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Quantum algorithm for obtaining the energy spectrum of molecular systems

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Simulating a quantum system is more efficient on a quantum computer than on a classical computer. The time required for solving the Schrödinger equation to obtain molecular energies has been demonstrated to scale polynomially with system size on a quantum computer, in contrast to the well-known result of exponential scaling on a classical computer. In this paper, we present a quantum algorithm to obtain the energy spectrum of molecular systems based on the multiconfigurational self-consistent field (MCSCF) wave function. By using a MCSCF wave function as the initial guess, the excited states are accessible. Entire potential energy surfaces of molecules can be studied more efficiently than if the simpler Hartree–Fock guess was employed. We show that a small increase of the MCSCF space can dramatically increase the success probability of the quantum algorithm, even in regions of the potential energy surface that are far from the equilibrium geometry. For the treatment of larger systems, a multi-reference configuration interaction approach is suggested. We demonstrate that such an algorithm can be used to obtain the energy spectrum of the water molecule.

I. Introduction

Since the discovery of a polynomial quantum algorithm for factorization,[1] other quantum algorithms that provide exponential speedup over their classical counterparts have been found. Examples in diverse areas include the computation of approximations to the Jones polynomial[2] and certain instances of the hidden subgroup problem.[3] Feynman observed that simulating a quantum system might be more efficient on a quantum computer than on a classical computer.[4] Further work by others has born out this early suggestion.[5–11] Although a quantum computer to carry out the calculations that we propose is not currently experimentally realizable, many recent developments in quantum information technology[12–15] continue to get closer towards the implementation of such a device.

In quantum chemistry, where molecular quantum systems are simulated on a classical computer, one is restricted to employ a finite basis to span the formally infinite Hilbert space that would describe the electronic structure of a molecular system. The full configuration interaction (FCI) method[16] diagonalizes the molecular Hamiltonian to provide solutions to the electronic structure problem that are exact within this basis. FCI scales exponentially with respect to the size of the molecular system studied and therefore is restricted to the treatment of small diatomic and triatomic systems.[17] Recently, a quantum algorithm for the solution of the FCI problem in polynomial time was proposed by Aspuru-Guzik *et al.*[9] This algorithm employed the HF wave function as a reference for further treatment of the correlation effects by the FCI Hamiltonian on the quantum computer. The excited states of molecular systems are difficult to resolve by employing the HF wave function as an initial trial state. The main reason for this difficulty is due to the fact that contributions from several configuration state functions (CSF) must be considered if one is seeking a reasonable overlap of the trial state with the exact wave function. In the quantum chemical study of molecular systems, people are often interested in computing molecular properties, such as the energy of the ground state and a few low-lying excited states. *i.e.*, in study of the spectroscopic properties of molecules. In such cases, an FCI calculation might become too expensive even for a quantum computer for some large systems. A multi-reference configuration interaction (MRCI)—truncated CI—calculation based on an a multi-configurational self-consistent field (MCSCF) wave function can sometimes provide results within chemical accuracy, but with much less computational work than FCI due to the smaller Hilbert space associated with the calculation. It is difficult to describe various regions of molecular potential energy surfaces, sometimes even qualitatively correct, by using a single reference determinant. Many reference determinants or configuration state functions are often required for the description of bond-dissociation regions.

In this paper, we suggest a quantum algorithm to obtain energy eigenvalues of a MRCI wave function of a molecular system using the MCSCF wave function as initial input to a quantum computer. We show that by improving the quality of the trial wave function, the proposed algorithm yields substantially higher success probabilities than by employing the

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HF wave function. The use of a MCSCF wave function simultaneously reduces the amount of quantum computing resources needed and extends the range of reliable quantum computations to excited states and treacherous regions of the potential energy surface. Simulating a chemical system with a quantum computer requires the mapping of the Fock space of the MCSCF wave function to the Hilbert space of the quantum bits (qubits) of a quantum computer. We introduce a more compact mapping technique for molecules by employing symmetry properties. This approach reduces the computational resources for representing the wave function on a quantum computer and avoids the state crossing-problem.

The structure of this work is as follows. In section II we will review the implementation of the FCI scheme on a quantum computer. Section III describes the properties of the MCSCF wave function. In section IV we describe a quantum algorithm for using MCSCF trial wave functions in a FCI quantum algorithm. In section V we discuss numerical evidence for the feasibility of this scheme as applied to calculations for the water molecule. We finalize with a conclusions section.

II. Implementation of CI scheme on a quantum computer

A closed quantum system in the non-relativistic limit can be described by its Schrödinger equation (atomic units are used),

$$i\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{1}$$

Feit[18] and coworkers suggested a method to solve the Schrödinger equation based on the spectral properties of the solutions to the time-dependent Schrödinger equation. Its solution can be expressed as a linear superpositions of eigenfunctions of the Hamiltonian,

$$\psi(r,t) = \sum_n A_n u_n(r)\exp(-iE_n t) \tag{2}$$

where the function $u_n(r)$ satisfies the equation $\hat{H}u_n = E_n u_n$. The method requires a numerical solution of $|\psi(r,\ t)\rangle$ and the correlation function $P(t)$:

$$P(t) = \langle\psi(r,\ 0)|\psi(r,\ t)\rangle = \int\psi^*(r,\ 0)\psi(r,\ t)\mathrm{d}r, \tag{3}$$

where $|\psi(r,\ 0)\rangle$ is the wave function at $t = 0$. $P(t)$ can then be expressed as

$$P(t) = \sum_n \langle A_n\rangle^2 \exp(-iE_n t), \tag{4}$$

which can be Fourier transformed to display the energy spectrum of the system as a set of sharp local maxima at $E = E_n$.

$$P(E) = \sum_n \langle A_n\rangle^2 \delta(E - E_n). \tag{5}$$

A scheme similar to the one proposed by Feit can be implemented on a quantum computer. Abrams and Lloyd[7] suggested finding eigenvalues and eigenvectors using a quantum phase estimation technique. Eigenfunctions of the Hamiltonian are also eigenfunctions of the unitary time-evolution operator, $U(t) = \exp(-i\hat{H}t)$, whose eigenvalues can be expressed as a phase factor. A quantum Fourier transform[22] (QFT) is used to retrieve the phase in a binary expansion and thus obtain the eigenenergy. This scheme has been proposed to simulate quantum systems, especially Fermion systems, on a quantum computer.[5,9,19,20] If the Hamiltonian can be decomposed by means of a split-operator technique,[6,8,11,18] the quantum computational cost is polynomial, it can provide an exponential speed increase over its classical counterpart.

The details of the algorithm proceeds as follows:[7,21] First, one must prepare two quantum registers, one is the index register composed of m qubits, which are used as control qubits and to perform a QFT operation. Another register of n qubits is the target register that is used to represent the wave function of the system. The index register is initially prepared in the zero state $|0\rangle$. The quantum bits of the index register are entangled with successive binary powers of the unitary evolution operator on the target register. After the time-evolution of the target register, the index register encodes an eigenvalue of the time evolution operator U of the target system as a phase represented in a binary notation. By performing a QFT, the phase, and therefore the eigenvalue of the system can be obtained.

The algorithm begins by initializing the quantum computer into the state:

$$|\Psi_0\rangle = |0\rangle|\psi\rangle \tag{6}$$

Performing a $\pi/2$ rotation on each qubit in the index register results on the state

$$|\Psi_1\rangle = \frac{1}{\sqrt{M}}\sum_{j=0}^{M-1}|j\rangle|\psi\rangle \tag{7}$$

where $M = 2^m$. By performing a series of controlled-U operations on this state, it is transformed into:

$$|\Psi_2\rangle = \frac{1}{\sqrt{M}}\sum_{j=0}^{M-1}\hat{U}^j|j\rangle|\psi\rangle \tag{8}$$

The approximate vector $|\psi\rangle$ can be written as a sum of eigenvectors of U,

$$|\psi\rangle = \sum_k c_k|\phi_k\rangle \tag{9}$$

where k sums over the dimensionality of the target register. The eigenvalue associated with $|\phi_k\rangle$ is $e^{i\phi_k}$, which can be written as $e^{2\pi i\omega_k/M}$, where $\omega_k \in [0,\ M)$. Using this fact, the state can be rewritten as:

$$|\Psi_2\rangle = \sum_k c_k|\phi_k\rangle\frac{1}{\sqrt{M}}\sum_{j=0}^{M-1}e^{2\pi ij\omega_k/M}|j\rangle. \tag{10}$$

A QFT performed on the index qubits will reveal the phases ω_k and thereby the eigenvalues. The QFT requires $\sim m^2$ operations.[22] Consequently, only a polynomial number of trials are required to obtain any eigenvalue for which the corresponding eigenvector is not exponentially small in the initial guess. If the initial guess is close to the desired state, then only a few trials may be necessary. Once a measurement is made and an eigenvalue is determined, the target register

qubits will collapse into the state of the corresponding eigenvector.

Aspuru-Guzik *et al.*[9] extended the algorithm to the study of molecular systems and simplified the algorithm by introducing a recursive phase-estimation technique that saves the qubits for performing the phase estimation. They also introduced an adiabatic state preparation (ASP) technique for obtaining molecular ground states. They demonstrated that such algorithms can be applied to problems of chemical interest using modest numbers of quantum bits.

III. MCSCF wave function

In the previous quantum computing for quantum chemistry work,[9] a HF wave function was used as the initial trial wave function. The HF method[23] represents the wave function as a single Slater determinant. In most cases, the HF wave function by itself is not sufficiently accurate to generate useful chemical predictions such as relative energies of products and reactants, and therefore a correlated calculation is necessary. Often, the HF wave function is not a good initial guess to the exact wave function of the system, especially for the excited states calculations, in which contributions from several Slater determinants must be considered, even for a qualitatively correct description. If a number of electron configurations are relatively close in energy (*i.e.* degenerate or near-degenerate), then the HF approximation is particularly poor. This is the usual case when one explores regions of avoided crossings (or anti-crossings), molecules close to the dissociation limit, in the limit of large system size, or in the study of a chemical reaction path[24] In such cases, it is more appropriate to describe the system with more appropriate wave functions in which several different electron configurations are taken into account.

One realization of such a wave function comes from MCSCF theory. The general form of an MCSCF wave function is:

$$\psi_{\mathrm{MCSCF}} = \sum_K D_K \Phi_K \tag{11}$$

$$\Phi_K = (N!)^{-1/2} \det\left|\prod_{i\subset K} \phi_i\right| \tag{12}$$

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} \tag{13}$$

which is a linear combination of several electron configuration state functions (CSF). Each CSF differs in how the electrons are distributed between the molecular orbitals (MOs), ϕ_i. For a particular system, the CSFs can be chosen based on physical consideration of the system. The MOs are usually expanded in a basis of atomic orbitals (AOs), χ_μ. To obtain a MCSCF wave function, both the configuration expansion coefficients D_K and the MO expansion coefficients $C_{\mu i}$ are variationally optimized. Hence, the optimized vector is the best approximation to the exact wave function of the system in a specific parameter space. For a given set of orbital and configuration parameters, even in a small variational space, the MCSCF wave function can give a much better approximation than the HF wave function. A truncated CI based on an MCSCF wave function, the so-called multi-reference CI method, normally gives better results than a CI using a HF wave function as a reference, when small Hilbert spaces are involved. The trade-off between the MRCI approach and the FCI approach is that chemical intuition is involved in selecting the apprpopriate CSFs for constructing the CI expansion.

As mentioned above, computational resource requirements are significantly less for any reasonable MCSCF calculation than for an FCI calculation in the same orbital space. Simple combinatorial arguments show that there are $\binom{2M}{N}$ possible Slater determinants formed from M molecular orbitals and N electrons, and although their number can be reduced by space- and spin-symmetry considerations, the growth in the number of determinants with system size remains exponential. Even a well-constructed algorithm that uses an iterative process for a subset of the roots (such as that by Lanzcos or Davidson)[25] will have CPU requirements that scale roughly as the square of the number of determinants. Moreover, the storage requirements scale as the number of determinants. Consequently, the FCI problem scales exponentially with system size.

In contrast, MCSCF uses an iterative process to obtain an optimal (in the variational sense) space of specific size, *e.g.*, 8 electrons in 12 orbitals. Even if one adopts the most costly (but simply definable) MCSCF calculation, the so-called complete active space SCF (CASSCF), and the resulting number of determinants is given by the same formula as for full CI, the CASSCF space is a tiny fraction of the full CI space. The number of iterations required to determine the optimal space is usually on the order of 10. The non-CI part of an MCSCF calculation is typically dominated by the transformation of electron repulsion integrals from the atomic basis in which they are calculated to the molecular orbital basis, which scales as M^5. In fact, in real MCSCF calculations, the integral transformation step is often the limiting step. It is worth noting that more complex MCSCF calculations can be made possible by the use of the macroconfiguation approach,[26] which can reduce the number of determinants in an MCSCF to a polynomial number even for larger orbital spaces. This essentially guarantees that a physically meaningful and mathematically robust MCSCF calculation will be integrally bound, and therefore scale as M^5 with system size[27,28] for systems of tens of atoms. Asymptotically, MCSCF has an exponential cost as well and therefore a quantum computer still provides an exponential speedup for this method.

In the MCSCF method, several states can be calculated simultaneously through a state-averaged approach.[29,30] For the nth MCSCF CI root, the energy function can be written as,

$$E_n = \frac{\langle\psi_n|H|\psi_n\rangle}{\langle\psi_n|\psi_n\rangle} \tag{14}$$

A more general energy-like function can be constructed by use of weighting vector,[31]

$$E = \sum_i w_i E_i \tag{15}$$

where w_i is the weight for state i. So, if we are interested in a few evenly or non-evenly weighted states, the MO expansion coefficients are optimized for all these states. By diagonalizing

the one-particle density matrix, we can obtain the occupation numbers in Fock space for each state. This will be used as initial guess and map to the qubits on a quantum computer in the quantum algorithm proposed in this work.

IV. Implementation of a general CI algorithm based on an MCSCF wave function on a quantum computer

The first step for the proposed simulation algorithm is to map the wave function of the system to the state of the target register. In quantum chemistry basis set methods, many-particle molecular wave functions are represented in terms of a single-particle basis expanded in terms of atomic orbitals and a many-particle basis expanded in terms of Slater determinants or CSFs. In direct mapping,[9] each qubit represents the fermionic occupation state of a particular atomic orbital. The Fock space of the molecular system is mapped to the Hilbert space of the qubits. The direct mapping has the advantage of yielding a simple Trotter expannsion in terms of a polynomial number of second-quantized Fermion operators.

The compact mapping considers the restriction of the multiplicity of the system and reduces the number of qubits to represent the wave function to a Hilbert space where all the quantum states of the target register correspond to valid electronic configurations within a given spin symmetry. The challenge of employing the compact mapping to general quantum systems is that the representation of the time-evolution operator may involve a larger number of non-local quantum gates.

Here we introduce a more compact mapping technique, which considers the symmetry restriction of the molecules. The electronic states can be categorized into different irreducible representation of their point group. The subspace associated with a particular irreducible representation can be mapped to the Hilbert space of the target register. This results in considerable savings in the number of qubits required to represent the wave function. Since there is no interaction between states that belong to different irreducible representations, this mapping technique can aid in solving certain cases of the state crossing problem.[16]

For the proposed scheme, the wave function of the desired state is implemented as the initial input to the phase estimation algorithm using the MCSCF approach. The approximation to the exact wave function of the ith state $|\Psi_i\rangle$, is $|\Psi_i^{\mathrm{MCSCF}}\rangle$. The probability of observing the exact ith state is $|\langle\Psi_i|\Psi_i^{\mathrm{MCSCF}}\rangle|^2$. Since the MCSCF wave function provides a much better approximation to the ground state wave function of the system than does the HF wave function, and also provides a better description of excited states than a Koopmans' theorem estimate[16] from a HF wave function, the probability of obtaining the correct energy of the system in the phase estimation procedure is higher for MCSCF wave functions than for HF wave functions.

The first step for the quantum algorithm involves the preparation of a MCSCF calculation for N states that are of interest for the system. The MCSCF wave function for the state of interest are used as the initial guess for the trial wave function:

$$|\Psi\rangle = |\psi_n^0\rangle, \tag{16}$$

where $|\psi_n^0\rangle$ is the MCSCF wave function for the nth state. The next step is to map the MCSCF wave function for the nth state as the initial input to the quantum computer This will have to be prepared using a state-preparation algorithm.[32] General state preparation is a hard problem, but generally the MCSCF wave function contains a polynomial number of non-zero terms in the Hilbert space, and therefore may be prepared efficiently.[33] Feeding the MCSCF wave function into the phase estimation algorithm as initial guess, the eigenenergies of the corresponding CI state can be retrieved.

An MCSCF vector can be expanded as follows:

$$|\psi_n^0\rangle = \sum_k c_k|\psi_k\rangle, \tag{17}$$

where $|\psi_k\rangle$ is the eigenvector of the CI matrix. $|c_n|^2 = |\langle\psi_n|\psi_n^0\rangle|^2$ is the probability of obtaining the eigenvector $|\psi_n\rangle$. A CI vector for the nth state can be written as:

$$|\psi_n\rangle = |\psi_n^m\rangle + |\psi_n^p\rangle = |\psi_n^0\rangle + |\psi_n^{\mathrm{dev}}\rangle + |\psi_n^p\rangle, \tag{18}$$

where $|\psi_n^m\rangle$ is the part of the CI vector in the model space, which is used to construct the MCSCF wave function; $|\psi_n^p\rangle$ is the part of the CI vector in the space external to the model space; $|\psi_n^{\mathrm{dev}}\rangle$ is the deviation of MCSCF wave function $|\psi_n^0\rangle$ from $|\psi_n^m\rangle$, the projection of the CI vector in the model space. Then we have:

$$\langle\psi_n^0|\psi_n\rangle = 1 + \langle\psi_n^0|\psi_n^{\mathrm{dev}}\rangle + \langle\psi_n^0|\psi_n^p\rangle \tag{19}$$

The vectors in model space and external space are orthogonal, $\langle\psi_n^p|\psi_n^0\rangle = \langle\psi_n^p|\psi_n^m\rangle = 0$. We can see that if the deviation vector goes to 0, the overlap of the MCSCF vector with the CI vector is 1, the algorithm will be deterministic.

V. Application to the water molecule

We have performed a quantum simulation for the ground state and the first singlet excited state of the water molecule using the cc-pVDZ basis set.[34] For the ground state, considering the C_{2V} symmetry of the water molecule, the HF wave function of water is:

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2 \tag{20}$$

We consider a complete active space (CAS) type MCSCF method: the first two a_1 orbitals are frozen, the active space consists of $3a_1 - 6a_1$ orbitals, $1b_1$, and $1b_2$ and $2b_2$ orbitals. The MRCI is performed using the same model space but considering the single and double excitations to the external space. The MCSCF space contains 152 CSFs. The CI space contains 13872 CSFs, here $\log_2^{13872} = 13.76$, so 14 qubits are required to represent the CI wave function on a quantum computer. The geometry used in the calculation is near the equilibrium geometry ($R_0 = 1.8435a_0$ and $\angle HOH = 110.57$). We varied both OH bonds from 0.5 to 10 times of the equilibrium distance simultaneously, keeping the C_{2v} symmetry, $R = aR_0$, $a = 0.5$–10. The success probability of the quantum algorithm for using HF and MCSCF wave function as initial input $|\langle\Psi_i^{\mathrm{HF}}|\Psi_i^{\mathrm{CI}}\rangle|^2$ and $|\langle\Psi_i^{\mathrm{MCSCF}}|\Psi_i^{\mathrm{CI}}\rangle|^2$, are shown in

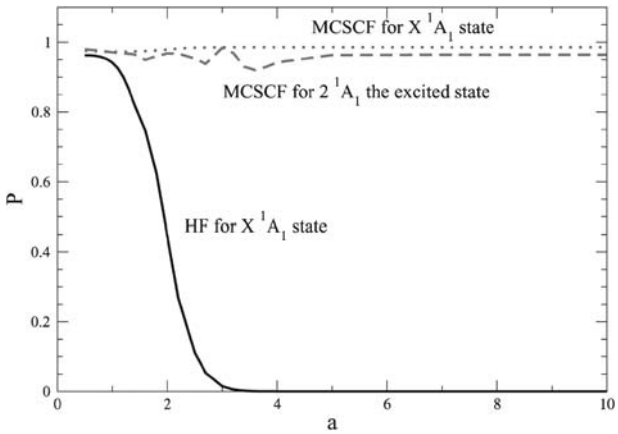

Fig. 1 Success probability ($P = |\langle\Psi^{HF}|\Psi^{CI}\rangle|^2$ and $P = |\langle\Psi^{MCSCF}|\Psi^{CI}\rangle|^2$) of using HF and MCSCF wave function as the initial guess. Black line is for HF wave function, red line is for the MCSCF wave function of the ground state, green line is the MCSCF wave function for the excited state. The system is the water molecule, where $a = R/R_0$ is the ratio between the stretched bond length R and the bond length near equilibrium distance $R_0 = 1.8435a_0$.

Fig. 1. By following the stretch coordinate, we observe that the success probability for using MCSCF wave function as initial guess is very high (>0.9) through the stretching, while the success probability for using HF wave function as initial guess decreases very fast as the OH bond is stretched. We can still obtain high probability of success by using just a few CSFs instead of all 152 CSFs in the MCSCF model space. In Fig. 2, we show the success probability for both the ground state and excited states using 6 and 8 CSFs, respectively. With a relatively small number of CSFs one can have a reasonable overlap with the desired state.

We further studied the performance of the method for excited states. We explored the first excited state of the water molecule at the equilibrium geometry using the STO-3G basis set.[35] The first two a_1 orbitals were frozen. The model space for the MCSCF is a complete active space that includes the $3a_1$, $4a_1$, $1b_1$ and $1b_2$ orbitals. The MRCI calculation uses the

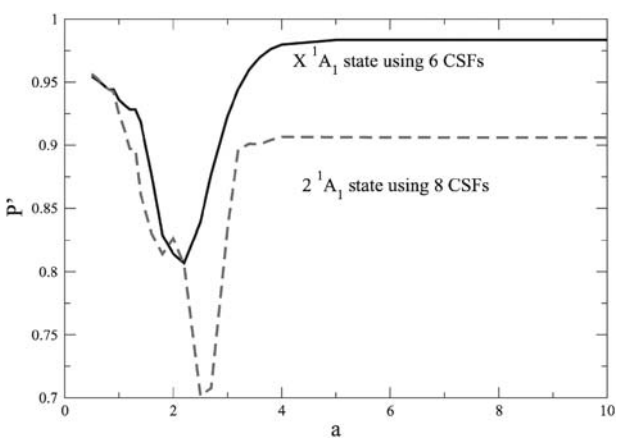

Fig. 2 Success probability ($P' = |\langle\Psi^{MCSCF}|\Psi^{CI}\rangle|^2$) of using a few CSFs as the initial guess. Black line is for the ground state and red line is for the excited state. The system is the water molecule, where $a = R/R_0$ is the ratio between the stretched bond length R and the bond length near equilibrium distance R_0.

Table 1 Results for the first singlet excited state of the water molecule using the phase estimation algorithm. The MCSCF and HF wave function are used as initial guesses. The FCI energy is −83.464130 a.u., the exact energy for using MCSCF wave function is −83.449186 a.u. and for using HF wave function is −83.443206 a.u.

Digits (qubits)	Energy (MCSCF)	Energy (HF)
2	$-83 \pm 2.07 \times 10^1$	$-83 \pm 2.07 \times 10^1$
8	$-83.6386 \pm 5.04 \times 10^{-1}$	$-83.6386 \pm 5.04 \times 10^{-1}$
16	$-83.4486 \pm 1.28 \times 10^{-3}$	$-83.4435 \pm 1.27 \times 10^{-3}$
24	$-83.44919786 \pm 4.95 \times 10^{-6}$	$-83.44318182 \pm 4.95 \times 10^{-6}$

same model space, but considers the single and double excitation to the external space.

We use the scheme introduced by Parker and Plenio[36] to implement the QFT. This method is known as the measured quantum Fourier transform (mQFT) approach. In this scheme, only one control qubit is used, more qubits are saved for representing the wave function. The mQFT approach is based on the fact that the gates within the Fourier transform are applied sequentially on the qubits. Thus, instead of performing the entire transform and then making measurements on all control qubits afterwards, one can apply the single qubit operation to the first qubit and then measure it. The operations controlled by this first qubit are then replaced by single qubit operations given the result of the measurement on the first. The measurement outcome is fed back into the quantum calculation and this procedure is recycled till all the required binary digits are resolved. The target register must remain coherent during the whole procedure. For more details on this procedure, the reader is referred to ref. 36.

For the excited-state simulation, the CI space is composed of 18 CSFs, so 5 qubits are required to represent the wave function. In Table 1, we present the results for the calculation of the first excited state of the water molecule in the STO-3G basis using the mQFT algorithm. The MCSCF wave function and HF wave function are used as different initial guesses. The MRCI energies are obtained to different digits of accuracy depending on the number of ancillary control qubits employed. The error bars in the table come from the numbers of the qubits in the index register. The more control qubits in the index register, the more binary digits can be retrieved. For example, if n qubits are used as control qubits, then one can only obtain up to n binary digits of accuracy in the phase estimation, all the binary digits after these n digits will be uncertain. Therefore, the error is the same regardless of the initial trial state (HF or MCSF) employed. The FCI energy is in this case is −83.464130 a.u. The first singlet excited state energy for the water molecule using 24 qubits ($E = -83.44919786$ a.u.) is lower, even including the error bars, than the exact energy using the MCSCF wave function ($E = -83.449186$ a.u.), this is because the error in expansion of the unitary matrix is only up to the second order in Trotter expansion.[9]

VI. Discussion and conclusions

In certain regions of molecular potential energy surfaces, electronic states can cross each other or have low gaps, like in the case of avoided crossing regions or at the bond-

dissocation limit. In these cases, the interactions between states should be considered simultaneously. Consequently, the use of single determinant based methods is challenging.

Using an MCSCF wave function as the initial guess can deal with the strong interaction between states straightforwardly. This can avoid possible convergence of the state wave function to some undesired and unphysical states when the energy gap between these states is small.

By using the more compact mapping technique, crossing states that belong to different irreducible representations can be addressed separately since there is no interaction between the states. For states in an avoided crossing region and at the dissociation limit where states are near degenerate, since the interaction has been considered qualitatively in the MCSCF calculation, the overlap of the MCSCF wave functions with the corresponding CI wave functions are still large, so that even in such regions the probability for the reference states is high. Therefore, we conclude that the MCSCF wave function can be used as a good initial guess for correlated wave functions using quantum computing to explore the whole potential energy surfaces for ground and excited states with high probability of success.

Using an HF wave function as the initial guess chooses a path $\hat{H}^{\mathrm{HF}} \rightarrow \hat{H}$, for the evolution from the HF state to the CI state. In our scheme, we choose the path $\hat{H}^{\mathrm{MCSCF}} \rightarrow \hat{H}$, and the states evolve from the MCSCF state to the MRCI state. Unlike in the case of HF wave function in which the evolution is started from a single element of the CI matrix, the MCSCF wave function starts the evolution from a small matrix. This makes the evolution safer and faster, especially for a MRCI space. From the simulation we can see that by including a few CSFs in the initial guess, the success probability can be increased from very small to near unity. This idea might be used in developing other quantum algorithms.

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