm i \arccos(E_k)}$

So, apply QPE to find $\arccos(E_0)$

An extension (quantum singular value transformation) can be used to implement e^{itH} at cost $O(t + \log(\varepsilon^{-1}))$ (which is optimal).

We set $\lambda = 1$, equivalent to $H \to \frac{H}{\lambda}$

$E_0 \to \frac{E_0}{\lambda}$ $\quad$ E_0 to precision $\varepsilon \to \frac{E_0}{\lambda}$ to precision $\frac{\varepsilon}{\lambda}$

Cost of QPE : $O(\frac{\lambda}{\varepsilon})$ iterations of W

Concrete resource estimates

For FeMoco (part of a nitrogen fixation protein, challenging for classical methods)

$N \approx 100$ orbitals needed (localized atomic orbitals)

Trotter : $\sim 10^{12}$ Toffoli gates

Qubitization $\sim 10^{8} - 10^{9}$ Toffoli gates

↳ with various tricks & optimizations!

& ~ 1000 logical qubits

Quantum signal processing

Recall: RU implements $W(x) = \begin{pmatrix} x & \sqrt{1-x^2} \\ \sqrt{1-x^2} & x \end{pmatrix}$

let $e^{i\phi R} = \begin{pmatrix} e^{+i\phi} & & & \\ & e^{-i\phi} & & \\ & & e^{-i\phi} & \\ & & & \ddots \end{pmatrix}$ $x = E_k$

Can consider $e^{i\phi_n R} W(x) \ldots e^{i\phi_2 R} W(x) e^{i\phi_1 R}$

$$\begin{gathered} \| \\ \begin{pmatrix} P(x) & Q(x)\sqrt{1-x^2} \\ \overline{Q(x)}\sqrt{1-x^2} & \overline{P(x)} \end{pmatrix} \end{gathered}$$

for polynomials $P(x), Q(x)$ of degree n

Fact: can make any deg. n polynomials P, Q s.t.

① $\forall x \in [-1, 1]$ $|P(x)|^2 + (1-x^2)|Q(x)|^2 = 1$

② P is even/odd when n is even/odd, and Q is odd/even.

Note: clear that P, Q need to satisfy these conditions

Hamiltonian simulation: $\left.\begin{array}{l} P(x) \approx \cos(tx) \\ P(x) \approx \sin(tx) \end{array}\right\}$ $e^{itx} = \cos(tx) + i\sin(tx)$

error $\varepsilon \to$ degree $n = O(t + O(\log(\varepsilon^{-1}))$

References

absolutely not comprehensive... but you will find many more references in the review articles!

Review articles:

arXiv: 1808.10402
arXiv: 1812.09976
arXiv: 2001.03685

A perspective on the hardness of chemistry in practice
arXiv: 2208.02199

Hamiltonian simulation
Chapter 9 in lecture notes Ronald
arXiv: 1912.08854 (technical details Trotterization)
arXiv: 1805.03662 (qubitization for electronic structure)