Molecular Energies via the Variational Quantum Eigensolver

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Abstract

Finding the lowest-energy arrangement of electrons in a molecule is an exponential-time problem on a classical computer. We describe here the variational quantum eigensolver, a method that can work on small noisy quantum computers. Using the fact that quantum computation can efficiently find energy expectation values of trial states, this method gives an upper bound for the ground-state electronic energy. As a demonstration, we demonstrate the method by computing an estimate of the ground-state energy of the H_2 molecule.

1 The electronic structure problem

The central problem of computation chemistry is this: given an arrangement of atoms, find the energy of the ground-state arrangement of electrons. Solving this problem would give reveal the reactivity, geometry, and spectroscopy of any molecules. More formally, the problem is to find the ground state of the Hamiltonian

$$-\sum_i \nabla_i^2 - \sum_{i,J} \frac{Z_i}{|i - J|} + \sum_{i,j} \frac{1}{|i - j|} \tag{1}$$

Here, the first term gives the kinetic energy of the electrons, the second describes the electric attraction between the electrons and nuclei, and the last describes repulsion between electrons. Here i, j represent coordinates of electrons, for which we hope to solve, and J represent coordinates of nuclei, which we take to be given and unmoving, because nuclei are so large and slow compared to electrons.

Solving such problems scales exponentially in the number of electrons. Methods to solve this problem efficiently on a classical computer, such as Hartree-Fock or density functional theory must essentially ignore the dimensionality of the problem, by assuming that electrons are repelled with an averaged electron density, not with $n - 1$ other discrete electrons.[1] This treatment of electron interaction is systematically incorrect, generally underestimating the interaction energy.

The ability of a quantum computer to store and operate on the whole, high-dimensional electronic wavefunction suggests a way to efficiently solve this problem. We describe here the variational quantum eigensolver, a method for tightly bounding above the ground-state energy. Essentially, this method relies on the fact that the expectation value of an operator on any state can be found quickly on a quantum computer. Minimizing energy over a family of states then estimates the true ground state energy.

There are other quantum algorithms to solve the electronic structure problem, but only this one can run on small, noisy computers of the kind available today. As a demonstration, we have written an implementation to find the ground state energy of molecular hydrogen and run it on quantum computers available to the public.

Here, we show how this algorithm works, as an example give some results from our implementation, and conclude by discussing future areas of study.

2 Mapping the problem to a quantum computer

2.1 Discretizing the problem

To solve the electronic structure problem, we would like to work in a finite-dimentional basis. To do this, assume that all possible wavefunctions can be written as a superposition of some number of orbitals. If the

number of orbitals is allowed to be very large, many collection of functions will include a close approximation to any state. A common basis is a large number of Gaussian functions centered at each atom.

On the other hand, if the basis must be small, then the choice of basis must be guided by physical principles. In choosing a small set of basis functions and hoping that their span contains a close approximation to the true ground-state energy, we are implicitly choosing our family of ansatze that will be used for the variational eigensolver. The choice of this basis is based on inexpensive classical methods for estimating ground-state wavefunctions. The basis set of atomic orbitals assumes that molecular orbitals look similar to those on single atoms. Hartree-Fock, again a method which takes into account electron-electron interaction in an averaged way, can also be used to generate a basis set. When we simulate hydrogen, we use this Hartree-Fock basis.

2.2 The Occupation Number Basis

Now that the space is discrete, it is possible to write down a finite basis and describe the Hamiltonian in terms of this basis. The Pauli exclusion principle says that an orbital can contain either zero or one electrons[1]. Given n orbitals, there are 2^n ways these orbitals can be occupied. To write one of these states in the occupation representation basis, write $|[0,1]^n\rangle$, and set entry i as 1 if orbital i is occupied, and 0 otherwise. A convenient operator in this basis are the creation and annihilation operators, which change the occupation of some state. All operators on an electronic system can be written in terms of products of the annihilation and creation operators. The creation operator $a_i^\dagger$ adds an electron to orbital i if it is empty. Likewise, the annihilation operator a_i removes a particle from orbital i if it is occupied. Applying a creation operator to a filled orbital, or removing from an empty orbital yields 0.

The electronic-structure Hamiltonian can be re-written in sums of products of these operators: The operators $a_i^\dagger a_j$ for some i,j act as basis for single-electron operators, like the kinetic energy and the electron-nucleus attraction, as this operator projects the one-electron state $|j\rangle$ onto $|i\rangle$. Likewise, the operators $a_i^\dagger a_j^\dagger a_k a_l$ act as a basis for the two-particle electron-electron interaction.[1]

On a quantum computer, the one qubit gate $Q^+ = \frac{1}{2}(X - iY)$ acts as a creation operator, sending $|0\rangle$ to $|1\rangle$ and $|1\rangle$ to 0. The gate $Q^- = \frac{1}{2}(X + iY)$ is the annihilation operator. Here, X, Y, Z are the Pauli matrices:

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Unfortunately, these annihilation and creation operators are not the right operators for an electronic system. Electrons are fermions with exchange anti-symmetry, so the creation and annihilation operators must obey the relations

$$a_i a_j + a_j a_i = a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0, \quad a_i^\dagger a_j + a_j a_i^\dagger = \delta_{kj} I$$

One way to implement these commutation relations is to enforce that adding or removing an electron into state i introduces a phase $-1^{\text{total occupation of state 0 to i-1}}$. On the quantum computer, the creation operator with the right anti-symmetry becomes the many-qubit gate

$$Z_0 \otimes \cdots \otimes Z_i \otimes \frac{1}{2}(X_j - iY_j) \otimes I_{j+1} \otimes \cdots \otimes I_n$$

The task then becomes to find a different representation of the occupation states of the system which will reduce the number of gates on the quantum computer needed to simulate the fermionic annihilation and creation operators.

2.3 The parity basis

The central idea is transform to a basis which represents the occupation of site i, but reduces the number of necessary Z operations by recording the parity of the number of electrons in all earlier states.[3] The parity

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[1]Orbitals here also include spin: one physical orbital can contain two electrons of opposite spin, but we split it into two spin orbitals.

basis is the most obvious choice choice. In this representation, set entry i in the state $|[0, 1]^n\rangle$ to 0 if the number of electrons from 0 to i is even and 1 otherwise.

This choice of basis is even worse than the occupation number basis. While adding or removing an electron now requires only one application of the Z gate to state $i - 1$, X gates must be applied to qubits $i + 1 \ldots n$, flipping these bits so that they can account for the presence the change in parity of the number of electrons in lower states. Therefore this basis does not reduce the number of gates.

In addition, which gate to apply to state i in order to create or annihilate a particle there now depends on whether $|0\rangle$ represents an occupied or unoccupied orbital: If state $i - 1$ has $|0\rangle$, then the entry $|1\rangle$ in state i represents a occupied state i as before, and the Q^+, Q^- gates can be applied as above. If state $i - 1$ has $|1\rangle$, then simulating a creation requires applying the annihilation gate Q^-, and vice versa. The two-qubit gate

$$Q^\pm_* = \frac{1}{2} \left(Z_{j-1} \otimes X_j \mp I_{j-1} \otimes iY_j \right)$$

implements this operation.

While this most obvious choice of basis fails to reduce the number of operations, it illustrates a trade-off between applying many Z gates to keep track of phase or many X gates to keep track of parity. There exists a basis which compromises between these two, and manages to require only $O(\log n)$ gates total.

2.4   The Bravyi-Kitaev basis

The interpretation of the elements of the state vector in this basis is not as physically clear as for the occupation or parity bases. This basis, first described in [2], is designed to efficiently write fermionic operators in terms of qubits. In this basis, a state i records the parity of of the electrons in states i through $i - k$, where $k = min_n (i \mod 2^n \equiv 0)$. In other words, each state is the sum (mod 2) of the number of electrons in k orbitals, where k is the first place missing from the binary representation of i. To illustrate, what information states 0–7 record is tabulated:

i	i_2	k	Encodes information about
0	000	1	0
1	001	2	0, 1
2	010	1	2
3	011	4	0, 1, 2, 3
4	100	1	4
5	101	2	4, 5
6	110	1	6
7	111	8	0, 1, 2, 3, 4, 5, 6, 7

Three pieces of information are necessary in order to determine the action of a_i on this basis: First, which states must flip parity when the number of electrons in state i changes? In other words, which states include information about state i? Secondly, which states must pick up a phase when state i changes, because they contain information about states less than i? Finally, when should Q^+_i or Q^-_i be applied to annihilate or create in state i?

The first question is the simplest. The set which encodes information about state i can be found by calculating which states are included in every state j, as in the table above, and then taking the inverse. If there is a conveniently written exact formula, it is not known. There are at most $\log n$ states which include information about state i, so annihilating or creating in state i causes at most $\log n$ applications of gate X.

The second question asks which states include information about states with index lower than i. When i updates, these must add a phase factor -1 so that the correct commutation relations hold. The easiest way to determine this set is to construct the matrix taking the Bravyi-Kitaev basis to the parity basis. Again, there are at most $\log n$ such states which must be operated on by Z each the occupation of i changes.

Finally, again at most $\log n$ states determine whether the state $|0\rangle$ in place i represents an unoccupied or occupied orbital i, in order to correctly apply Q^+ or Q^-. Also again, there is no easy way to see what this set should be, other than by constructing the matrix taking the Bravyi-Kitaev basis to the occupation basis, and noting which states include information about state i and $i - 1$.

Once these three sets is identified, writing out the exact gates corresponding to the operators a_i and $a_i^\dagger$ is both straightforwards and tedious. The exact form, as well as the forms for the two- and four-operator products can be found in [3]. Importantly, this transformation has reduced the number of necessary gates from scaling with n to scaling with $\log n$, at the cost of only a little more pre-processing. It is not known if the Bravyi-Kitaev is the basis mapping which minimizes the number of necessary gates.

3 Finding expectation values

As described above, the electronic structure Hamiltonian can be written in terms of the creation and annihilation operators, and by Brevyi-Kitaev, there is a mapping of these gates onto Pauli gates applied on a quantum computer. Estimating the ground state energy now requires finding

$$\min_{\psi} \langle\psi|H|\psi\rangle$$

This section describes three ways to calculate expectation values of arbitrary states under any operator U. Our implementation uses the last.

3.1 The Hadamard test

After preparing the state ψ, apply controlled U, with an ancilla $|+\rangle$ state as the control and ψ as the target. Apply the Hadamard gate to the ancilla. This qubit is now in the state

$$Hd\left(|0\rangle \otimes |\psi\rangle + |1\rangle \otimes U\,|\psi\rangle\right) = |0\rangle \otimes |(\psi + U\psi)\rangle + |1\rangle \otimes |(\psi - U\psi)\rangle$$

so the probability of measuring in state 0 is

$$P(|0\rangle) = \langle(I+U)\psi\rangle\,(I+U)\psi = \langle\psi\rangle\,(I+U^\dagger)(I+U)\psi = \langle\psi\rangle\,(I+U^\dagger+U+U^\dagger U)\psi = 2 + \langle\psi|U|\psi\rangle + \langle\psi|U|\psi\rangle^\dagger$$

If all expectation values are real i.e. if U is also Hermitian, then this procedure gives $2(1 + \langle\psi|U|\psi\rangle$. If not, then using this procedure returns $2 + 2\text{Re}(\langle\psi|U|\psi\rangle)$.

The Pauli matrices are indeed both Hermitian and unitary, so this procedure works well for the electronic structure problem. However, it involves putting an additional qubit into superposition with ψ, and so increases the error on a noisy quantum computer. For this reason, we do not use this method.

3.2 Using $|\psi\rangle = V\,|0\rangle$

If we are to measure the expectation value of the state ψ, we must be able to produce it by applying some operator to $|0\rangle$. Therefore,

$$\langle\psi|U|\psi\rangle = \langle V0|U|V0\rangle = \langle 0|V^\dagger U V|0\rangle$$

Applying $V^\dagger U V$ and measuring in the standard basis will then give $|\langle\psi|U|\psi\rangle|^2$ This method does not preserve all information about $\langle\psi|U|\psi\rangle$, because the spectrum of a unitary U cannot be all real and positive.

3.3 Measuring in the eigenbasis

If the eigenvectors of the matrix U are known, then measuring in the basis of eigenvectors can give the expectation value. Say that $U\,|\phi_i\rangle = \lambda_i\,|\phi_i\rangle$. Then

$$\langle\psi|U|\psi\rangle = \langle\sum_i a_i\phi_i|U|\sum_i a_i\phi_i\rangle = \sum_i |a_i|^2\,\langle\phi_i|U|\phi_i\rangle = \sum_i |a_i|^2\lambda = \sum_i P(|\phi_i\rangle)\lambda_i$$

Thus, measuring in the basis of eigenstates can give the expectation values. Note that this algorithm never applies the matrix U, but instead applies the transformation sending the eigenstates to the standard basis states. This transformation is guaranteed to exist, but might be expensive to find for large dimensional U.

In our implementation, we take the expectation of products of Pauli gates. In addition, the eigenstates of a tensor product of matrices are the tensor products of the eigenstates of each component, and the eigenvalues are the product of the corresponding component eigenvalues. Finding the eigenvectors of the component 2×2 matrices is not difficult, so finding the right eigenbasis for the tensor products of Pauli matrices is not difficult.

4 The Variational Principle

The above section demonstrates how to use a quantum computer to efficiently find expectation values for arbitrary states. The connection of this task to finding the ground state is not apparently obvious. Notice, however that any state can be written in the basis of eigenstates of the energy operator

$$\phi = \alpha_0\phi_0 + \alpha_1\phi_1 + \alpha_2\phi_2 + \dots$$

for some constants α_i. If the energy of state ϕ_i is E_i, then the energy expectation value of ϕ is

$$\langle\phi|H|\phi\rangle = \sum_i \alpha_i^2 E_i$$

Taking that the ground state E_0 is smaller than the other E_i,

$$\langle\phi|H|\phi\rangle > E_0$$

.

Physically, this is a result of the tautology that all states have a higher energy than the lowest energy state. For this purpose of the variational eigensolver, we use that the expectation value of any state is an upper bound on the true energy, and that the bound becomes tighter with larger α_0, i.e. that the bound is tighter when the state is closer to the the real ground-state energy.

The variational eigensolver uses these ideas in the following procedure: First, generate some ansatz states which for some physical reason we believe to include some state very close to the ground energy state. Next, calculate the energy expectation values of them all. The lowest one is the estimate for the ground-state energy, and the state giving the lowest energy is most similar to the true ground state. Again, the advantage that quantum computation provides is in calculating expectation values. Generating ansatz states is performed classically.

5 Implementing for Hydrogen

We closely follow [4] in simulating the energy of a H_2 molecule. The family of ansatze states is based on Hartree-Fock, assuming that taking superposition of the four lowest-energy Hartree-Fock orbitals is close enough to the true ground state.

5.1 Reducing the number of qubits

Using Hartree-Fock to find n orbitals with which to solve the electronic structure problem would then require 2^n states to describe all possible occupations of those states. 2^n qubits would be needed to act on this state. However, a little chemical knowledge about the molecule can greatly reduce the necessary information. In the case of H_2, four Hartree-Fock orbitals yielding 16 qubits will be reduced to only two.

The occupation states can describe systems with any number of electrons. Typically, we know in advance the number of electrons in a certain molecule, so we can set the occupation of states without that number of electrons to $|0\rangle$ and not include them. H_2 has two electrons and only $\binom{4}{2} = 6$ states are needed to describe two-electron states.

Additionally, we know not only the number of electrons but also the number of electrons with each spin. Ground state H_2 has one electron of each spin, allowing us to remove two more states in which both electrons are in spin orbitals of the same spin. This leaves four possible configurations. Following the paper, we assume a family of ansatz states of the form $\cos\theta\,|0100\rangle + \sin\theta\,|0010\rangle$, a state mostly composed of the ground state $|0\rangle\otimes|1\rangle$ in superposition with a small amount of the singly-excited state $|1\rangle\otimes|0\rangle$. This choice of ansatz can be justified by the coupled-cluster correction to the Hartree-Fock state[6], or by arguments from symmetry of wavefunctions.

Results

The circuit shown below generates this family of states, parameterized by the RZ_θ gate, and then transforms to the right basis to measure the expectation value of some qubit, as described above. This circuit, diagrammed below, was run on IBM's 5-qubit open-access computers.
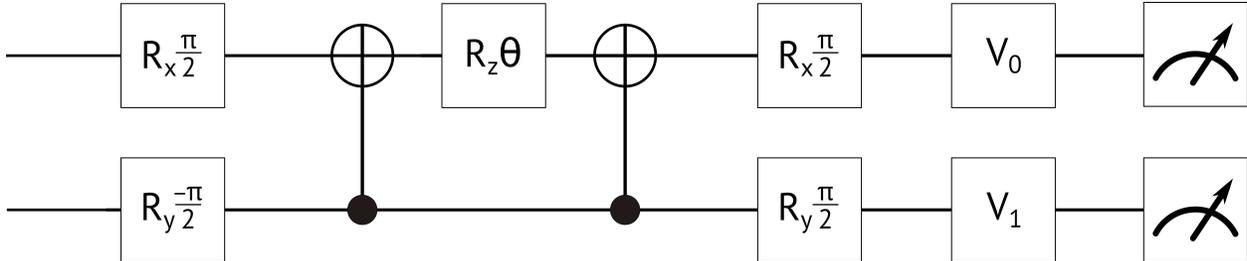

Figure 1: The circuit run on the IBM computers. Here, V_0 and V_1 are the matrices which take the eigenbasis of the gate under investigation to the standard basis. Here, R_σ are the matrices $e^{-i\theta\sigma}$ generated by the Pauli matrices.

In order to save computational cost, we calculate only for θ on the range $(0, 2)$, because classical simulation of the quantum computer to determines that this is where the minima lie. To give an example of the output, we show tabulated some of the output expectation values:

θ	Quantum Computer					Classical Simulation				
	$\langle Z_0\rangle$	$\langle Z_1\rangle$	$\langle Z_0Z_1\rangle$	$\langle X_0X_1\rangle$	$\langle Y_0Y_1\rangle$	$\langle Z_0\rangle$	$\langle Z_1\rangle$	$\langle Z_0Z_1\rangle$	$\langle X_0X_1\rangle$	$\langle Y_0Y_1\rangle$
0.0	-0.92	0.97	-0.91	0.19	0.15	-1.00	1.00	-1.00	0.01	-0.03
0.2	-0.86	0.93	-0.84	-0.05	-0.13	-0.99	0.97	-1.00	-0.18	-0.21
0.4	-0.83	0.89	-0.86	-0.27	-0.20	-0.93	0.93	-1.00	-0.41	-0.42
0.6	-0.80	0.78	-0.84	-0.25	-0.34	-0.83	0.83	-1.00	-0.59	-0.54
0.8	-0.69	0.13	-0.80	-0.44	-0.47	-0.67	0.71	-1.00	-0.70	-0.75
1.0	-0.55	0.53	-0.78	-0.50	-0.58	-0.55	0.56	-1.00	-0.81	-0.85

The quantum computer has problems properly generating the state. Recall that the ansatz has the form $a(\theta)|01\rangle + b(\theta)|10\rangle$, a eigenstate of the Z_0Z_1 operator with eigenvalue -1. The measurement of the expectation value of this operator on the quantum computer is not -1 and the error increases with θ. It is not clear why higher θ leads to more error.

Nevertheless, remember that

$$E_{total} = g_0 + g_1\langle Z_0\rangle + g_2\langle Z_1\rangle + g_3\langle Z_0Z_1\rangle + g_4\langle Y_0Y_1\rangle + g_5\langle X_0X_1\rangle$$

It follows then that after determining the expectation value for each set of Pauli gates on each ansatz $\phi(\theta)$, the energy can be determined at any internuclear distance distance r by multiplying by the coefficients $g_i(r)$, which depend on the two- and four-election interaction orbitals. These are tabulated in [4]. Plotting the energies as a function of r and θ gives the chart in figure 2.

Finding the minimum at each r gives the potential energy curve for molecular hydrogen in figure 3. The minimum of this graph, the predicted H_2 bond length, is very close to the experimental value of $7.4\,\text{Å}$. Qualitatively, the shape matches the exact theoretical and accepted experimental result. The vertical shift of the result of the quantum computer is probably related to the failure of $\langle Z_0Z_1\rangle$ to be exactly -1.
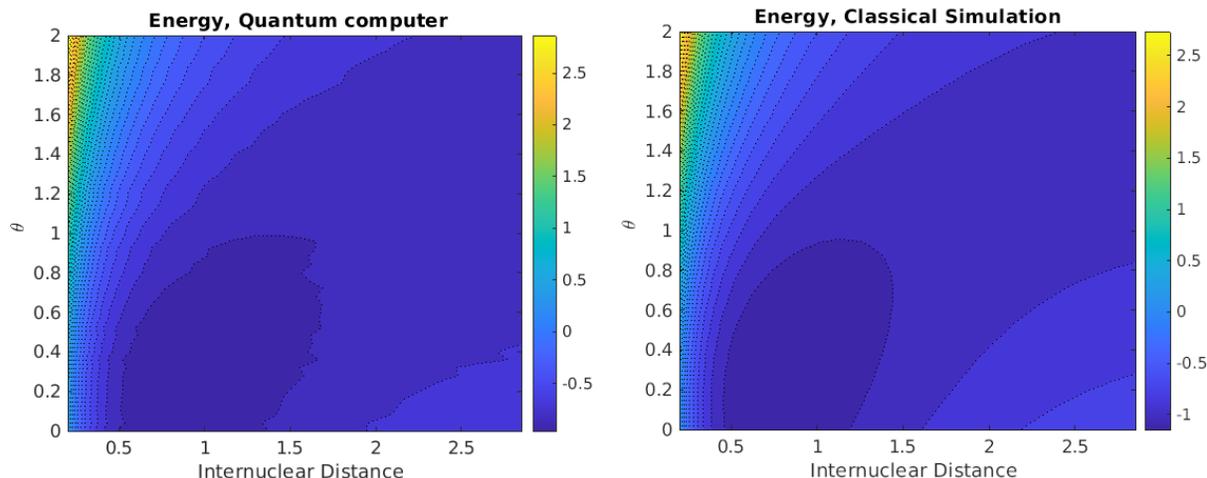
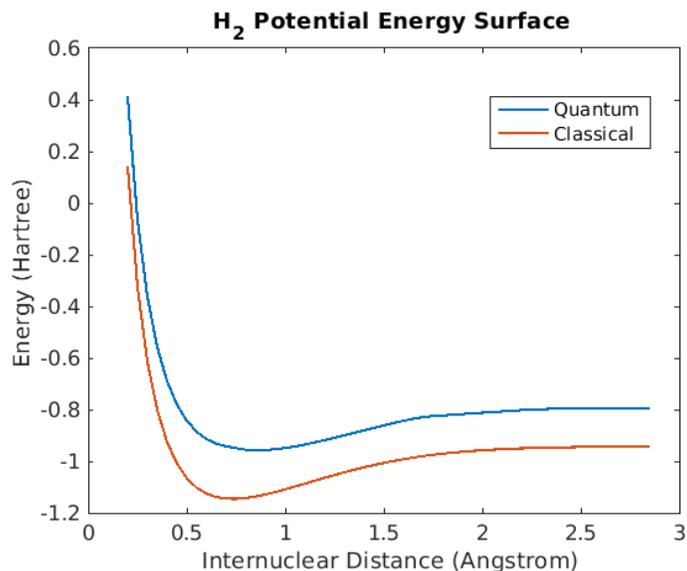Figure 2: Energy of various ansatz at different internuclear distances.

Figure 3: Potential energy curve for molecular hydrogen.

6   Conclusion

We have described how to implement the variational quantum eigensolver to solve the central problem of computational chemistry, finding the ground-state energy of a molecule. This method works even on a physical, noisy quantum computer. To conclude, we describe some related open areas of research.

6.1   Better computers and phase estimation

The proceeding sections have described a method that works on small, noisy quantum computers, but requires preparing many ansatz states, and only gives an upper bound on the energy. Phase estimation requires an error-free quantum computer, but gives the energy exactly. It still requires preparation of an ansatz, but the only requirement is that the overlap of the ansatz with the true ground state is high.

Mapping the molecular Hamiltonian to the basis proceeds exactly as for the variational eigensolver, as

does finding some ansatz state. At first, the initial state is

$$|\psi\rangle = (1 - \epsilon) |\phi_{gs}\rangle + \epsilon' |\phi'\rangle$$

where $|\phi_{gs}\rangle$ is the true ground state and $|\phi'\rangle$ is the difference between the ansatz and the true ground state. Now, applying $U = e^{inH}$ yields

$$\left((1 - \epsilon) e^{2\pi in\theta} |\phi_{gs}\rangle + \epsilon' |\phi''\rangle\right)$$

where $2\pi\theta$ is the ground state energy. As long as ϵ is small, quantum phase estimation will give θ to any desired precision with high probability.

As we discussed in class, quantum phase estimation requires access to high powers of controlled U and a large register of ancilla bits. It is possible to work around these problem for molecular simulation: Trotterization gives one way to estimate large powers of U. In addition, the phase estimation algorithm can be run in series one bit at a time, from least significant bit to most, using only one ancilla bit.[5] The only additional step necessary is a rotation by the phases determined by the previous steps: That is, if two previous steps have determined that the binary expansion of the phase ends in $\theta n - 1\theta n$, then the third iteration must rotate the ancilla bit by $2^{-2}\theta_{n-1}\theta n$ before measuring in the $|+\rangle, |-\rangle$ basis.

Unlike variational methods, where it is possible to run the calculation many times in hope of mitigating the effect of noise, this algorithm is more sensitive to noise because an error at any iteration will cause the rest of the calculation to be incorrect. Finding the energy to 2^{-n} precision requires a computer which reliably do $O(n)$ operations without a single error. For reasonable n this is far beyond the ability of current computers.

Stability in the presence of noise is the only advantage of the variational eigensolver over methods based on phase estimation. As quantum computers improve, phase estimation replace variational methods. However, the variational eigensolver is a useful technique in the noisy, intermediate scale regime of current technology.

6.2 Directions for future work

6.2.1 Optimization

In our implementation we considered only a one-dimensional family of trial states. In this space, it is simple to scan over every possible ansatz. For higher-dimensional systems this would be unworkable. It's not clear how to efficiently optimize in the presence of noise. Gradient descent does not work well here. In addition, it would be interesting to know if there is a quantum optimization algorithm that could be applied to this problem.

6.2.2 Mapping the problem onto qubits

Is the Brevyi-Kitaev basis the one which minimizes the number of operations? Is it possible to prove that $O(\log n)$ gates are needed to represent the action of an annihilation or creation operator? Is it possible to develop mappings that correspond to the hardware of a certain quantum computer, to guarantee that operations are applied locally on cubits physically connected to each other?

6.2.3 Choosing an ansatz

Is it possible to choose ansatz states such that they can be reliably produced on particular hardware? Are there faster ways to choose an ansatz that don't rely on calculating the Hartree-Fock state?

References

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