

VQE Algorithm in Quantum Chemistry

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Abstract. For a complex quantum system, the dimensionality of the Hamiltonian grows exponentially with the size of the system, making it difficult to perform fast large-scale simulations and calculations on a classical computer. The first Variational Quantum Eigenvalue solver (VQE) proposed by Peruzzo et al. This gives the possibility of highly accurate molecular simulations and calculations in the field of quantum chemical computing. VQE is roughly based on the principle of using a quantum computer and set up a trial wave function $|\psi(\theta)\rangle = U(\theta)|\psi_0\rangle$ to measure the energy expectation of the wave function $|\psi(\theta)\rangle$ at the corresponding initialization parameter, and then using a classical optimization algorithm to iterate $\theta_0 \rightarrow \theta_n$ over the energy to minimum until convergence. The significance of this paper is to verify the accuracy as well as the feasibility of the VQE algorithm for the calculation of LiH molecules in STO-3g basis, and to perform an error analysis and to verify the exponential acceleration of the classical algorithm implementation. These results shed light on guiding further exploration focusing on quantum computing.

Keywords: Quantum computing, Variational methods, Electronic structure, Quantum chemistry.

1. Introduction

The Schrödinger equation plays a very important role in quantum mechanics and so does the method of solving for the minimum eigenvalue of a quantum matrix [1-3]. Quantum chemistry is often the application of the fundamental theories and methods of quantum mechanics to solve numerical solutions of various specific types of Schrödinger equation [4-6]. Quantum chemical simulations on high-performance computers have become an important tool for studying the physical and chemical properties of materials. However, solving the Schrödinger equation exactly has exponential complexity so that the scale of the chemical systems that can be simulated is severely limited by this. Contemporarily, the state-of-art researches in quantum computing have provided a feasible path to solve this problem, promising a high precision solution of the Schrödinger equation at polynomial complexity on quantum computers.

VQE is a type of variational quantum algorithm, which was designed to train a parametric circuit using a classical optimizer for solving matrix eigenvalues and eigenvectors. The Hamiltonian H can be expressed as the sum of several bubble operators, and the ground state energy of H corresponds to the sum of the minimum energies of each of the bubble operators. Afterwards, using the classical gradient descent algorithm, iterations make $\theta_0 \rightarrow \theta_n$ and then update the parametric quantum circuit $U(\theta)$.

The rest part of the paper is organized as follows. The Sec. 2 will introduce the principle and the methodology will be presented in Sec. 3. Subsequently, the results and discussion will be demonstrated in Sec. 4. Afterwards, a brief summary will be given in Sec. 5.

2. Principle

2.1 Born-Oppenheimer approximation

The total molecular energy can be expressed in the BO approximation as a sum of polynomials with several independent terms:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{nuclear\ spin} \quad (1)$$

Since the mass of the nucleus is much greater than that of the electron and the speed of motion is much lower than that of the electron (the mass of the proton is 1836 times that of the electron), Assuming that the motion of the nucleus or that of the electron can be discussed separately, so that the two can be separated into variables and the following equation of motion for the electron without time, also known as the stationary Schrödinger equation, can be obtained as:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2)$$

Where $\hat{H}$ is equals to the sum of the following three independent terms, electron kinetic energy, electron-electron potential energy and electron-nuclear potential energy, respectively:

$$\hat{H} = \hat{K}_e + \hat{V}_{ee} + \hat{V}_{Ne} \quad (3)$$

2.2 Second quantization

The key idea of the method was first proposed by Paul Dirac in 1927. The ordinary methods of quantum mechanics can only be applied to those quantum systems in which the number of particles is always conserved. In relativistic quantum mechanics, however, the number of particles is no longer always conserved. Particles can be created and annihilated, so those mathematical formulations of ordinary quantum mechanics will no longer be applicable either. Second quantization deals with the creation and annihilation of particles by introducing creation and annihilation operators. Under the quadratic quantization formulation, the Hamiltonian of the system has the following form:

$$\hat{H} = \sum_{p,q} h_q^p E_q^p + \sum_{p,q,r,s} \frac{1}{2} g_{rs}^{pq} a_p^\dagger a_q^\dagger a_r a_s \quad (4)$$

where $a_p^\dagger$ is the Creation Operator and a_q is the Annihilation Operator. Thus, the wave function of the excited state can be expressed as:

$$|\Psi_{ijk\dots}^{abc\dots}\rangle = a_a^\dagger a_b^\dagger a_c^\dagger \dots a_i a_j a_k \dots |\Psi\rangle \quad (5)$$

2.3 Ansatz for UCC

Unitary Coupled-Cluster theory defaults to real numbers for the angle parameter in the operator. The first chemical simulation experiments on a quantum computer using VQE combined with the UCCSD (Unitary coupled-cluster with singles and doubles) formulation were carried out by Peruzzo et al. in 2014 [7]. The function can be expressed as:

$$|\Psi_{UCC}\rangle = \exp(\hat{T} - \hat{T}^\dagger) |\Psi_{HF}\rangle \quad (6)$$

where the coupled cluster operator $\hat{T}$ is a summation over the excitation operator

$$\hat{T} = \sum_{\substack{p \notin occ \\ q \in occ}} \theta_q^p E_q^p + \sum_{\substack{pq \notin occ \\ rs \in occ}} \theta_{rs}^{pq} a_p^\dagger a_q^\dagger a_r a_s + \dots \quad (7)$$

Changing this to the UCC form, one derives unitary coupled cluster (UCC) ansatz:

$$U(\theta) = e^{\hat{T} - \hat{T}^\dagger} \quad (8)$$

2.4 The Variational Quantum Eigenvalue solver

The variational principle shows that the ground state energy obtained from any trial wave function is always greater than or equal to the actual ground state energy (under certain conditions).

$$\lambda \leq \lambda_\theta \equiv \langle \psi(\theta) | H | \psi(\theta) \rangle \quad (9)$$

Using $|\Psi_t\rangle$ in the below equation to represent the trial wave function. The energy eigenvalue can therefore be expressed as:

$$E_0 \leq \frac{\langle \Psi_t | H | \Psi_t \rangle}{\langle \Psi_t | \Psi_t \rangle} \quad (10)$$

The variational principle provides a method for solving the Schrödinger equation for the molecular ground state: using a parameterized function $f(\theta)$ as an approximation to the exact ground state wave function, the exact ground state energy is approximated by optimizing the parameter θ .

3. Method

3.1 Hartree-Fock method

The core idea of the Hartree-Fock method is approximating a multi-particle state by a set of single-particle states of Slater determinant and aims to solve the time-independent Schrödinger equation for a multi-electron quantum system with BO-approximation [8].

$$\langle x_1 x_2 \dots x_N | HF \rangle = \frac{1}{\sqrt{N}} \begin{bmatrix} \chi_1(x_1) & \dots & \chi_N(x_1) \\ \vdots & \ddots & \vdots \\ \chi_1(x_N) & \dots & \chi_N(x_N) \end{bmatrix} \quad (11)$$

That's the Hartree-Fock matrix where these single-particle wave functions χ_i are generally referred to as "orbitals". Denoting the Fock operator as: (include single-particle/Coulomb/exchange operator)

$$f = h + \sum_i J_i - K_i \quad (12)$$

and the Hamiltonian for one-electron Fock operator in this method is:

$$\hat{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \quad (13)$$

Substituting the above equation into the Schrödinger equation gives the equation that needs to be satisfied for the orbit χ_i is:

$$f\chi_j = \sum_i \epsilon_{ij}\chi_i \quad (14)$$

3.2 Full Configuration Interaction method

Full configuration interaction (FCI) is a linear variational method, it can calculate non-relativistic exact solutions of the time-invariant Schrödinger equation. In contrast to the Hartree-Fock method, it allows for a good introduction of correlations between electrons [9-11]. By means of the variational wave function, it is a linear combination of configuration state functions constructed from spin orbitals (denoted by the upper SO). Noting that Ψ is usually the electronic ground state of the system,

$$\Psi = \sum_{I=0} c_I \Phi_I^{SO} \quad (15)$$

The eigenequations generated by the CI method can be obtained as follows:

$$Hc = eSc \quad (16)$$

where e is the eigenvalue matrix, c is the coefficient, and the elements of the Hamiltonian and overlap matrices are respectively as:

$$H_{ij} = \langle \Phi_i^{SO} | H^{el} | \Phi_j^{SO} \rangle \quad (17)$$

$$S_{ij} = \langle \Phi_i^{SO} | \Phi_j^{SO} \rangle = \delta_{ij} \quad (18)$$

The above matrix is of course simplicial, since the Slater series consists of a set of orthogonal spin orbitals. The eigenvalues and eigenvectors obtained are the solutions required for the CI method.

3.3 VQE process

First, one needs to create the initial state of the corresponding molecule if one wants to use VQE to solve it, i.e., to define the wave function fitting (FCI, UCC, UCCSD, etc.), transform the wave function fitting into a parametric quantum line, and then initialize the variational parameters [12, 13]. The energy $E(\theta)$ of the molecular Hamiltonian under the set of variational parameters and the derivative of the energy with respect to the parameters are measured several times on a quantum computer, and the sum is updated on a classical computer using a gradient descent optimization algorithm. Finally, the new variational parameters are passed into the quantum line and updated and repeated until convergence to the desired accuracy.

4. Results and Discussion

Based on the algorithms, the results For HF molecule (the bond length of the molecule is 112 picometres) is listed in Table. 1 and 2. The optimize step is 63 for both CCSD and FCL with the energy of -7.8823529091527007 Ha and -7.8823622867987213 Ha.

Table 1. The optimization for CCSD energy

Step	0 energy	-7.8173098564147949
Step	5 energy	-7.8740758895874023
Step	10 energy	-7.8818783760070801
Step	15 energy	-7.8821649551391602
Step	20 energy	-7.8822622299194336
Step	25 energy	-7.8823080062866211
Step	30 energy	-7.8822288513183594
Step	35 energy	-7.8758554458618164
Step	40 energy	-7.8761253356933594
Step	45 energy	-7.8807921409606934
Step	50 energy	-7.8818383216857910
Step	55 energy	-7.8821811676025391
Step	60 energy	-7.8823504447937012
Optimization completed at step 63		
Optimized energy: -7.8823523521423340		
Optimized amplitudes:		
-2.42472161e-04	1.89258391e-03	-3.46013680e-02 1.59353409e-02
-8.40432079e-08	9.09362687e-04	2.01798011e-05 1.41534032e-02
-2.81526667e-07	9.08639806e-04	2.00776722e-05 1.41590768e-02
5.45396935e-04	4.26715094e-04	-2.84755090e-03 5.38354851e-02
2.29954778e-04	9.55212727e-07	-1.24844689e-07 -9.20767249e-08
-4.53033465e-07	-7.44455733e-08	-8.83169875e-08 1.17984437e-05
-1.04996754e-04	7.94677646e-04	-4.50417019e-06 -4.49753043e-06
-5.48430867e-02	3.08870710e-03	-6.50319926e-05 1.26427835e-06
1.25660222e-06	-2.82077963e-07	7.96948143e-08 -3.28978906e-08
-3.63568660e-07	5.76087541e-06	3.08870478e-03 8.82309266e-08
5.73797401e-08	-2.53652850e-08	5.72846511e-06 3.71275470e-04

The VQE algorithm combined with the theory of the unitary coupled clusters can effectively avoid the exponential increase in complexity associated with solving Schrödinger's equation exactly, and in the future, it may be possible to achieve high accuracy in solving Schrödinger's equation with polynomial complexity on quantum computers. In the NISQ era, this type of hybrid computing algorithm between quantum and classical computing can increase the speed of computation to a certain extent and compensate for the disadvantage of insufficient quantum numbers. However, the most essential application of VQE is to quickly solve for the ground state energies of all types of polyatoms and molecules containing many electrons

In a VQE algorithm such as the one used in this paper, the energy solutions for different atomic bond lengths are completely independent. Various disturbances and troubles are therefore encountered, for example the optimization is often affected by local minima, statistical errors in measurements, chip noise, etc., which will affect the accuracy of the calculation and the degree of maximum convergence.

Table 2. The optimization for FCL energy

Step	0 energy	-7.8173098564147949	
Step	5 energy	-7.8740758895874023	
Step	10 energy	-7.8818783760070801	
Step	15 energy	-7.8821649551391602	
Step	20 energy	-7.8822622299194336	
Step	25 energy	-7.8823080062866211	
Step	30 energy	-7.8822288513183594	
Step	35 energy	-7.8758554458618164	
Step	40 energy	-7.8761253356933594	
Step	45 energy	-7.8807921409606934	
Step	50 energy	-7.8818383216857910	
Step	55 energy	-7.8821811676025391	
Step	60 energy	-7.8823504447937012	
Optimization completed at step 63			
Optimized energy: -7.8823523521423340			
Optimized amplitudes:			
-2.42472161e-04	1.89258391e-03	-3.46013680e-02	1.59353409e-02
-8.40432079e-08	9.09362687e-04	2.01798011e-05	1.41534032e-02
-2.81526667e-07	9.08639806e-04	2.00776722e-05	1.41590768e-02
5.45396935e-04	4.26715094e-04	-2.84755090e-03	5.38354851e-02
2.29954778e-04	9.55212727e-07	-1.24844689e-07	-9.20767249e-08
-4.53033465e-07	-7.44455733e-08	-8.83169875e-08	1.17984437e-05
-1.04996754e-04	7.94677646e-04	-4.50417019e-06	-4.49753043e-06
-5.48430867e-02	3.08870710e-03	-6.50319926e-05	1.26427835e-06
1.25660222e-06	-2.82077963e-07	7.96948143e-08	-3.28978906e-08
-3.63568660e-07	5.76087541e-06	3.08870478e-03	8.82309266e-08
5.73797401e-08	-2.53652850e-08	5.72846511e-06	3.71275470e-04

5. Conclusions

In summary, the calculation of the base-state energy is carried out by Hartree-Fock method, UCCSD and FCI method respectively. If the running times are counted, the calculation times $HF < UCCSD \ll FCI$, and for the total energy calculated, there is $HF > UCCSD > FCI$. These differences will be more evident when calculating molecules with more electrons and more complexity. This paper verifies that exponential acceleration is achieved on a real quantum computer using the VQE algorithm. The accuracy and computation time of the algorithms are also measured and compared for specific molecules at different Ansatz. As the number of quantum bits contained in a quantum computer rises, faster computation speeds and higher accuracy of ground state energies can be achieved. It does not exclude the possibility of gradually moving away from the aid of classical algorithms in the future.

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