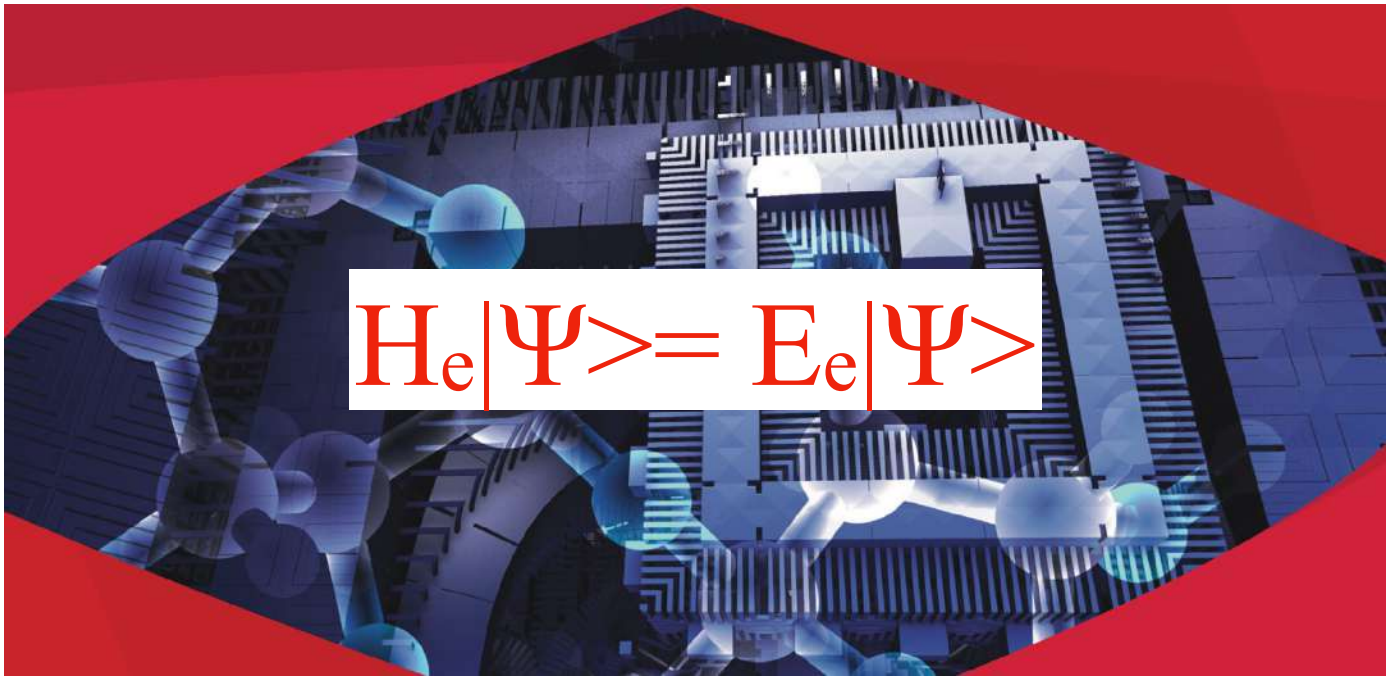
Quantum Chemistry on a Quantum Computer



Artur Izmaylov

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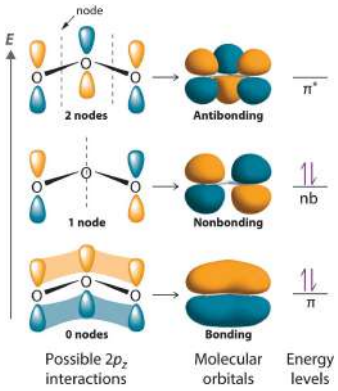
New hope: Digital quantum computers

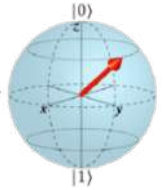


$$\hat{H}_e(\mathbf{R})\,|\Phi_j(\mathbf{R})\rangle = E_j(\mathbf{R})\,|\Phi_j(\mathbf{R})\rangle$$

$$|\Phi_j(\mathbf{R})\rangle = \sum_{\bar{n}}^{2^{No}} C_{\bar{n},j}\,|n_1, n_2, \ldots n_{N_o}\rangle,\ \ n_i = \{0,1\}$$

For |Ψ>: occupations to qubit orientations

|1100> → |↑↑↓↓>



Entanglement

|Ψ> = α|↑↑>+β|↓↑>+ γ|↑↓> + δ|↓↓>

N qubits can store 2^N complex numbers

Quantum Algorithms

"Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical…

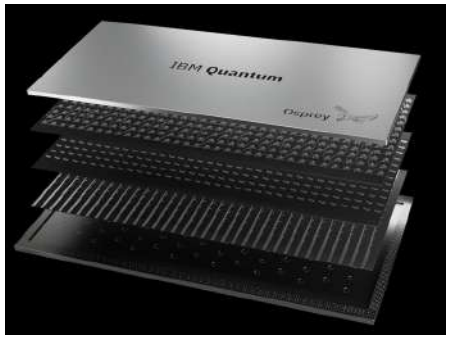
$$|\text{answer}\rangle = U|\text{question}\rangle$$

$$U = U_1 \ldots U_n$$

…and by golly it's a wonderful problem, because it doesn't look so easy."

Quantum Computers: What can they do?

Short answer: not much (in spite of all the hype)

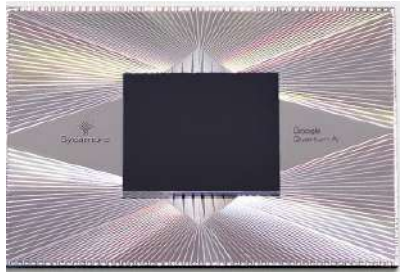


IBM 433Q

|answer>= U|question>

U = $U_1 \ldots U_n$

Error correction is needed



Google 72Q

Error correction: 1-10K qubits for 1 "corrected qubit" ~ 1M qubits

Expectations: hardware will come, develop algorithms for quantum advantage

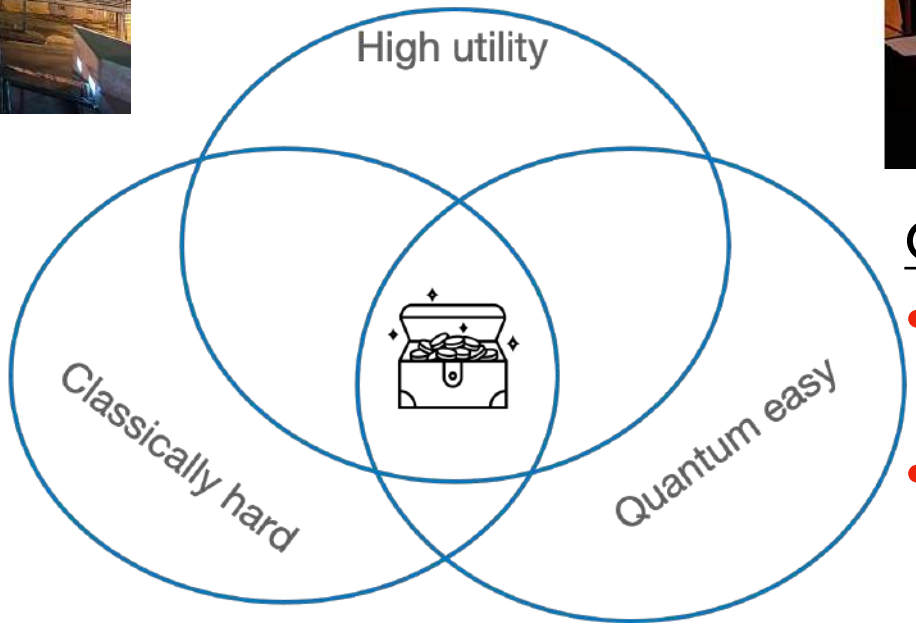
Another possibility: quantum inspired methods for classical computers

Quantum Sci. Technol. **6** (2021) 024012

Quantum Advantage in Quantum Chemistry

Chemical space:

- Catalysts
- OLEDs



Classical heuristics:

inaccurate (DFT) or expensive (DMRG, MRCI, stochastic methods,…)

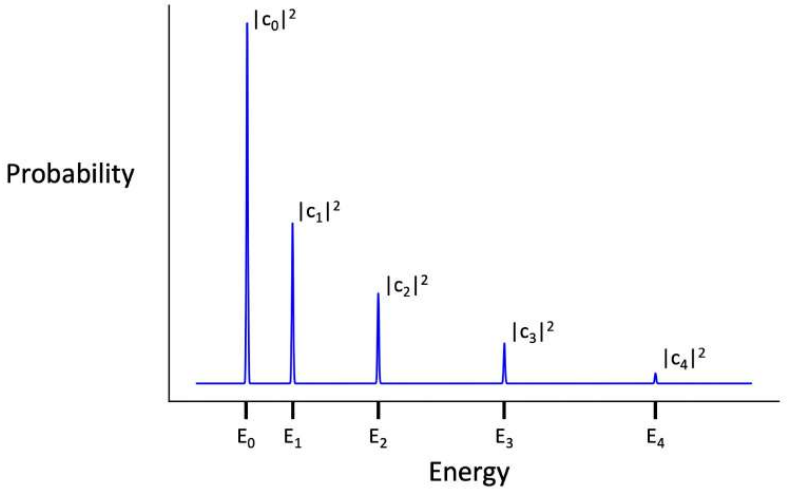
Quantum methods:

- What makes system "quantum easy"?
- Different algorithms different complexities

Quantum Phase Estimation

$$\hat{H}\,|\phi_n\rangle = E_n\,|\phi_n\rangle$$

$$|\psi\rangle = \sum_n c_n\,|\phi_n\rangle$$



$$\int \langle\psi\, e^{-i\hat{H}t}\, |\psi\rangle\, e^{i\omega t}\mathrm{d}t = \sum_n |c_n|^2 \delta(E_n - \omega)$$

Q1: How to prepare the initial state?

Q2: How to propagate?

Outline

$$\int \langle\psi| e^{-i\hat{H}t} |\psi\rangle e^{i\omega t} \mathrm{d}t = \sum_n |c_n|^2 \delta(E_n - \omega)$$

- Variational Quantum Eigensolver (near-term / quantum inspired)
  - State preparation: Qubit Coupled Cluster ansatz
  - Measurement

- Quantum Phase Estimation (assuming error correction)
  - Trotterization (cost ~ t^2)
  - Linear Combination of Unitaries (cost ~ t)

Fermion-qubit mapping

$$\hat{H}_e = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \sum_{pqrs} g_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

Polynomial scaling of # of integrals with system size is another reason to use quantum computing

Jordan-Wigner (1928):

$$\hat{a}_j \rightarrow (\hat{x}_j - i\hat{y}_j) \otimes \hat{z}_{j-1} \ldots \otimes \hat{z}_1$$

$$\hat{a}_j^\dagger \rightarrow (\hat{x}_j + i\hat{y}_j) \otimes \hat{z}_{j-1} \ldots \otimes \hat{z}_1$$

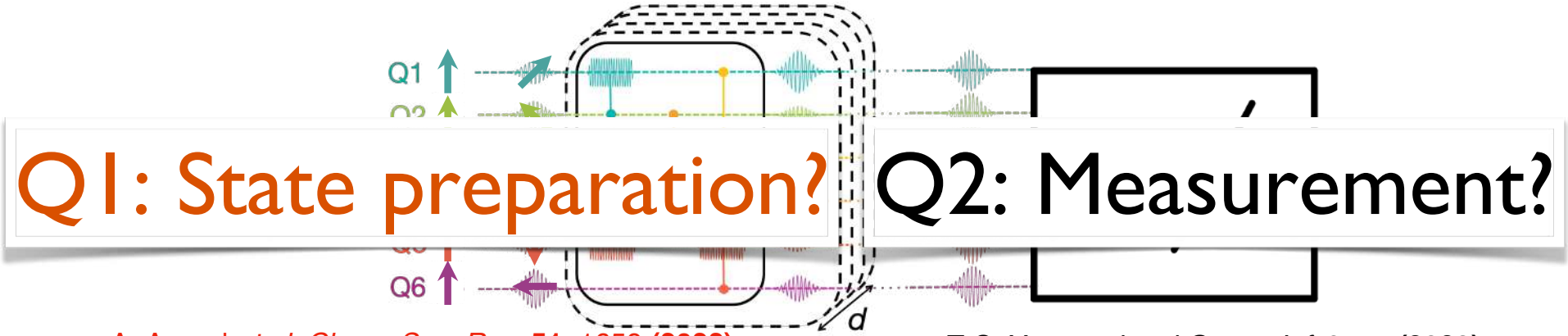
$$\hat{x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{y} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \qquad \hat{z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Iso-spectral to H_e qubit-Hamiltonian:

$$\hat{H}_q = \sum_k c_k \hat{P}_k, \quad \hat{P}_k = \prod_i \hat{\sigma}_i, \quad \hat{\sigma}_i = \{\hat{x}_i, \hat{y}_i, \hat{z}_i\}$$

1. Variational Quantum Eigensolver

$$E_e = \min_{\theta} \langle 0|U(\theta)' H_q U(\theta)|0\rangle$$



Q1: State preparation?

Q2: Measurement?

A. Anand *et al. Chem. Soc. Rev.* **51**, 1659 **(2022)**

T.C. Yen *et al. npj Quant. Inf.* **9**, 14 **(2023)**

$|0\rangle$ $U(\theta)|0\rangle$ H_q measurements

classical computer

$$\min_{\theta} \langle 0|U(\theta)' H_q U(\theta)|0\rangle$$

Alan Aspuru-Guzik *et al. Nat. Commun.* **5**, 4213 (2014)

More on VQE: *Chem. Rev.* ***2019***, *119, 10856* *Rev. Mod. Phys.* ***2020***, *92, 015003*

1.1 State preparation

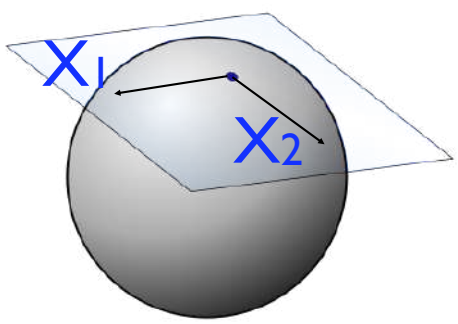
$U_e|\Phi_e\rangle$ (fermions) → $U_q|\Phi_q\rangle$ (qubits) → Sequence of gates $|0\rangle$

(hardware-efficient)

$$\hat{U}(\bar{\theta}) = \prod_k e^{\theta_k \hat{X}_k}, \;\; \hat{X}_k^\dagger = -\hat{X}_k$$

Which X's and in what order?

H= H_0+V:



$\hat{A}_+$

$$[\hat{H}_0, \hat{A}_\pm] = \lambda_\pm \hat{A}_\pm$$

raising/lowering

Energy gradient wrt X's amplitude (θ): $\frac{d}{d\theta}\langle\Phi|e^{-\theta\hat{X}}\hat{H}e^{\theta\hat{X}}|\Phi\rangle\Big|_{\theta=0} = \langle\Phi|[\hat{H},\hat{X}]|\Phi\rangle$

Fermionic and Qubit Algebras

$$\hat{U}(\bar{\theta}) = \prod_k e^{\theta_k \hat{X}_k}, \;\; \hat{X}_k^\dagger = -\hat{X}_k$$

Fermionic algebra

$|\Phi_e\rangle$ Hartree-Fock

$$\hat{X}_k = \hat{a}_a^\dagger \hat{a}_i - \hat{a}_i^\dagger \hat{a}_a, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j - \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_b \hat{a}_a, \ldots$$

Methods: UCC, ADAPT-VQE, GUCC…

Qubit algebra

$|\Phi_q\rangle$ simple product state

$$\hat{X}_k = i \bigotimes_{j=1}^{N} \hat{\sigma}_j, \quad \hat{\sigma}_j = \hat{x}_j, \hat{y}_j, \hat{z}_j, \hat{1}_j$$

Methods: QCC, Qubit-ADAPT,…

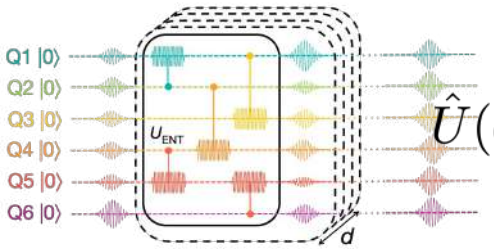
Ryabinkin et al. *JCTC* 16, 1055 (2020)

symmetry conservation

gate cost

A. Anand *et al. Chem. Soc. Rev.* **51**, 1659 **(2022)**

Two-qubit gate count: QCC vs UCCSD



$$\hat{U}(\bar{\theta}) = \prod_k e^{\theta_k \hat{X}_k}, \quad \hat{X}_k^\dagger = -\hat{X}_k$$

$$\hat{X}_k = \hat{a}_a^\dagger \hat{a}_i - \hat{a}_i^\dagger \hat{a}_a, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j - \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_b \hat{a}_a$$

$$\hat{X}_k = i \bigotimes_{j=1}^{N} \hat{\sigma}_j$$

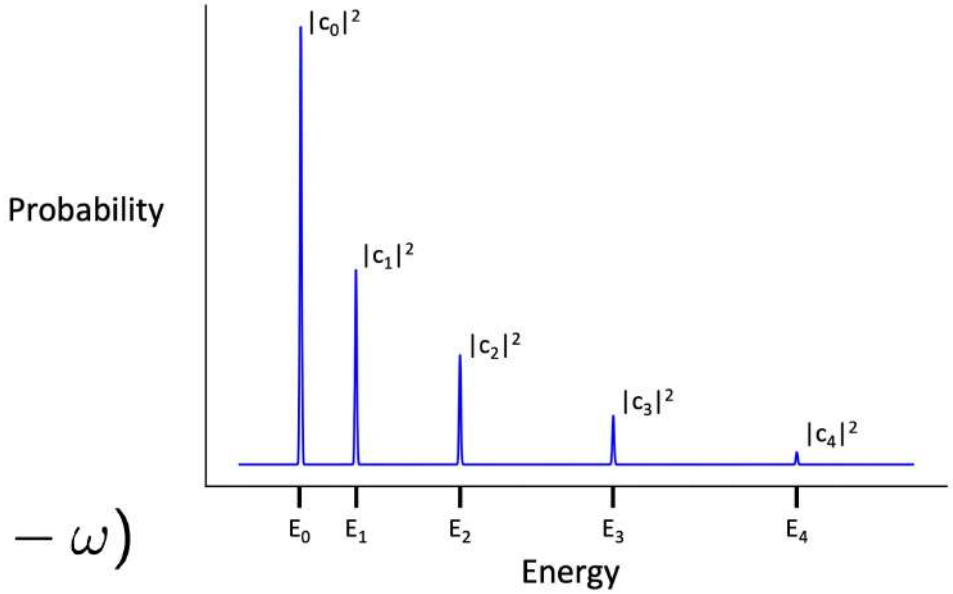
Ryabinkin et al. *JCTC* 14, 6317 (2018)

2.Unitary evolution

$$\hat{H}\,|\phi_n\rangle = E_n\,|\phi_n\rangle$$

$$|\psi\rangle = \sum_n c_n\,|\phi_n\rangle$$

$$\int \langle\psi|\, e^{-i\hat{H}t}\,|\psi\rangle\, e^{i\omega t}\mathrm{d}t \;=\; \sum_n |c_n|^2\delta(E_n-\omega)$$



Unitaries! Can be done on a quantum computer

2.1 Trotterization

$$\boxed{e^{-it\hat{H}}} = e^{-it\sum_n \hat{H}_n} = \lim_{K\to\infty}\left(\prod_n e^{-i\frac{t}{K}\hat{H}_n}\right)^K$$

H_n Hamiltonians: easy to bring to the diagonal form

$$\hat{H}_n = \hat{U}_n^\dagger \hat{Z}_n \hat{U}_n \qquad e^{-it\hat{H}_n} = \hat{U}_n^\dagger e^{-it\hat{Z}_n}\hat{U}_n$$

Diagonal:

$$\hat{Z}_n = \sum_i a_i \hat{z}_i + \sum_{ij} b_{ij}\hat{z}_i\hat{z}_j + \ldots \qquad \text{qubits}$$

$$\hat{Z}_n = \sum_i c_i \hat{n}_i + \sum_{ij} d_{ij}\hat{n}_i\hat{n}_j + \ldots \qquad \text{fermions}$$

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$$

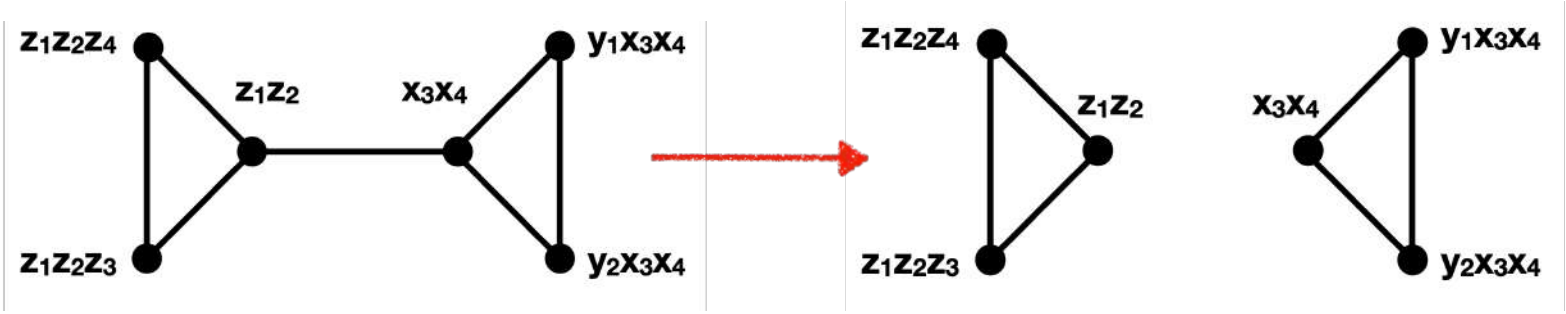
What Hamiltonians can we rotate to the diagonal form?

Qubit algebra: Commuting Pauli products

(Qubitization-then-partitioning)

$$\hat{H}_n = \sum_k c_k \hat{P}_k, \qquad \hat{H} = \sum_n \hat{H}_n$$

$$\left[\hat{P}_k, \hat{P}_{k'}\right] = 0 : \qquad \hat{U}^{\dagger}_{\text{Cliff}} \hat{H}_n \hat{U}_{\text{Cliff}} = \hat{Z}_n$$



Verteletskyi, et al. *J. Chem. Phys.* 152 124114 **(2020)**

Yen, et al. *J. Chem. Theory Comput.* 16, 190 **(2020)**

Hamiltonian decomposition: Fermionic algebra

(Partitioning-then-qubitization)

$$\hat{H} = \sum_n \hat{H}_n$$

Hartree-Fock solvable fragments

1e : $$\hat{h}_{1e} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q = \hat{U}_{\rm HF}^\dagger \left(\sum_p \epsilon_p \hat{n}_p \right) \hat{U}_{\rm HF}$$

$$\hat{U}_{\rm HF} = \prod_{p>q} e^{\theta_{pq}(\hat{a}_p^\dagger \hat{a}_q - \hat{a}_q^\dagger \hat{a}_p)}$$

occ. number

$\hat{n}_i \to \hat{z}_i$

orbital rotations

1e+2e: $$\hat{H}_{\rm HF} = \hat{U}_{\rm HF}^\dagger \left(\sum_{pq} \lambda_{pq} \hat{n}_p \hat{n}_q \right) \hat{U}_{\rm HF}$$

Yen & Izmaylov, PRX Quantum 2, 040320 **(2021)**

Which fragments are better, Qubit or Fermionic?

$$\hat{H} = \sum_n \hat{H}_n$$

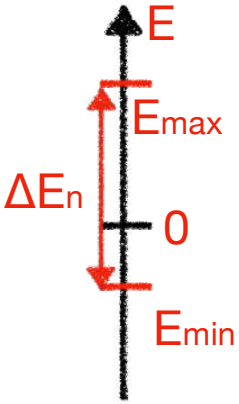
Practical choice: 1st order Trotter

$$e^{-iHt} \approx \prod_n e^{-iH_n t} = \prod_n \hat{U}_n^\dagger e^{-iZ_n t} \hat{U}_n$$

Optimizing Trotter error

$$||e^{-i\hat{H}t} - \prod_n e^{-i\hat{H}_n t}|| \leq t^2 \sum_{k\neq n} |||[\hat{H}_k, \hat{H}_n]|||$$

A.Childs *et al.* PRX 11, 011020 (2021)



$$2\sum_{n\neq k} |||[\hat{H}_n, \hat{H}_k]||| \leq \left(\sum_n \Delta E_n\right)^2 \left[1 - \sum_n \omega_n^2\right]$$

Total Spectral Range

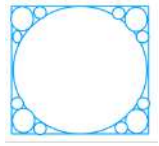
Entropic part

$$S = -\sum_n \omega_n \ln(\omega_n) \approx 1 - \sum_n \omega_n^2 = S_L$$

$$\omega_n = \frac{\Delta E_n}{\sum_k \Delta E_k} : \quad \sum_n \omega_n = 1, \ \omega_n \in [0,1]$$

Smaller spread of eigenvalues

Non-uniform distribution

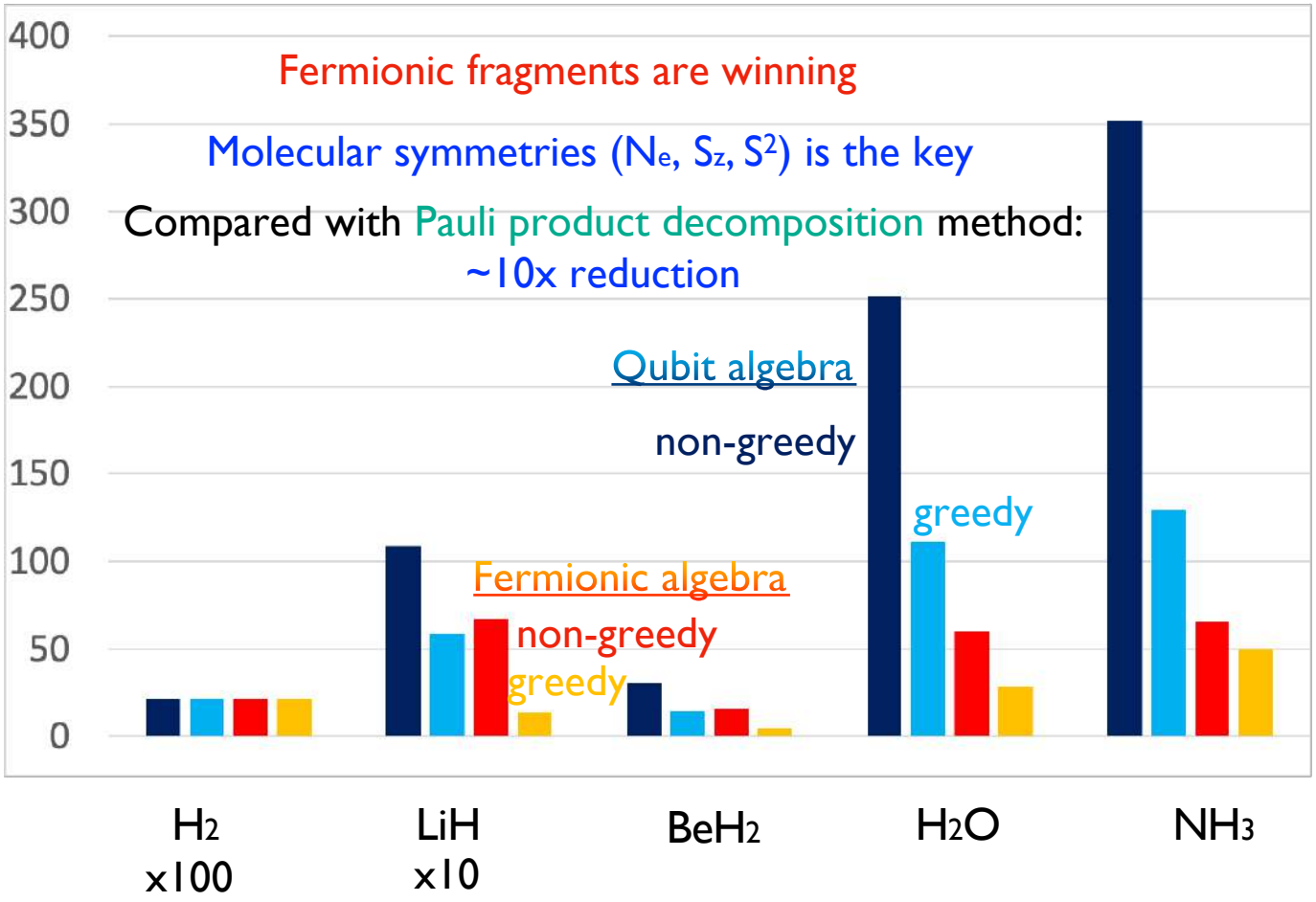


"Greedy" algorithms

Quantum 7, 1086 (2023)

Trotterization error

$\Sigma_{nn'}|||[H_n,H_{n'}]|||$



Quantum 7, 1086 (2023)

2.2 Linear Combination of Unitaries

$$\hat{H} = \sum_k c_k \hat{U}_k$$

$$e^{-i\hat{H}t} = \mathbb{1} - i\hat{H}t + \ldots$$

1. Taylor expansion

PRL 114, 090502 (2015) PHYSICAL REVIEW LETTERS week ending 6 MARCH 2015

Simulating Hamiltonian Dynamics with a Truncated Taylor Series

Dominic W. Berry,[1] Andrew M. Childs,[2,3,4,5] Richard Cleve,[2,5,6] Robin Kothari,[2,6,7] and Rolando D. Somma[8]

2. Qubitization

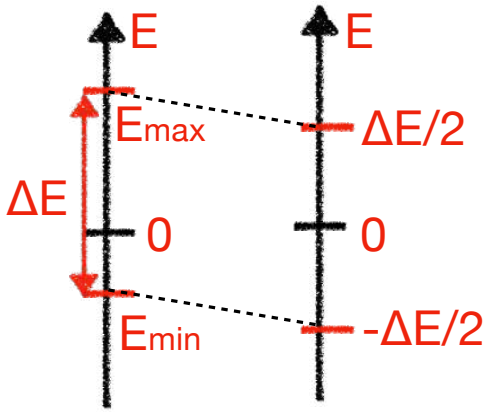
Hamiltonian Simulation by Qubitization

Guang Hao Low[1] and Isaac L. Chuang[2]

$$\hat{W} = \begin{pmatrix} \hat{H} & \sqrt{1-\hat{H}^2} \\ -\sqrt{1-\hat{H}^2} & \hat{H} \end{pmatrix} = e^{i\cos^{-1}(\hat{H})\hat{\sigma}_y}$$

LCU game: reduce the 1-norm of coefficients, $\sum_k |c_k|$ ~cost

1-norm lower bound



$$\hat{H} = s\hat{I} + \sum_k c_k \hat{U}_k$$

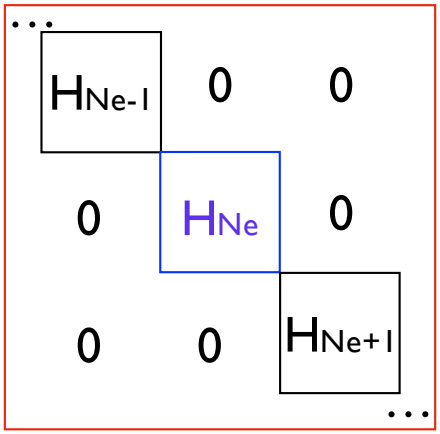
$$\Delta E/2 \leq ||\hat{H} - s\hat{I}|| \leq \sum_k |c_k| \cdot ||\hat{U}_k|| = \sum_k |c_k|$$

$$\frac{E_{\max} - E_{\min}}{2} = \Delta E/2 = \min_s ||\hat{H} - s\hat{I}||$$

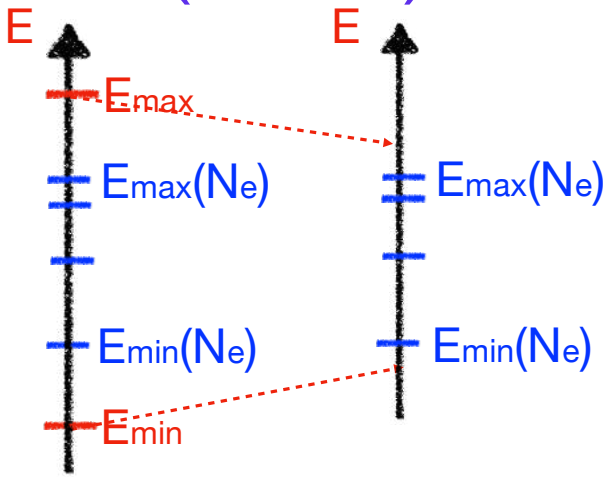
Hard limit: 1-norm cannot be lower than a half of the spectral range (ΔE/2)

(One way around is to change H)

BLock-Invariant Symmetry Shift (BLISS)



$$\hat{H}\Psi_k = (\hat{H} - \hat{K})\Psi_k = E_k\Psi_k$$



$$\hat{K} = \left[\alpha_1 + \sum_{pq} \beta_{pq}\hat{a}_p^\dagger \hat{a}_q\right](\hat{N}_e - N_e) + \alpha_2(\hat{N}_e^2 - N_e^2)$$

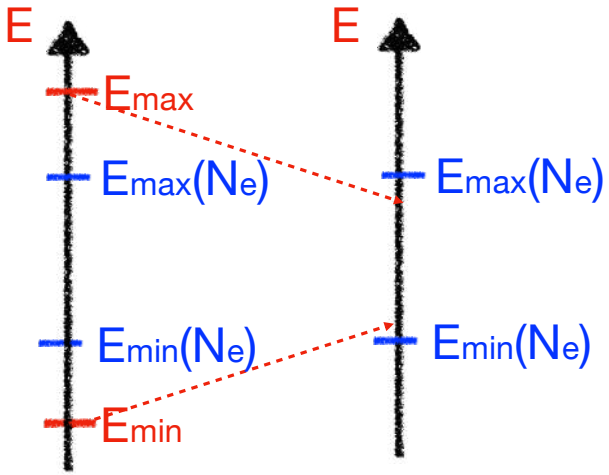
Finding K: optimizing to reduce 1-norm

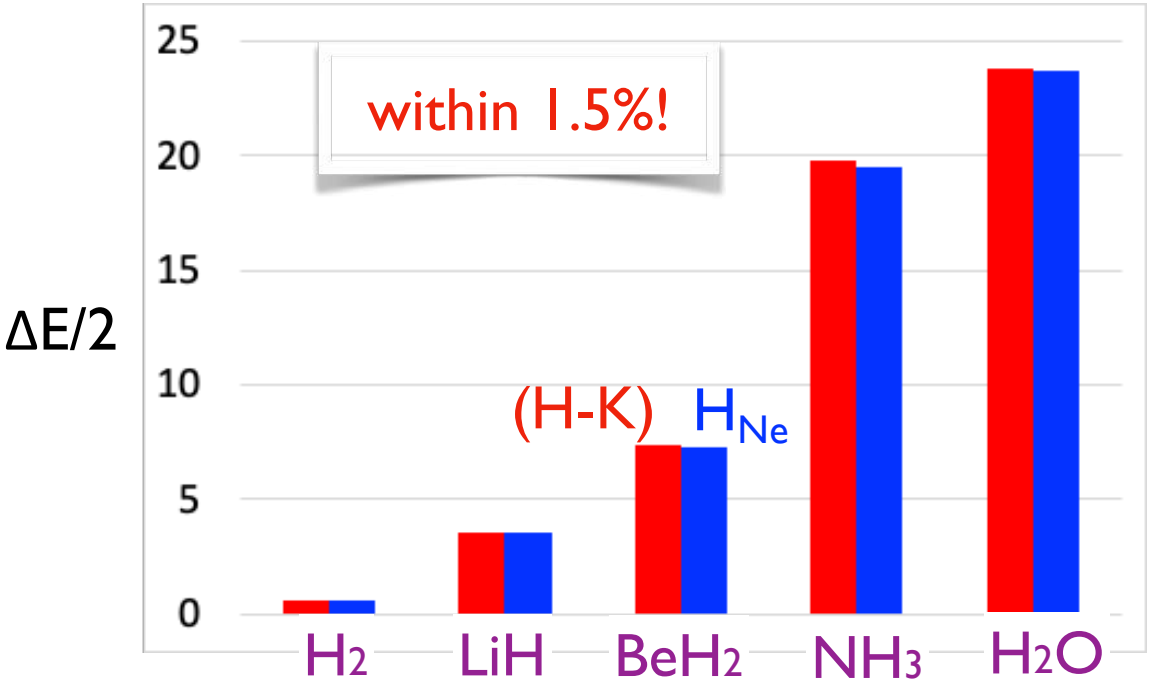
$$(\hat{H} - \hat{K}) = \sum_n c_n \hat{P}_n, \quad \lambda = \sum_n |c_n|$$

Note that 1) K is not a symmetry, 2) using other symmetries is possible

K search: Lower bound results

Success is when (H-K) has the same ΔE/2 as in H for a particular # of electrons:





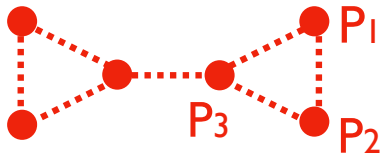
STO-3G basis

What U's to use?

$$(\hat{H} - \hat{K}) = \sum_n c_n \hat{U}_n$$

P's are good but can we do better?

Qubit anti-commuting grouping



$$\{\hat{P}_k, \hat{P}_{k'}\} = 2\delta_{kk'}$$

$$\sum_k \tilde{c}_k^2 = 1$$

anti-commuting Paulis form reflections

$$\hat{R}_i = \sum_k \tilde{c}_k \hat{P}_k$$

Grouping always reduces 1-norm

arXiv:2208.08272

Fermionic reflections:

$$\min_{\hat{U}_{\rm HF}^{(k)},\lambda^{(k)}} ||\hat{H} - \sum_k \hat{H}_{\rm HF}^{(k)}|| \qquad \hat{H}_{\rm HF}^{(k)} = \left(\hat{U}_{\rm HF}^{(k)}\right)^\dagger \left(\sum_{pq} \lambda_{pq}^{(k)} \hat{n}_p \hat{n}_q\right) \hat{U}_{\rm HF}^{(k)}$$

$$\hat{n}_p^2 = \hat{n}_p \qquad \hat{r}_p = 2\hat{n}_p - 1 \qquad \hat{r}_p^2 = 1$$

$$\hat{H} = \sum_k c_k \hat{R}_k$$

1e: $\hat{R} = \hat{U}_{\rm HF}^\dagger \hat{r}_p \hat{U}_{\rm HF}$ 2e: $\hat{R} = \hat{U}_{\rm HF}^\dagger \hat{r}_p \hat{r}_{p'} \hat{U}_{\rm HF}$

arXiv:2208.08272

LCU decompositions results

1-norm improvement w.r.t. naïve Pauli decomposition for H

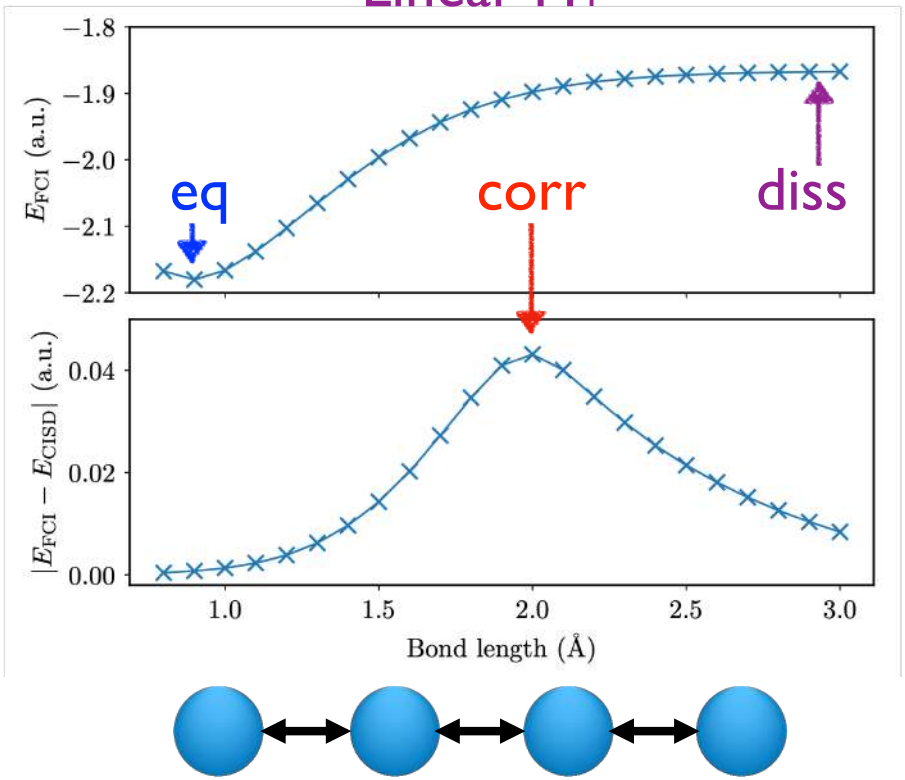
H ΔE/2	x1.8
H-K ΔE/2	x3.1
H-K Pauli	x1.9
H-K Qubit AC	x2.8
H-K Fermionic	x2.7

STO-3G basis H_2 LiH BeH_2 NH_3 H_2O

arXiv:2304.13772

Testing complexity: classical vs quantum

Linear H_4



Other systems:

Rectangular H_4

H_2O, sym OH stretch

N_2 stretched

Quantum "hardness":

1. # $\exp(\theta_k X_k)$
2. Trotter error
3. LCU cost (1-norm)
4. # measurements VQE

arXiv:2311.00129

Summary

Quantum chemistry is still attractive for demonstrating quantum advantage: We are looking for classically hard and quantum easy systems

Algebraic techniques are essential for many quantum algorithms due to non-trivial algebraic structure of the Hamiltonian: Lie and Clifford algebras and groups

$$\hat{H} = \sum_n \hat{H}_n \qquad \hat{H} = \sum_k c_k \hat{U}_k$$

Great news is that in all quantum algorithms we have checked so far quantum hardness is not correlated with classical hardness (except initial state preparation)

More info: YouTube

Tequila (developed with Alan Aspuru-Guzik group)

Acknowledgments

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Aadithya Ganeshram

Ignacio Loaiza

Robert Lang

Seonghoon Choi

Luis Martinez Martinez

Zachary Pierce Bansingh

Postdoc Position Opening

Smik Patel

ZAPATA

Funding:

Google AI

NSERC CRSNG

DARPA