Limitations of Hartree-Fock with quantum resources

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The Hartree-Fock problem provides the conceptual and mathematical underpinning of a large portion of quantum chemistry. As efforts in quantum technology aim to enhance computational chemistry algorithms, the fundamental Hartree-Fock problem is a natural target. While quantum computers and quantum simulation offer many prospects for the future of modern chemistry, the Hartree-Fock problem is not a likely candidate. We highlight this fact from a number of perspectives including computational complexity, practical examples, and the full characterization of the energy landscapes for simple systems.

The present study aims to highlight the difficulty of conducting optimization problems in the context of electronic structure, with and without quantum resources. Specifically, we will focus on Hartree-Fock, an optimization problem using the mean-field approximation. The Hartree-Fock problem provides the mathematical setting for molecular orbitals widely used in chemistry and beyond. The ubiquitous self-consistent field (SCF) methodology used to solve Hartree-Fock is also applied to most implementations of density functional theory based on Kohn-Sham theory.\textsuperscript{10} While the solution to an instance of the Hartree-Fock problem is often insufficient for many applications, it often serves as the reference state for post-Hartree-Fock methods. Widely used post-Hartree-Fock methods include coupled cluster ansätz,\textsuperscript{21} Møller–Plesset perturbation theory,\textsuperscript{11}\textsuperscript{12}\textsuperscript{13} equation of motion,\textsuperscript{14}\textsuperscript{15} multi-reference configuration interaction, and many more. Here, we forgo improving the Hartree-Fock ansatz and instead ask how difficult it is to find the true Hartree-Fock global minimum and its importance.

Many instances of the Hartree-Fock problem can be solved quickly using heuristic approaches. In practice, conventional algorithms for Hartree-Fock scales cubically with the number of basis functions. However, this cost only reflects the correct scaling if the number of iterations is bounded by a constant or if local minimums are acceptable in place of a global solution. Linear scaling methods\textsuperscript{22}\textsuperscript{23} avoid the diagonalization of hessian entirely and rely on localized properties of the system. This assumption may not be true generally for every case. Iterative procedures, regardless of cost per step, are prone to convergence issues. This article highlights the above mentioned properties in the context of standard numerical and hybrid-quantum approaches to the Hartree-Fock problem.

Typical approaches to improve SCF convergence uses direct inversion of the iterative subspace (DIIS), level shifting,\textsuperscript{24}\textsuperscript{25} quadratically convergent Newton-Raphson techniques,\textsuperscript{28} or varying fractional occupation number,\textsuperscript{29} among many other approaches. The success of any above mentioned methods varies at each instance and depends on the initial parameters chosen, e.g. the size of the iterative subspace, and often work well in combination leading to attempts to build black-box SCF procedures.\textsuperscript{30}\textsuperscript{31}

Unfortunately, these methods cannot work in all cases without violating fundamental assumptions in the theory of computation. In previous work, arbitrary spin-glasses have been mapped to instances of the Hartree-Fock problem.\textsuperscript{27} In addition to other works,\textsuperscript{32}\textsuperscript{33} this shows that the Hartree-Fock problem is difficult in the worst case setting. The complexity class of non-deterministic polynomial time (NP) problems are the set of problems that can be solved efficiently with a hint.\textsuperscript{34} It is possible that every problem that can be solved efficiently with a hint, can also be efficiently solved without the hint. However, from all signs of practical experience suggest that problems in the NP class can do not admit efficient black-box solutions. Thus, due to the NP-completeness of the Hartree-Fock problem, it is unlikely that any classical algorithm can solve all instances in a time proportional a polynomial of the input size. Note that because it in the NP complexity class, the Hartree-Fock problem can be solved efficiently in polynomial time with a sufficiently strong hint e.g. as gleaned from experience or luck. It has been known since the late 1990’s that quantum computers can promise no more than a quadratic speed up over their classical counterparts on such NP-complete problem.\textsuperscript{35}

It has long been known that any classical algorithm can be simulated using quantum hardware. With the the heavy reliance of the variational quantum eigensolvers on classical optimization routines, it is marginal how the quantum approach differs from the conventional approaches. In the recent VQE study the optimization strategy used was an augmented Hessian approach rather than the typical DIIS.\textsuperscript{36} However, both of these optimization strategies can be employed by conventional computers to optimize the orbitals.

In this brief communication, we consider how the use of quantum hardware enhances the ability of chemists to solve instances of the Hartree-Fock problem. Quantum hardware has many prospects for applications to physical and chemical simulations; however the Hartree-Fock problem is not likely to admit drastic advances using quantum computers.

The present article is inspired by a recent study of the Google group and collaborators\textsuperscript{40} using a variational quantum-classical hybrid formulation of the Hartree-Fock problem. There the authors point out the primary purpose of considering the Hartree-Fock problem was to benchmark their quantum device. Here, we highlight obstructions to its use as a general purpose replacement for standard SCF solvers. We

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do so by first introducing the Hartree-Fock problem and characterizations of the solution landscape for an instance of the Hartree-Fock problem. We then give examples that are (1) simple, (2) small, and (3) well-motivated instances of Hartree-Fock that present convergence problems for black-box approaches.

I. HARTREE-FOCK THEORY

The Hartree-Fock ansatz is important for conventional quantum chemistry and has been thoroughly developed over the past 100 years. The Hartree-Fock problem can be stated succinctly as: minimize the electronic energy in the space of single Fock states.

$$E_{HF} = \min_{\Psi \in \mathcal{F}_1} \langle \Psi | \left( \sum_{ij} h_{ij} a_i^\dagger a_j + \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l \right) | \Psi \rangle$$ (1)

The space $\mathcal{F}_1$ is the set of all rank 1 (versus rank $\binom{M}{N}$ in the general case) $N$-electron Fock states. Here and throughout, $N$ is the number of electrons and $M$ is the number of spatial basis functions. Each single Fock state is of the form: $\Psi = | b_i b_j \cdots b_N | \Omega \rangle$ where we have $| b_i b_j \rangle_+ = b_i b_j + b_j b_i = \delta_{ij}$ and $| b_i b_j \rangle_+ = 0$.

After the restriction to this ansatz, the variational space is characterized by rotations from an initial set of orbitals (e.g. the atomic orbitals). If the initial set corresponds to operators $\{ a_j : [a_i, a_j^\dagger]_+ = \int dx \phi_i(x) \phi_j^* (x) = S_{ij}, [a_i, a_j]_+ = 0 \}$, then

$$b_j^\dagger = \sum_i W_{ij} a_i^\dagger,$$ (2)

Here we require that $WW^\dagger = 1$ only when $S = 1$. For applications to molecular physics, single-electron spin-orbitals $\phi_i(x)$ corresponding to the fermionic operators $a_i^\dagger$ and $a_j$ are of Gaussian form e.g. STO-3G.

A. Rotation of charge density matrix

In practice, most algorithms utilize the SCF method to solve eq. (1) using a effective potential term that takes into account the averaged two-body interaction (mean-field). In this approach, the $N$-body problem is reduced to a non-linear single particle problem. At each iteration of the simplest implementation, the Fock matrix, $F$, is formed as a function of a previous bond density matrix ($D_{prev}$).

$$D_{prev} = [ (a_j^\dagger a_i + a_i^\dagger a_j)_{ij} ]^M = C_{prev} \eta C_{prev}^\dagger$$ (3)

with $\eta$ as the orbital occupancies written as a diagonal matrix. The new transformation matrix, $C$, is determined using the gradient of eq. (1) with respect to bond density matrix $D$. The new coefficient matrix is used to form a new bond density matrix. At each iteration, the (real-valued) bond density matrix satisfies the following three properties:

$$D = D^T$$ (4)

$$\text{Tr}(DS) = N/2$$ (5)

$$D = SDS$$ (6)

We convert to an orthogonal basis using e.g. canonical orthogonalization $X_{\text{canonical}} = U_0^\dagger \sqrt{3}$ with $S = U_0 U_0^\dagger$, converts from the non-orthogonal to an orthogonal one. e.g. canonically with $X_{\text{canonical}} = \sqrt{3}, P = X^T DX$.

The three properties of the bond-density matrix below imply, in an orthogonal basis, that $P$ is a rank $N/2$ projector with trace $N/2$. We use $D$ to denote an arbitrary bond density matrix and $P$ as a bond density matrix in an orthogonal basis.

Next, we consider transformation between bond density matrices. A convenient parameterization of the set of bond density matrices that avoids redundancy is

$$P(A) = e^{-A_{\text{block}} P_0 e^{A_{\text{block}}}}$$ (7)

with $A_{\text{block}} = P_0 A (1 - P_0) + (1 - P_0) A P_0$ for arbitrary skew-symmetric $A = -A^T$.

Once an instance of a Hartree-Fock problem has been specified, the objective for the optimization problem is given by the energy matrix functional

$$E[P] = 2\text{Tr}[hP] + \text{Tr}[G P].$$ (8)

Here the mean-field, $G$, is a function of the bond density matrix:

$$G = G[P]_{\mu\nu} = \sum_{\kappa\lambda} h_{\mu\kappa\lambda}^\text{off} P_{\kappa\lambda}$$ (9)

with the antisymmetrized two-electron integral over spatial degrees of freedom defined by $h_{\mu\kappa\lambda}^\text{off} = h_{\mu\kappa\lambda} - h_{\mu\kappa\lambda}$. Note that expression eq. (8) follows directly from evaluating the energy’s expectation value in eq. (1) using e.g. Slater-Condon rules. The matrix derivative of eq. (8) gives the Fock operator

$$F_{ij} = 2(h_{ij} + G_{ij}).$$ (10)

By rotating the charge density matrix with all possible rotations, we are able to do brute force exploration of whole space for some small examples. Below we expand about $P_0 = P_{\text{core}}$ where the $N$ lowest eigenmodes of $H_{\text{core}} = h_{ij} a_i^\dagger a_j$ are occupied. Before turning to examples, we will introduce the quantum ansatz for the Hartree-Fock method.

II. QUANTUM CIRCUIT ANSATZ FOR HARTREE-FOCK

The quantum circuit for creating the Hartree-Fock ansatz state was applied in the context of VQE. The description of the ansatz circuit will be aided through the use of QR decomposition.
The Givens rotations provide a useful canonical characterization of an arbitrary orthogonal matrix, \( W \). The QR decomposition of a real \( n \times n \) orthogonal matrix \( W \) can be done using 
\[
T = n(n-1)/2 \text{ Givens rotations such that }
W = G_1 G_2 G_3 \ldots G_T D
\]
(11)

When \( W \) has determinant of one, \( D \) is just the identity matrix. Each Givens rotation, \( G_i \), is of the form 
\[
G_i = g(a, b, \theta) \text{ with } g_{kk} = 1 \text{ unless } k \text{ is either } a \text{ or } b \text{ when instead } g_{kk} = \cos(\theta).
\]
All off-diagonal elements are zero except 
\[
g_{ab} = -g_{ba} = -\sin(\theta).
\]

Applications of the Givens decomposition to fermionic orbital rotations has been worked out elsewhere \( ^{13,16} \) resulting in a quantum circuit that is able to prepare arbitrary Slater determinants following the parameters of the QR decomposition. By ordering the QR decomposition appropriately, a fermionic swap network can be used to rotate each pair of orbitals using the appropriate Givens rotation parameters. This results in an efficient state preparation circuit of the form depicted in fig. 1. The full compilation down to gates including hardware optimization is given elsewhere \( ^{44,46} \).

Our characterization of the fermionic space in eq. (7) gives us a set of parameters, \( \Theta \) that also characterizes the mixing between pairs of orbitals. The resulting orthogonal transformation \( W(\Theta) \) is then given to the QR decomposition and forwarded to the quantum circuit construction.

### III. Calculations and Results

All calculations of the molecular system are done in the STO-3G basis \( ^{42} \). Energies are reported in Hartrees, angles of rotation in radians, and bond lengths in Angstroms.

The Hartree-Fock energy surfaces (HES) were computed using PySCF \( ^{32} \). In this paper we only consider Restricted Hartree-Fock (RHF) solutions where the alpha and beta spatial orbitals are restricted to be identical. The quantum optimization routines were that of OpenFermion-Cirq and we only modify the initial state routines and the input molecular data \( ^{39} \). The data that support the findings of this study are available from the authors upon reasonable request.

#### A. Landscape analysis

We consider \( \text{H}_2, \text{H}_3^+ \) as minimal basis model systems whose Hartree-Fock instances we can completely characterize. We begin with the \( \text{H}_2 \) example.

When considering \( \text{H}_2 \) in the minimal basis with there is only a single orbital mixing parameter. In fig. 2 we have plotted the 1D HES surface as a function of bond length for \( \text{H}_2 \). The number of minimums in \( \text{HES}(\theta) \) changes with bond length. Before a bond length of approximately 1.2 Å, there is only a single minimum. But at larger bond lengths an additional minimum begins to appear.

We continue with our two electron examples with the iso-electronic \( \text{H}_3^+ \). Now, instead of a 1D HES, we now have two parameters that mix the one occupied orbital with the two virtual orbitals. We plot the HES in fig. 3 for a linear configuration with hydrogen atoms separated by 2.5 Å. There are three minimums for \( \text{HES}(\theta_1, \theta_2) \). In fig. 3 we give the HES of \( \text{H}_3^+ \) at 4.36 Å where there are several minimums with the same globally optimal value.
The eigenvalues of this matrix are $\lambda_{\pm} = \{0, \pm i \sqrt{\theta_1^2 + \theta_2^2}\}$. Since the matrix exponential of $A_{\text{block}}$ merely exponentiates the eigenvalues, when $\lambda_{\pm} = i \pi$, the rotation acts trivially on the density matrix. This underlies periodicity to the plots seen in\cite{3} and \cite{4}.

We can explain the periodicity in terms of this invariant by converting to polar coordinates where $\theta_1 = R \cos \phi$ and $\theta_2 = R \sin \phi$. Now the nontrivial eigenvalue is $\lambda_{\pm} = \pm i R$ and we can express the periodicity of the plots as $\exp(\theta R + i n \pi \phi) = \exp(\theta R + i (n+1) \pi \phi)$ where $n$ is an integer.

There is a nice generalization of this fact. For a single spatial orbital that is doubly occupied with two electrons and $m$ virtual orbitals, the generalization of eq. (12) is

$$A_{\text{block}} = \begin{pmatrix}
0 & -\theta_1 & -\theta_2 & -\theta_3 & \ldots & -\theta_m \\
\theta_1 & 0 & 0 & 0 & \ldots & 0 \\
\theta_2 & 0 & 0 & 0 & \ldots & 0 \\
\theta_3 & 0 & 0 & 0 & \ldots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
\theta_m & 0 & 0 & 0 & \ldots & 0
\end{pmatrix}$$ (13)

It is straightforward to calculate that the eigenvalues of this matrix are zero except $\lambda_{\pm} = \pm i \sqrt{\theta_1^2 + \theta_2^2 + \theta_3^2 + \ldots + \theta_m^2}$.

Following the same argument as in the $m = 2$ case above, we can say that

$$\text{HES}(\Theta) = \text{HES}(R, \Phi) = \text{HES}(R + n\pi, \Phi)$$ (14)

where $R = \sqrt{\theta_1^2 + \ldots + \theta_m^2}$.

Therefore, the range of the minimal required search space for each $\theta_j$ is restricted to a hyper-sphere with radius $\pi$ of dimension $m$. But, the default search space was a hyper cube of dimension $m$ with side $2\pi$. Now, the ratio of minimal required search space with default search goes to zero as $m$ tends to infinity. This is a well known consequence of the vanishing ratio of the volume of a hyper-sphere to the volume of the corresponding hyper-cube.\cite{5}

B. Convergence analysis

We used the quantum algorithm outlined in ref\cite{10} for obtaining RHF solutions for four examples. Depending on initial guess it may converge to local rather global solutions.

The different initial guess were generated using the Givens rotations corresponding to different minimums in figs.\cite{2} and \cite{3} respectively. The results for $H_2$, converging to two different minimums on quantum simulator is shown in fig. \cite{5} Similarly results for $H_3^+$, converging to two different minimums on quantum simulator is shown in fig. \cite{6} In fig. \cite{5} the values of $\lambda = 1$ and $\lambda = 1.2$ were chosen as states far enough in parameter space to have energy sufficiently large. If we select states with small $\lambda$, the convergence to the minimum is highly likely so long as the system does not climb uphill in energy since the initial state has energy less than all minimums except the global minimum.

As final examples, we choose diatomic carbon and its cation. We also consider $C_2$ and $C_2^+$ as instances that are commonly known to confound solvers due to the appearance of saddle points with in the optimization landscape. To illus-
trate the complications of convergence we modified the initial parameters following the method used in Ref. \[40\]. Namely, we begin with the solution provided by the classical SCF solver, perturb from those solutions and observe if the quantum algorithm still converges to the correct minimum.

This example allows us to highlight the importance of using the information of Hessian to avoid saddle points during SCF optimization in either quantum or classical methods. In Figs. 7 and 8, convergence results are shown for \( C_2 \) and \( C_{2^+} \), respectively. In each of the plots, we have plotted the performance of the quantum circuit optimization routine and the classical optimization routines as implemented in PySCF. At an inter-nuclear separation of 1.5 Å, there is a saddle point appearing the potential energy landscape.

| Energy (a.u.) | Iterations |
|--------------|------------|
| \(-74.2\)   | 0          |
| \(-74.3\)   | 20         |
| \(-74.4\)   | 40         |
| \(-74.5\)   | 60         |
| \(-74.6\)   | 80         |

**FIG. 7**: SCF convergence for different optimizers for the minimal basis \( C_2 \) at \( r_{CC} = 1.5 \) Å. Plotted are the optimization trajectories for the quantum circuit optimizer, and PySCF with and without an extra step. The energy of the saddle point and of the global minimum of the HES are also shown. PySCF guess is \( P_{\text{core}} \).

The use of the orbital Hessian helps solvers avoid saddle points where the gradient may vanish at a non-optimal values. The solver uses Hessian which provides a notion of the curvature of the landscape. This allows the solver to avoid saddle points. The augmented Hessian conjugate-gradient method was used for the quantum optimization of the Hartree-Fock circuit. This allows the solver to avoid convergence to saddle points as illustrated in Figs. 7 and 8. Many of the quantum chemistry do not check the the RHF solutions by default. This makes them prone to failure by convergence to a saddle point rather than the RHF solution.

**IV. DISCUSSION**

In this study, we showed that the convergence to a local minimum or global minimum is a function of initial guess. The proposed algorithm on quantum simulator carries this feature from classical algorithm. There is no \textit{a priori} guarantee that it will find global solution.

Since the Hartree-Fock problem is an optimization problem, quantum computing via a modified Grover search can be used to find the global solution quadratically faster than the classical brute force approaches. However, in both conventional and quantum solvers, local searches are employed for local search whereby no guarantees on finding the globally optimal solutions are given.

In analyzing the Hartree-Fock functional for \( H_2 \), \( H_3^+ \), \( C_2 \), and \( C_{2^+} \) we note that the number of critical points in the solution space changes as the nuclear separation changes. This also implies that there are additional difficulties in applying Hartree-Fock for nuclear dynamics or other non-equilibrium configurations. Most solvers for the Hartree-Fock problem do not explore the entire space and usually only choose a single starting point (rather than multiple starting points). While this is not often an issue, it can cause serious pathology when used in post-Hartree-Fock methods e.g. coupled cluster method. This will be true for both on conventional computers and in its unitary formulation for quantum computers.

**V. CONCLUSIONS**

The recent application of quantum technology to the Hartree-Fock problem may serve as a hardware benchmark but is unlikely to have a dramatic impact on the practical approaches to this problem.

While the application to Hartree-Fock is not likely to change the workhorse routines used on conventional computers, there are still interesting use cases for the results from Ref. \[40\]. The projection methods and purity extrapolation presented in \[40\] will still be useful.

Hartree-Fock is NP-hard and is not likely to admit more than a quadratic speed up. When considering application areas of quantum computers, it is far more likely to make major breakthroughs when considering time-dependent phenomena. For example, the quantum-classical hybrid algorithm for obtaining the Kohn-Sham potential of time-dependent density
functional\textsuperscript{23,24}, also requires measuring the bond density matrix.

This article highlights the wide body of knowledge on the SCF method, its difficulty, and shows the lack of verification of the solution are material in both the quantum and conventional computing domains.

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1. D. Hartree, “The wave mechanics of an atom with a non-coulomb central field, part I: Theory and methods,” Proc. Camb. Phil. Soc. 24, 89–312 (1928).
2. V. Fock, “Näherungsmethode zur lösung des quantenmechanischen Mekkorperproblems,” Z. Phys. 61, 723–734 (1930).
3. W. Kohn and L. J. Sham, “Self-consistent equations including exchange and correlation effects,” Phys. Rev. 140, 1133 (1965).
4. F. Coester, “Bound states of a many-particle system.” Nuclear Physics 7, 421–424 (1958).
5. F. Coester and H. Kümml, “Short-range correlations in nuclear wave functions,” Nuclear Physics 17, 477–485 (1960).
6. J. Čížek, “On the correlation problem in atomic and molecular systems, calculation of wavefunction components in ursell-type expansion using quantum-field theoretical methods,” The Journal of Chemical Physics 45, 4256–4266 (1966).
7. R. J. Bartlett, “Many-body perturbation theory and coupled cluster theory for electron correlation in molecules,” Annual Review of Physical Chemistry 32, 359–401 (1981).
8. J. Paldus and N. Li, “A critical assessment of coupled cluster method in quantum chemistry,” Advances in Chemical Physics 110, 1–175 (1999).
9. J. Shavitt and R. J. Bartlett, “Many-body methods in chemistry and physics: MBPT and coupled-cluster theory (Cambridge university press, 2009).
10. W. Kutzelnigg, “How many-body perturbation theory (mbpt) has changed quantum chemistry,” International Journal of Quantum Chemistry 109, 3588–3588 (2009).
11. I. Lindgren and J. Morrison, “Springer series in chemical physics,” in Atomic many-body theory, Vol. 13 (Springer Berlin, 1982).
12. J. Binkley and J. Pople, “Moller–plesset theory for atomic ground state energies,” International Journal of Quantum Chemistry 9, 229–236 (1975).
13. P. Pulay, “Convergence acceleration of iterative sequences. The case of SCF iteration,” Chem. Phys. Lett. 73, 393 (1980).
14. R. Saunders and I. H. Hillier, “A level-shifted method for converging closed shell Hartree–Fock wave functions,” Intl. J. Quantum. Chem. 7, 699–705 (1973).
15. G. B. Bacskaia, “A quadratically convergent Hartree-Fock (QC-SCF) method: Application to closed shell systems,” Chem. Phys. 61, 385–404 (1981).
16. A. D. Rabuck and G. E. Scuseria, “Improving self-consistent field convergence by varying occupation numbers,” J. Chem. Phys. 110, 695 (1999).
17. L. Thagersen, J. Olsen, D. Yeager, P. Jorgensen, P. Selk, and T. Helgaker, “The trust-region self-consistent field method: Towards a black-box optimization in Hartree-Fock and Kohn-Sham theories,” J. Chem. Phys. 121, 16–27 (2004).
18. K. N. Kudin, G. E. Scuseria, and E. Cancs, “A black-box self-consistent field convergence algorithm: One step closer,” J. Chem. Phys. 116, 8255 (2002).
19. J. D. Whitfield, N. Schuch, and F. Verstraete, “The computational complexity of density functional theory,” in Many-Electron Approaches in Physics, Chemistry and Mathematics: A Multidisciplinary View, Lecture Notes in Physics, edited by V. Bach and L. D. Site (Springer, 2011) pp. 245–260.
20. N. Schuch and F. Verstraete, “Computational Complexity of interacting electrons and fundamental limitations of density functional theory,” Nature Phys. 5, 732 (2009) also see appendix of arxiv:0712.0483.
21. J. D. Whitfield and Z. Zimborsa, J. Chem. Phys. 141, 234103 (2014).
22. In this article, we use the term problem to refer to a specific collection of problem instances.
23. M. Sipser, Introduction to the Theory of Computation (PWS Publishing Company, 1997).
24. C. H. Bennett, E. Bernstein, G. Brassard, and U. Vazirani, “Strengths and weaknesses of quantum computing,” SIAM J. Computing 26, 1510–1524 (1997).
25. Q. Sun, “Co-iterative augmented hessian method for orbital optimization,” (2016), arXiv:1610.08423 [physics.chem-ph].
26. S. Lloyd, “Universal quantum simulators,” Science 273, 1073–8 (1996).
27. E. Cancs, M. De Franceschi, W. Kutzelnigg, C. L. Bris, and Y. Maday, “Computational quantum chemistry: A primer,” in Special Volume, Computational Chemistry, Handbook of Numerical Analysis, Vol. 10 (Elsevier, 2003) pp. 3 – 270.
28. W. J. Hehe, R. F. Stewart, and J. A. Pople, “Self-consistent molecular-orbital methods. i. use of gaussian expansions of Slater-type atomic orbitals,” J. Chem. Phys. 51, 2657–2664 (1969).
29. A. Szabo and N. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory (Dover Publications, 1996).
30. D. Kivelichan, J. McClean, N. Wiebe, C. Gidney, A. Aspuru-Guzik, G. K.-L. Chan, and R. Babbush, “Quantum Simulation of Electronic Structure
with Linear Depth and Connectivity," Phys. Rev. Lett. 120, 110501 (2018).

45 R. A. Horn and C. R. Johnson, *Matrix Analysis* (Cambridge University Press, 2005).

46 Z. Jiang, K. J. Sung, K. Kechedzhi, V. N. Smelyanskiy, and S. Boixo, "Quantum algorithms to simulate many-body physics of correlated fermions," Phys. Rev. Applied 9, 044036 (2018).

47 S. [50], "Hartree-fock on a superconducting qubit quantum processor," https://github.com/quantumlib/OpenFermion-Cirq/tree/master/openfermioncirq/experiments/hfvqe (2020).

48 Q. Sun, X. Zhang, S. Banerjee, P. Bao, M. Barbry, N. S. Blunt, N. A. Bogdanov, G. H. Booth, J. Chen, Z.-H. Cui, J. J. Erliksen, Y. Gao, S. Guo, J. Hermann, M. R. Hermes, K. Koh, P. Koval, S. Lehtola, Z. Li, J. Liu, N. Mardirossian, J. D. McClain, M. Motta, B. Mussard, H. Q. Pham, A. Pulkin, W. Purwanto, P. J. Robinson, E. Ronca, E. Sayfutyarova, M. Scheurer, H. F. Schurkus, J. E. T. Smith, C. Sun, S.-N. Sun, S. Upadhyay, L. K. Wagner, X. Wang, A. White, J. D. Whitfield, M. J. Williamson, S. Wouters, J. Yang, J. M. Yu, T. Zhu, T. C. Berkelbach, S. Sharma, A. Sokolov, and G. K.-L. Chan, "Recent developments in the pyscf program package," (2020), arXiv:2002.12531 [physics.chem-ph].

49 Q. Sun, T. C. Berkelbach, N. S. Blunt, G. H. Booth, S. Guo, Z. Li, J. Liu, J. McClain, E. R. Sayfutyarova, S. Sharma, S. Wouters, and G. K.-L. Chan, "The python-based simulations of chemistry framework (pyscf)," (2017), arXiv:1701.08223 [physics.chem-ph].

50 J. R. McClean, K. J. Sung, I. D. Kivlichan, Y. Cao, C. Dai, E. S. Fried, C. Gidney, B. Girvin, T. H"{a}ner, T. Hardikar, V. Havliček, O. Higgott, C. Huang, J. Izaaq, Z. Jiang, X. Liu, S. McArdle, M. Neeley, T. O’Brien, B. O’Gorman, I. Ozfidan, M. D. Radin, J. Romero, N. Rubin, N. P. D. Sawaya, K. Setia, S. Sim, D. S. Steiger, M. Steudtner, Q. Sun, W. Sun, D. Wang, F. Zhang, and R. Babbush, "OpenFermion: The Electronic Structure Package for Quantum Computers," arXiv:1710.07628 (2017).

51 D. W. Scott, *Multivariate density estimation: theory, practice, and visualization* (John Wiley & Sons, 2015).

52 R. E. Stanton, "Multiple solutions to the hartree-fock problem. i. general treatment of two-electron closed-shell systems," The Journal of Chemical Physics 48, 257–262 (1968).

53 L. K. Grover, "A fast quantum mechanical algorithm for database search," Proc. 28th ACM Symp. on Theory of Comp. (STOC ’96), 212 (1996), also see arxiv:quant-ph/9605043.

54 J. Yang, J. Brown, and J. D. Whitfield, "Measurement on quantum devices with applications to time-dependent density functional theory," arXiv e-prints:1909.03078 (2019).

55 J. Brown, J. Yang, and J. D. Whitfield, "Solver for the electronic V-representation problem of time-dependent density functional theory," arXiv e-prints:1904.10958.

56 J. D. Whitfield, M.-H. Yang, D. G. Tempel, S. Boixo, and A. Aspuru-Guzik, "Computational complexity of time-dependent density functional theory," New Journal of Physics 16, 083035 (2014).