Quantum Computing for Modeling of Molecules and Materials

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Sparse-rank factorization methods in physics

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UVIC

Outline

Quantum Chemistry

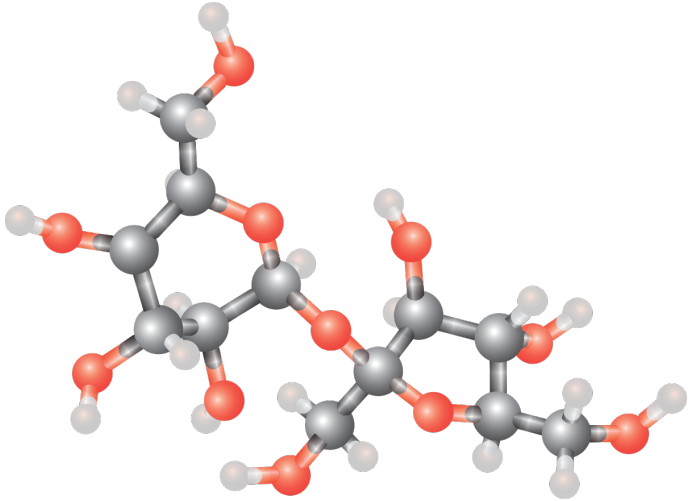
- Electron interactions
- Density functionals

Quantum Computing

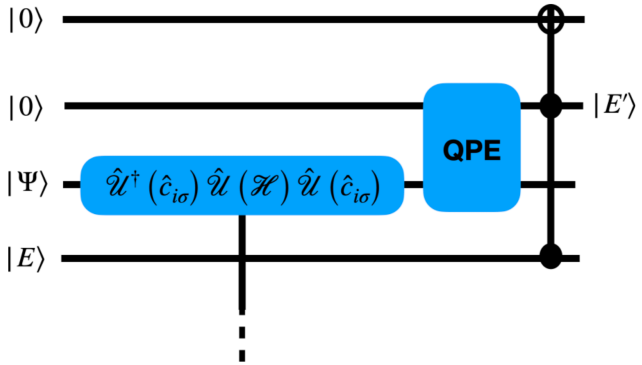
- Special rules
- Near-term computers

Quantum Algorithms

- Sparse-rank factorization: Lanczos
- Ground states and excitations
- Density functionals



https://en.wikipedia.org/wiki/Disaccharide



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Quantum chemistry

Electron-electron interactions

- Born-Oppenheimer approximation

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v(\mathbf{r}_i)$$

- Second quantization:

$$H = \sum_{ij\sigma}\left(t_{ij}\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \sum_{k\ell\bar{\sigma}} V_{ijk\ell}\hat{c}^\dagger_{i\sigma}\hat{c}^\dagger_{j\bar{\sigma}}\hat{c}_{\ell\bar{\sigma}}\hat{c}_{k\sigma}\right)$$

Hardness of many-body problem

QMA-hard

LETTERS
PUBLISHED ONLINE: 23 AUGUST 2009 | DOI: 10.1038/NPHYS1370
nature physics

Computational complexity of interacting electrons and fundamental limitations of density functional theory

Norbert Schuch[1]* and Frank Verstraete[2]*

One of the central problems in quantum mechanics is to determine the ground-state properties of a system of electrons interacting through the Coulomb potential. Since its introduction[1,2], density functional theory has become the most widely used and successful method for simulating systems of interacting electrons. Here, we show that the field of computational complexity imposes fundamental limitations on density functional theory. In particular, if the associated

(that is, antisymmetric) quantum states. Following the early work of ref. 3, it was shown[1,2] that this problem could be rephrased as a single-particle minimization problem, for the reason that the only problem-dependent part is the external potential V, whose expectation value only depends on the local density, whereas the kinetic and interaction terms T and I are fixed and universal for all systems. Thus, the ground-state energy is given by

Density functional theory

Walter Kohn:

- Nobel Prize in Chemistry (1998)
    A. Hohenberg & Kohn Theorem (1964)
        - Compact representation
        - Provably equivalent
    B. Kohn & Sham (1965)
- Also John Pople

Density functional theory

$$n(\mathbf{r}) = \iint \ldots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e}|^2 d\mathbf{r} d\mathbf{r}_2 \ldots d\mathbf{r}_{N_e}$$

Density functional theory

$$E = \min_{n} \left(F[n] + V[n] \right)$$

$$V[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

$$F[n] = \ldots ?$$

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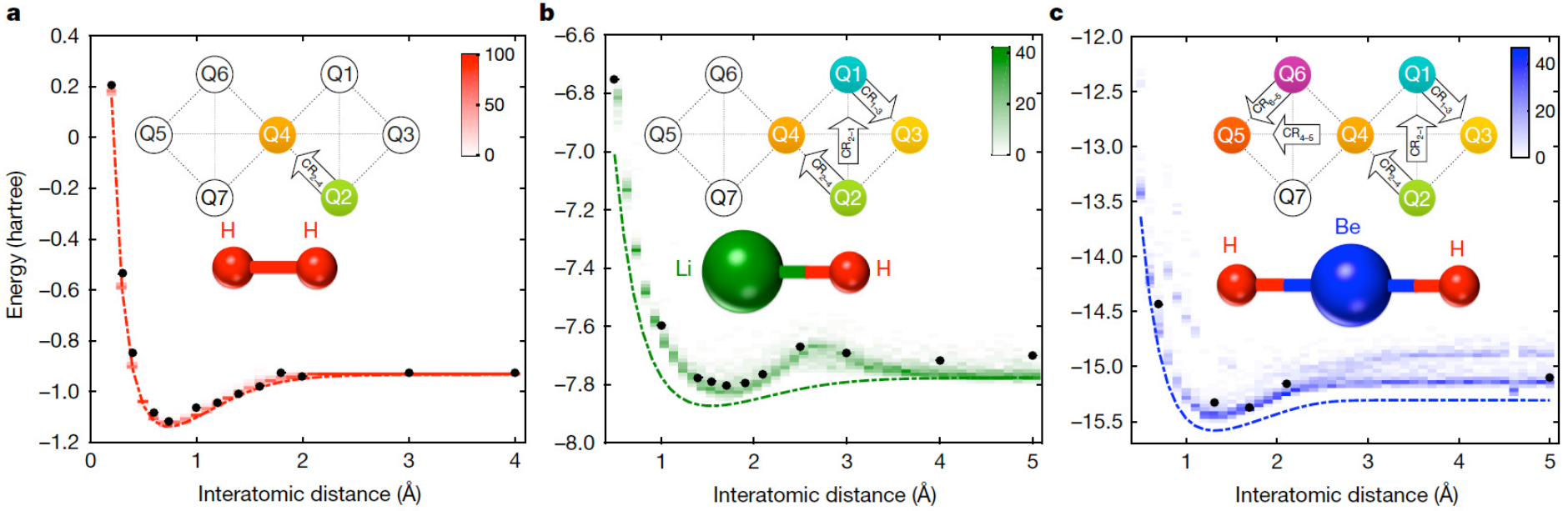
Quantum Computing



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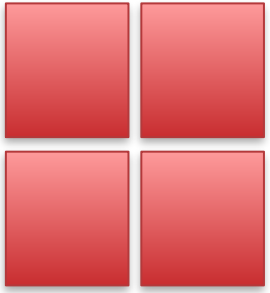
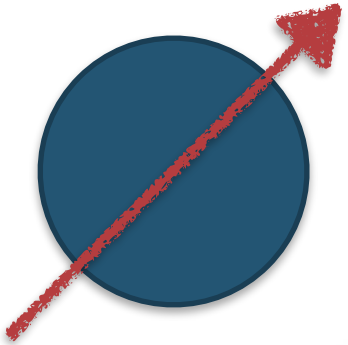
Lanyon, et. al., Nature Chemistry **2**, 106–111 (2010)

Constraints

Quantum computing

- Uncertainty
- No copying (no cloning)
- Less memory
- Simple operations are harder
  - Addition has a high gate count





- Reverse Copenhagen interpretation

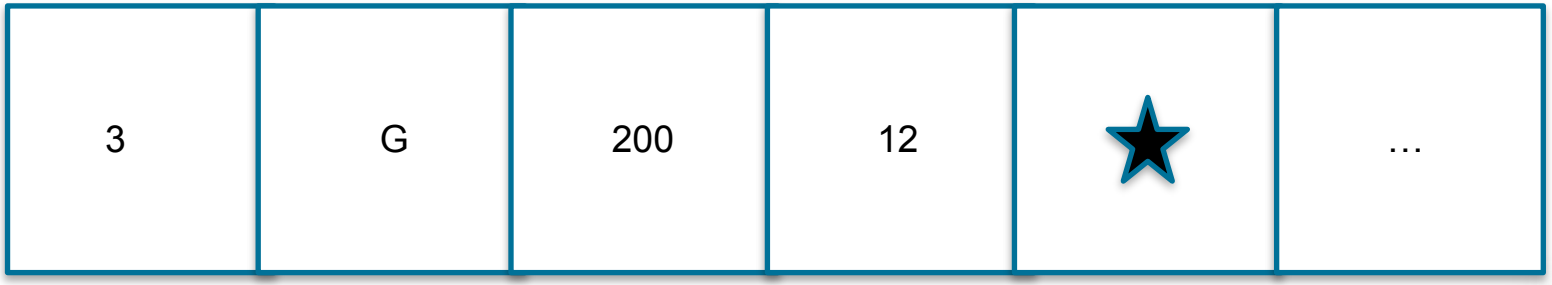
Algorithms

Grover's search algorithm

L. K. Grover, "Quantum Mechanics Helps in Searching for a Needle in a Haystack," *Phys. Rev. Lett.* **79**, 325 (1997)

- Classical analogy with coupled oscillators

L. K. Grover, "From Schrödinger's equation to the quantum search algorithm," *Pramana* **56**, 333 (2001)

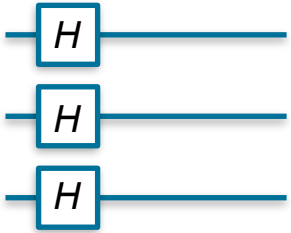


- Classical: O(N); Quantum: O($\sqrt{N}$)
- A few other notable algorithms (Shor's algorithm, Deutsch-Josza)

Grover's search for the density functional?

What is *N*?

- Superposition of all states



$$|\psi\rangle = H^{\otimes N}\left(\bigotimes_{i=1}^{N}|0\rangle\right) = \frac{1}{\sqrt{2}^{N}}\left(\sum_{\sigma_1\sigma_2\ldots\sigma_N}|\sigma_1\sigma_2\ldots\sigma_N\rangle\right)$$

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

Grover's search for the density functional?

What is *N*?

- *N* is exponentially sized in the quantum case
  - Uninformed search
  - Not just square integrable functions

$$E = \min_{n} \left(F[n] + V[n] \right)$$

- Not feasible…

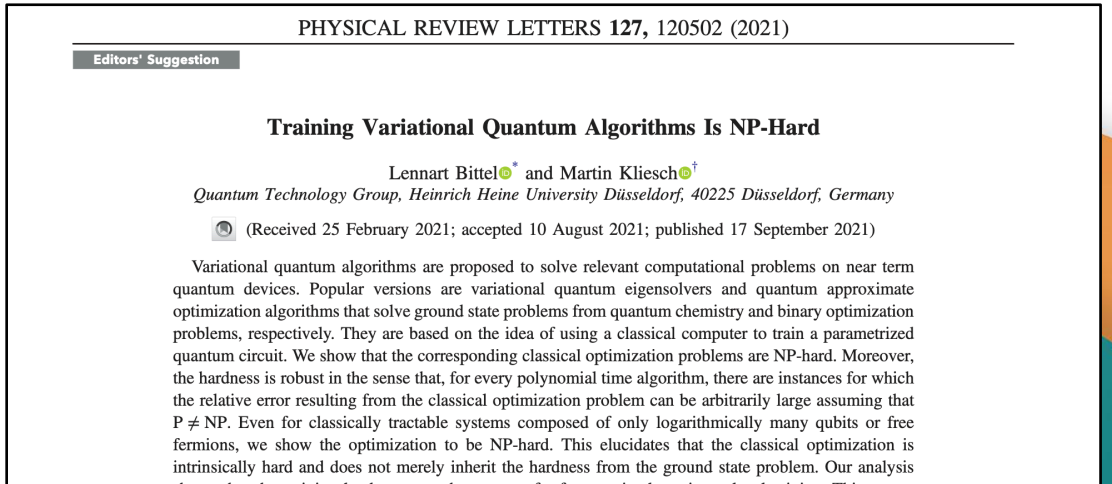
Near-term quantum algorithms

Variational Quantum Eigensolver (VQE)

- Minimize energy with classical parameters

$$E = \min_{\theta_1,\theta_2,\ldots,\theta_N} \langle \psi(\theta_1, \theta_2, \ldots, \theta_N) | H | \psi(\theta_1, \theta_2, \ldots, \theta_N) \rangle$$

- NP-hard in general
- Noisy



PHYSICAL REVIEW LETTERS **127,** 120502 (2021)

Editors' Suggestion

Training Variational Quantum Algorithms Is NP-Hard

Lennart Bittel* and Martin Kliesch†
Quantum Technology Group, Heinrich Heine University Düsseldorf, 40225 Düsseldorf, Germany

(Received 25 February 2021; accepted 10 August 2021; published 17 September 2021)

Variational quantum algorithms are proposed to solve relevant computational problems on near term quantum devices. Popular versions are variational quantum eigensolvers and quantum approximate optimization algorithms that solve ground state problems from quantum chemistry and binary optimization problems, respectively. They are based on the idea of using a classical computer to train a parametrized quantum circuit. We show that the corresponding classical optimization problems are NP-hard. Moreover, the hardness is robust in the sense that, for every polynomial time algorithm, there are instances for which the relative error resulting from the classical optimization problem can be arbitrarily large assuming that $P \neq NP$. Even for classically tractable systems composed of only logarithmically many qubits or free fermions, we show the optimization to be NP-hard. This elucidates that the classical optimization is intrinsically hard and does not merely inherit the hardness from the ground state problem. Our analysis

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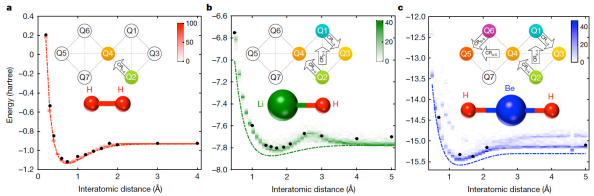
Real-time evolution

Trotter-Suzuki decomposition

- Decompose the time evolution operator

$$e^{-iHt} = e^{-iH_A t} e^{-iH_B t} + O(t^2)$$

- How long to run? Months on small molecules



Lanyon, et. al., Nature Chemistry **2**, 106–111 (2010)

The Trotter Step Size Required for Accurate Quantum Simulation of Quantum Chemistry

David Poulin,[1] M. B. Hastings,[2,3] Dave Wecker,[3] Nathan Wiebe,[3] Andrew C. Doherty,[4] and Matthias Troyer[5]

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[2] *Station Q, Microsoft Research, Santa Barbara, CA 93106-6105, USA*
[3] *Quantum Architectures and Computation Group, Microsoft Research, Redmond, WA 98052, USA*
[4] *Centre for Engineered Quantum Systems, School of Physics, The University of Sydney, Sydney, NSW 2006, Australia*
[5] *Theoretische Physik, ETH Zurich, 8093 Zurich, Switzerland*

(Dated: June 20, 2014)

The simulation of molecules is a widely anticipated application of quantum computers. However, recent studies [1, 2] have cast a shadow on this hope by revealing that the complexity in gate count of such simulations increases with the number of spin orbitals N as N^8, which becomes prohibitive even for molecules of modest size $N \sim 100$. This study was partly based on a scaling analysis of the Trotter step required for an ensemble of random artificial molecules. Here, we revisit this analysis and

Quantum Lanczos Recursion

T.E. Baker, *Phys. Rev. A* **103**, 032404 (2021)

Ground-states

- Run a Lanczos recursion

$$|\psi_{n+1}\rangle = \mathcal{H}|\psi_n\rangle - \alpha_n|\psi_n\rangle - \beta_n|\psi_{n-1}\rangle$$

- How to actually do this?
  - Linear combination of unitaries
  - Oblivious Amplitude Amplification
    - Guarantees operator applied is correct

$$H = \sum_i \alpha_i U_i$$

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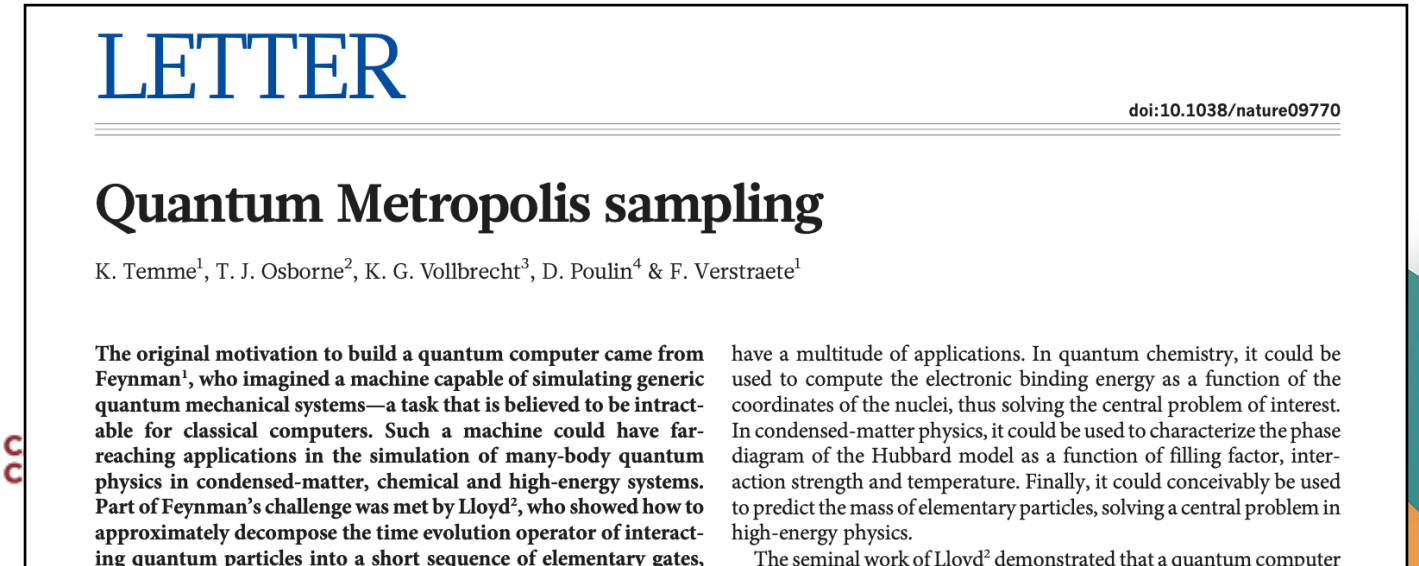
Quantum Lanczos Recursion

T.E. Baker, *Phys. Rev. A* **103**, 032404 (2021)

Minimal wavefunction preparation

- Sampling trick
- State-preserving quantum counting (QAM-sampling/Quantum Amplitude Estimation)



LETTER

doi:10.1038/nature09770

Quantum Metropolis sampling

K. Temme[1], T. J. Osborne[2], K. G. Vollbrecht[3], D. Poulin[4] & F. Verstraete[1]

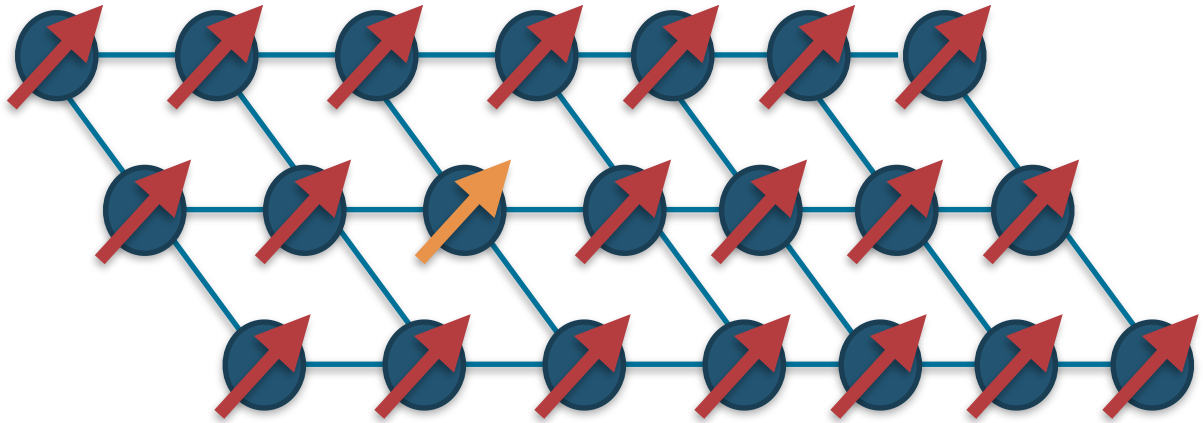
The original motivation to build a quantum computer came from Feynman[1], who imagined a machine capable of simulating generic quantum mechanical systems—a task that is believed to be intractable for classical computers. Such a machine could have far-reaching applications in the simulation of many-body quantum physics in condensed-matter, chemical and high-energy systems. Part of Feynman's challenge was met by Lloyd[2], who showed how to approximately decompose the time evolution operator of interacting quantum particles into a short sequence of elementary gates,

have a multitude of applications. In quantum chemistry, it could be used to compute the electronic binding energy as a function of the coordinates of the nuclei, thus solving the central problem of interest. In condensed-matter physics, it could be used to characterize the phase diagram of the Hubbard model as a function of filling factor, interaction strength and temperature. Finally, it could conceivably be used to predict the mass of elementary particles, solving a central problem in high-energy physics.

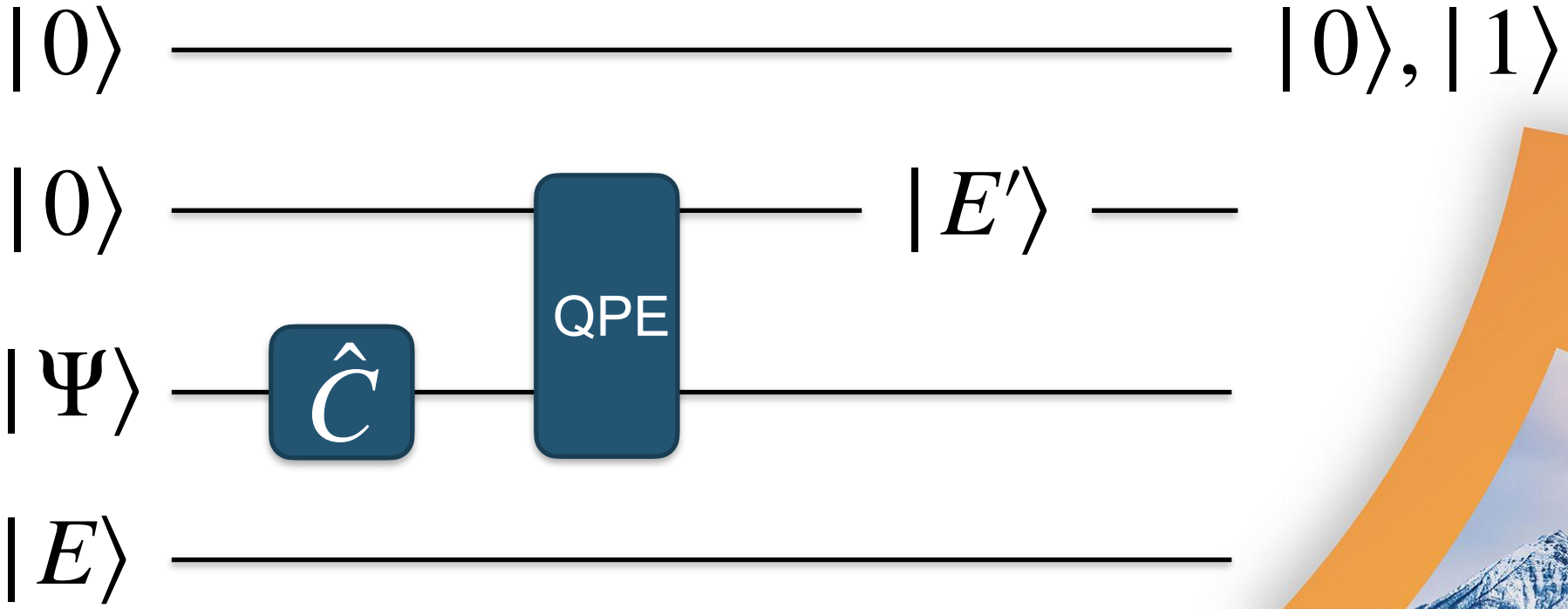
The seminal work of Lloyd[2] demonstrated that a quantum computer

Tangent: Quantum Metropolis sampling

- Temme, et. al. *Quantum Metropolis Sampling* Nature **471**, 87 (2011)
- Metropolis algorithm



Tangent: Quantum Metropolis sampling



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Tangent: Quantum Metropolis sampling

- Quantum counting
  - “Counts” the number of transitions between a wavefunction
  - QAM-sampling
  - Marriott and Watrous, *Quantum Arthur- Merlin games*, Comput. Complex **14**, 122 (2005)

$$\hat{C}|\Psi\rangle = \alpha|\Psi\rangle + \alpha^{\perp}|\Psi^{\perp}\rangle$$

- Generates expectation values of any operator!
  - No wavefunction destruction!
  - Reversible

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Quantum Lanczos Recursion

T.E. Baker, *Phys. Rev. A* **103**, 032404 (2021)

Green's functions

$$\mathcal{G}_{j\bar{\sigma};i\sigma}(\omega) = \cfrac{\langle\Psi|\hat{c}^{\dagger}_{j\bar{\sigma}}\hat{c}_{i\sigma}|\Psi\rangle}{\omega - \alpha_0 - \cfrac{\beta_1^2}{\omega - \alpha_1 - \cfrac{\beta_2^2}{\ddots}}}$$

Quantum computing: Excited States

T.E. Baker, arxiv: 2109.14114

Excitations at polynomial cost

- Block Lanczos method
  - Block matrices replace Lanczos coefficients
    - $O(d^2)$ for d excitations

$$\mathbf{\Psi}_{n+1}\mathbf{B}_{n+1} = \mathcal{H}\mathbf{\Psi}_n - \mathbf{\Psi}_n\mathbf{A}_n - \mathbf{\Psi}_{n-1}\mathbf{B}_n^\dagger$$

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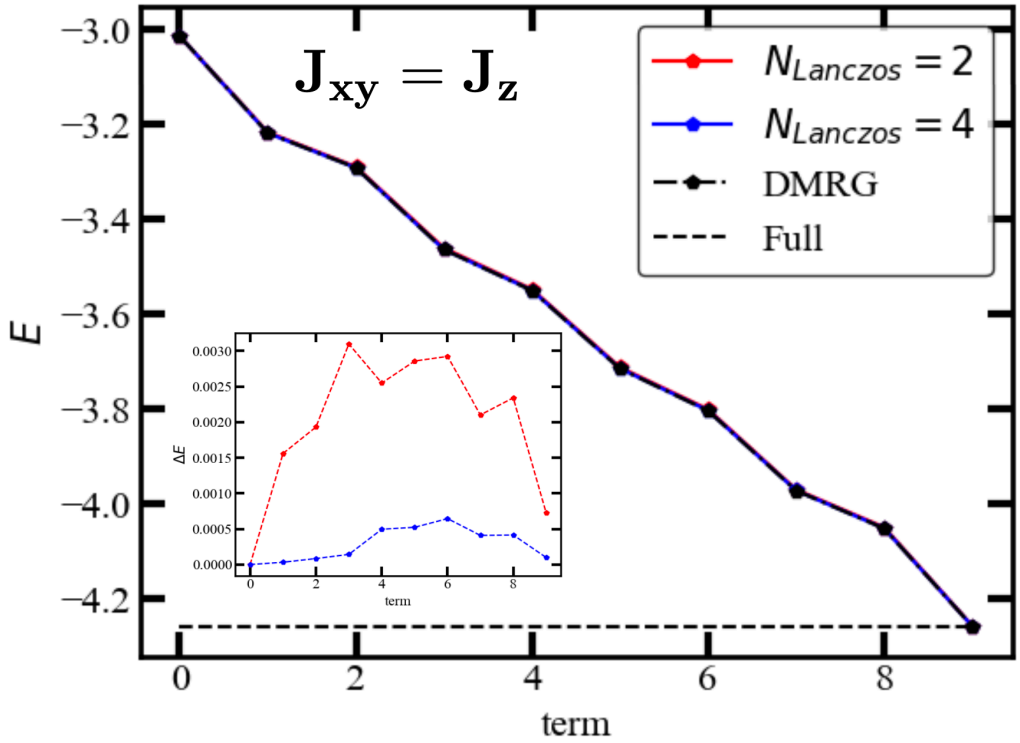
Quantum computing: Excited States

T.E. Baker, arxiv: 2109.14114

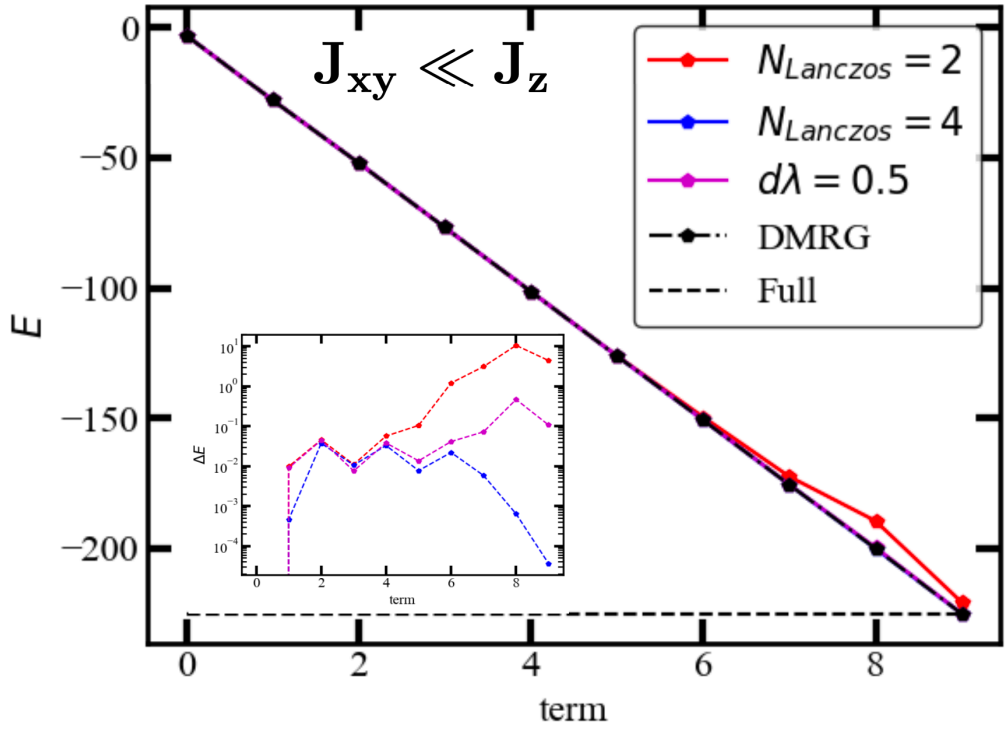
Fast convergence



Quantum computing: Excited States

T.E. Baker, arxiv: 2109.14114

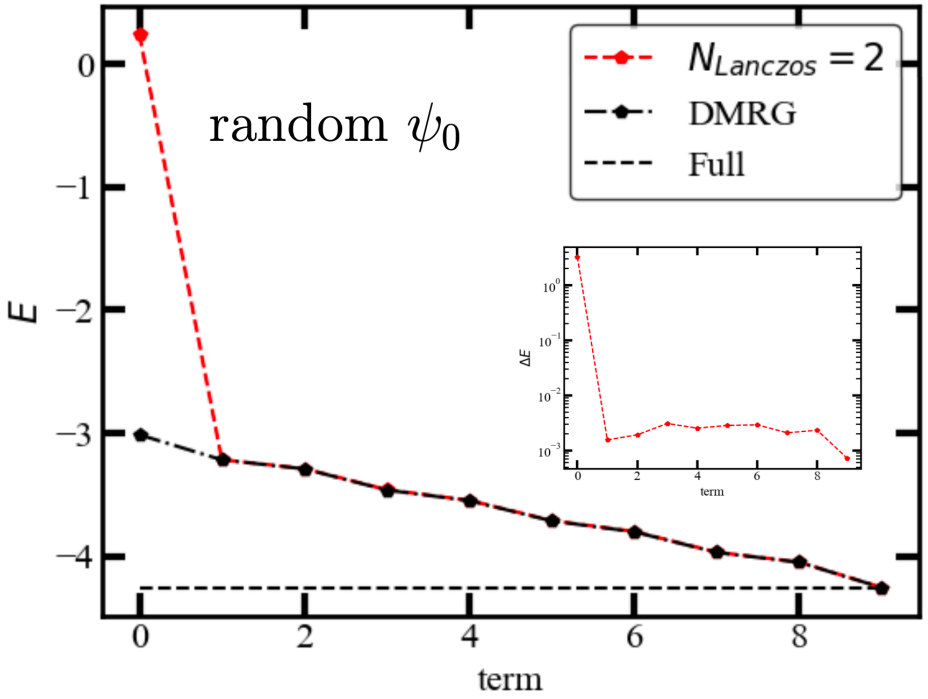
Fast convergence



Quantum computing: Excited States

T.E. Baker, arxiv: 2109.14114

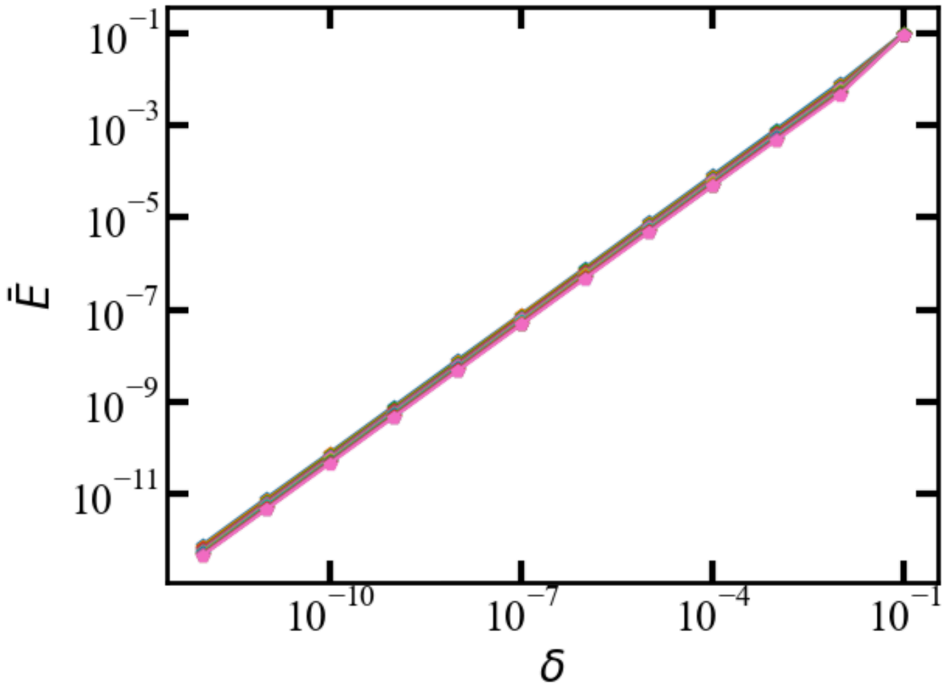
Fast convergence



Quantum computing: Excited States

T.E. Baker, arxiv: 2109.14114

Linear error relationship



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Density Functional Theory & Quantum Computing

PHYSICAL REVIEW RESEARCH **2**, 043238 (2020)

Density functionals and Kohn-Sham potentials with minimal wavefunction preparations on a quantum computer

Thomas E. Baker [1] and David Poulin [1,2,3]

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[2] *Quantum Architecture and Computation Group, Microsoft Research, Redmond, Washington 98052, USA*

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One of the potential applications of a quantum computer is solving quantum chemical systems. It is known that one of the fastest ways to obtain somewhat accurate solutions classically is to use approximations of density functional theory. We demonstrate a general method for obtaining the exact functional as a machine learned model from a sufficiently powerful quantum computer. Only existing assumptions for the current feasibility of solutions on the quantum computer are used. Several known algorithms including quantum phase estimation,

Density Functional Theory from the quantum computer

- Back to density functionals…

$$n(\mathbf{r}) = \sum_{ij} \rho_{ij} \phi_i(\mathbf{r}) \phi_j(\mathbf{r})$$

$$\rho_{ij} = \langle \Psi | \hat{c}_i^\dagger \hat{c}_j | \Psi \rangle$$

- Coefficients of the density matrix are just expectation values!
- Energy and density is sufficient

Exact Kohn-Sham potentials

- Always v-representable
- Cost function with Quantum Gradient Algorithm

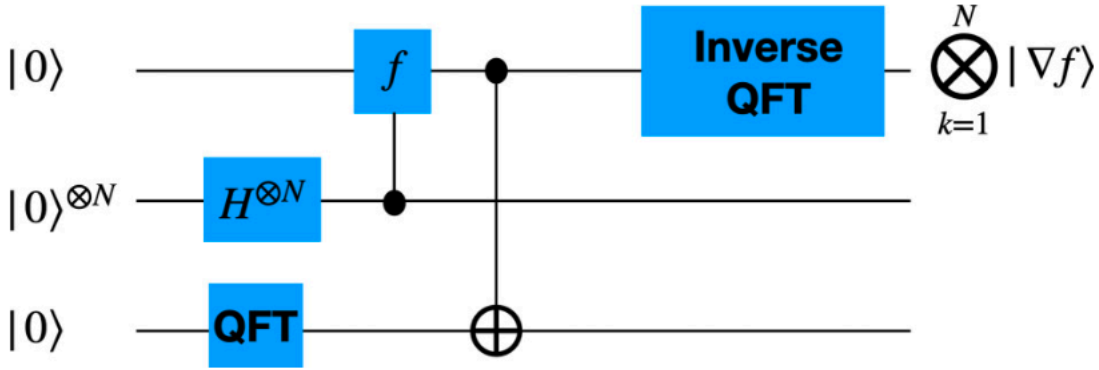
$$T_\Psi[v_s] = \langle \Psi[v] | \hat{T} + \hat{V}_s | \Psi[v] \rangle - \langle \Phi[v_s] | \hat{T} + \hat{V}_s | \Phi[v_s] \rangle$$

$$\langle \Psi[v] | \hat{T} + \hat{V}_s | \Psi[v] \rangle > \langle \Phi[v_s] | \hat{T} + \hat{V}_s | \Phi[v_s] \rangle$$

$$\frac{\delta T_\Psi[v_s]}{\delta v_s} = n_\Psi(\mathbf{r}) - n_\Phi(\mathbf{r})$$

Density Functional Theory from the quantum computer

- Type of density functional
  - Many varieties
- Technically, *potential functionals* so far
  - There is a Potential Functional Theory that has a Hohenberg-Kohn proof attached.
  - Proper labelling of training data
- Can get gradients from Quantum Gradient Algorithm



Density Functional Theory from the quantum computer

- Potential functional theory

$$E = \min_{n[v]} \left(F[v] + \int n[v](\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} \right)$$

$$F[v] = \min_{\Psi \to n[v]} \langle \Psi[v] | \hat{T} + \hat{V}_{ee} | \Psi[v] \rangle$$

$$\frac{\delta F[v]}{\delta v} + \int \frac{\delta n[v](\mathbf{r})}{\delta v(\mathbf{r}')} v(\mathbf{r}')\, d\mathbf{r}' = 0$$

Density Functional Theory from the quantum computer

- Time-dependent density functional theory

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \left\{-\frac{\nabla^2}{2} + v_s[n,\Phi_0](\mathbf{r},t)\right\}\phi_j(\mathbf{r},t)$$

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+}\sum_{k,j=1}^{\infty}(\xi_k-\xi_j)\frac{\phi_k^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega-(\epsilon_j-\epsilon_k)+i\eta}$$

$$f_{xc}[n](\mathbf{r},t,\mathbf{r}',t') = \left.\frac{\delta v_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n=n_{g.s.}}$$

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega) = \chi_s^{-1}(\mathbf{r},\mathbf{r}',\omega) - \chi^{-1}(\mathbf{r},\mathbf{r}',\omega) - v_{ee}(\mathbf{r}-\mathbf{r}')$$

Density Functional Theory from the quantum computer

- Finite-temperature density functional theory

$$\hat{\Omega}^{\tau}_{v,\mu} = \min_{n}\left\{F^{\tau}[n] + \int n(\mathbf{r})(v(\mathbf{r}) - \mu)d\mathbf{r}\right\}$$

$$F^{\tau}[n] \equiv \min_{\hat{\Gamma}\to n}\{T[\hat{\Gamma}] + V_{\mathrm{ee}}[\hat{\Gamma}] - \tau S[\hat{\Gamma}]\}$$

$$\hat{\Gamma} = \sum_{N_e,i} p_{N_e,i}|\psi_{N_e,i}\rangle\langle\psi_{N_e,i}|$$

Density Functional Theory from the quantum computer

- More!
  - Ensemble DFT
  - Non-Born-Oppenheimer DFT
  - Relativistic DFT
  - Molecular dynamics simulations that are accurate with DFT
- Summary:
  - Two algorithms: Quantum counting and quantum gradient algorithms
  - Any type of density functional
  - Minimal measurement

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Conclusion

DMRjulia

- New algorithms
  - DFT from the quantum computer
  - Lanczos-based wavefunction preparation (rapid convergence!)
- From old algorithms
  - Quantum Counting
  - Quantum Gradient Algorithm
- Continued Fraction Green's function
- Excitations
- Needs error correction
- Might have near-term application

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