
QUANTUM SIMULATIONS READING PROJECT

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ABSTRACT

Quantum simulation is a very interesting problem, while hard in nature to implement on classical computers one can find efficient ways to implement them in certain cases using quantum systems.

Here we aim to explore algorithms for the execution of Hartree-Fock methods, configuration interactions, and coupled-cluster type calculations on quantum computers.

1 Review on Quantum Simulation

This section is made with reference to [3].

1.1 Introduction

The problem of creating a simulation of a quantum system is a famous and very difficult task. If one were to make use of a classical computer the resources required would scale exponentially. For example if one were to store a state of N spin 1/2 particles we would need to store 2^N numbers for the state and 4^N for the unitary evolution (this is about 4TB for $N = 40$).

There do exist certain classical stochastic methods which can be used for certain systems (specifically those where the functions being integrated do not change sign and vary slowly). The Quantum Monte Carlo methods offer a polynomial time implementation for the quantum many body simulation.

One of the alternatives to simulate quantum systems was proposed by Feynman. Bluntly put we use quantum systems to simulate quantum systems. The method described uses a mapping of the desired state and desired evolution to a state of the system and it's evolution. We denote the system state by $|\varphi\rangle$ and it goes from $|\varphi(0)\rangle$ to $|\varphi(t)\rangle$ with evolution $U = \exp(-i\hbar H_{sys}t)$. The simulator state $|\psi\rangle$ goes from $|\psi(0)\rangle$ to $|\psi(t)\rangle$ with evolution $U' = \exp(-i\hbar H_{sim}t)$. If we can create a mapping between the final and initial states and the evolution operator, we can simulate this system.

1.2 Digital and Analog Quantum Simulations

1.2.1 Digital Quantum Simulation

Here we make use of qubits for simulating the systems. Suppose we want to simulate spin 1/2 particles, we assign each particle to one qubit and we prepare our simulator state $|\psi(0)\rangle$ using the 1,0 convention for spin up and down respectively. For getting $|\psi(t)\rangle = \exp(-i\hbar Ht) |\psi(0)\rangle$ we apply the unitary $U = \exp(-i\hbar Ht)$ to our initial state by decomposing it into single qubit and two qubit gates (eg: U3 and CNOT gates are universal). This is referred to as DQS (digital quantum simulation) and since we can make a circuit for all unitaries, DQS is universal however we need not be able to find an efficient decomposition for all unitaries.

State preparation in general is a task which need not be efficient but in some cases there are convenient efficient algorithm. For example there is an algorithm for efficiently preparing a state of m electrons occupying n orbitals using recursion to reverse engineer the given state to the $|0\rangle^{\otimes(n)}$

For the actual evolution of state we use the Trotter's formula for dealing with systems of form $H = \sum_{i=1}^n H_i$ by using the fact that $\lim_{n \rightarrow \infty} (\prod_i \exp(H_i/N))^N = \exp(\sum_i H_i)$ since all the commutation terms are second order with $1/N$ hence in the limit go to zero so we break our unitary into small time steps to make sure that the error doesn't go large. The algorithms functions like this (reference: [5])

Inputs: The initial state $|\psi_0\rangle$ along with the Hamiltonian $H = \sum_{k=1}^L H_k$, the error range δ and time t_f for which we have to find $|\psi(t_f)\rangle$. Here $U_{\Delta t} = \prod_{k=1}^L \exp(-i\hbar H_k \Delta t)$

Outputs: The state $|\psi(\tilde{t}_f)\rangle$ such that $|\langle \psi(\tilde{t}_f) | \psi(t_f) \rangle|^2 < 1 - \delta$

Procedure:

1. Initialize state as $|\tilde{\psi}_0\rangle = |\psi_0\rangle$.
2. Iterative update $|\psi_{j+1}\rangle = U_{\Delta t} |\psi_j\rangle$.
3. $j = j + 1$; goto 2. while $j\Delta t < t_f$.
4. $|\psi(\tilde{t}_f)\rangle = |\tilde{\psi}_j\rangle$ final result

Runtime: This typically functions in $O(\text{poly}(1/\delta))$ operations. Here $U_{\Delta t}$ is a unitary which describes the approximate evolution over a time of Δt

Now comes the process of measurement. Generally for quantum systems this is done via quantum state tomography however those require resources that scale exponentially with the size of the system. To get around this estimation is done of correlation functions or spectra of operators.

1.2.2 Analog Quantum Simulation

In analog quantum simulation a real quantum system is used to simulate another quantum system and the real quantum system would be controllable hence one can make inferences about the simulated system using this possibly easier to control system by using mappings. The mappings are made as $H_{sim} = f H_{sys} f^{-1}$ where the initial state is transformed using f and we get the final state by transforming back with f^{-1} . Essentially we must note that H_{sim} and H_{sys} have the same eigenvalues for this to be a valid mapping. An example of hamiltonians like this would be a hamiltonian describing a gas of interacting bosonic atoms in a periodic potential and the bose-hubbard hamiltonian.

$$H_{sim} = -J \sum_{i,j} \hat{a}_i^\dagger \hat{a}_j + \sum_i \epsilon_i \hat{n}_i + \frac{1}{2} \sum_i \hat{n}_i (\hat{n}_i - 1) \quad (1)$$

$$H_{BH} = -J \sum_{i,j} \hat{b}_i^\dagger \hat{b}_j - \mu \sum_i \hat{n}_i + \frac{1}{2} \sum_i \hat{n}_i (\hat{n}_i - 1) \quad (2)$$

The bosonic atoms hamiltonian is described in 1 where \hat{a}_j and \hat{a}_j^\dagger are the bosonic annihilation and creation operators respectively and J is the hopping strength and U is the interaction strength. ϵ_i represents the energy offset. One can see that eq1 is quite similar to eq2. The μ eq2 is the chemical potential and that is pretty much the only difference. One can execute the bose-hubbard hamiltonian as described by eq2 using atoms in an optical potential. However there need not be a straightforward mapping in most situations. AQS does have quite some advantages over DQS such as the fact that state preparation would occur naturally as the system would naturally gravitate toward the equilibrium state normally. Also measurement can be done directly unlike the computational manipulation required in DQS.

1.3 Resource estimation

There is a general rule of thumb that to outperform a normal computer with a quantum computer one would need somewhere between 40 to 100 qubits. There are plenty of interesting things that can be done with about 10 qubits too from proof of concept simulations to even quantum chaos. However when you only need a few qubits you might as well use a classical computer. In DQS the estimate for representing N particles with pairwise potential would require n qubits for representing the wave function as a discrete variable and we would need m qubits for estimation of values to some precision. The coulomb potential can be calculated in $\mathcal{O}(N^2 m^2)$ steps which is clearly an exponential improvement from the classical way of calculation. There is however an overhead cost in for the gates as the step size decreases in trotterization.

It is stated that AQS has less stringent resource requirements and can provide useful results with classical computers. In AQS one can manipulate a larger number of particles with more resources for example hundreds of thousands of atoms have been trapped using only three laser beams.

In AQS effects of decoherence are generally believed to be less dramatic and is even suggested that it might be useful as a way of modelling decoherence of the simulated system. If the noise level naturally present in the simulator is lower than the simulated system one can artificially supplement the noise so that it faithfully mimics the simulated system. In principle one can make use of the natural symmetries present in the system so as to modify the effective decoherence using appropriate mappings. There are cases where fault tolerant methods are inefficient compare to trotter approximation such as finding the low lying spectrum of a pairing hamiltonian in an NMR implementation. Two qubit entanglement was found to be exponentially sensitive to both small changes in the hamiltonian and locations of the chosen qubits due to natural ordering introduced on the qubits by coding of the simulated system.

1.4 Physical Realizations

All physical systems that can be used as a quantum computer would also be a universal machine for DQS. However there are various quantum systems that can be used to implement AQS.

1.4.1 Atoms and Ions

Neutral atoms in optical lattices are well suited to mimic solid state systems. These optical potentials can be adjusted to change geometry and dimensionality of lattice like creating triangular or kagome lattices. These are quite flexible systems where there are several controllable parameters and there are both bosonic and fermionic elements that can be used here. A general Hubbard hamiltonian is written as

$$H = H_{hop} + H_{interaction} + H_{pot} + H_{internal} \quad (3)$$

One can simulate the Mott insulator-superfluid phase transition using this system by tuning the on-site interactions using Feshbach resonances. Continuous tunability of interaction strength allows one to enter a regime called the

unitary regime where interaction strength is comparable to Fermi energy so we only have one energy scale in our system. Addressing individual atoms is a tough task however due to the best laser focusing widths are typically near the scale of lattice distance ($0.5 - 0.8\mu m$)

One can even use these for DQS since one can make controlled operations by using a double optical potential with interaction between neighbouring atoms.

Using ions one can make multiple qubit gates by making use of their Coulomb repulsion and ion qubits tend to have much longer coherence times (in the order of seconds) and can also make sequences of high fidelity quantum gates.

The quantum states for trapped ions are mostly manipulated using resonantly driving transitions between internal states of the ions or resonantly driving sideband transitions involving the internal states and vibrational states of the ions in the trapping potential. The hamiltonian describing coupling between internal and vibrational modes due to laser driving at red-sideband frequency is the following

$$H = \hbar\eta\Omega[\exp(i\phi)\sigma_+a - \exp(-i\phi)\sigma_-a^\dagger] \quad (4)$$

Here Ω is the Rabi frequency of transition between the internal states, σ_+ and σ_- are the two level atom transition operators. a, a^\dagger are the ladder operators for the vibrational modes and ϕ is laser phase and η is the Lambe-Dicke parameter. Using this one can realize quantum gates for DQS and even some hamiltonians for AQS. High fidelity one, two, three qubit (toffoli) gates have been implemented using this. Ions have generally been trapped using linear harmonic traps.

1.4.2 Nuclear and electronic spins

Nuclear spin qubits have long coherence times ($> 1s$) and high fidelity quantum gates of up to 12 qubits have been demonstrated. Here nuclear spins are manipulated using NMR (nuclear magnetic resonance). The general form of the hamiltonian is

$$H = -\hbar\gamma B \sum_i I_i^z + \sum_{i>j} J_{ij} I_i^z I_j^z \quad (5)$$

Here I is the angular momentum operator and J represents the spin-spin coupling coefficients. B is magnetic field and γ is the gyro-magnetic ratio. The different transitions between pairs of energy levels generally have distinct resonance frequencies which makes it possible to implement multi qubit gates using rf (radio frequency) pulses. Scaling is however a big issue here but can be possibly addressed by making use of nitrogen vacancy centers for strongly correlated systems.

Another system that is used are electron spins in semiconductor quantum dots. Quantum dots are semiconductor systems where excitations are confined in small regions in one or two dimensions and if they are roughly as wide as the wavelength of charge carrier they sort of have quantized levels similar to those of actual atoms. Readout can be manipulated both electrically and optically. They have decay times of $> 1s$. A hamiltonian for an array of quantum dots is given by

$$H = \sum_{j=1}^n \mu_B g_j(t) B_j(t) \cdot S_j + \sum_{1 \leq j < k \leq n} J_{jk}(t) S_j \cdot S_k \quad (6)$$

The first term comes from energy of applied magnetic field and the second term is exchange interaction due to virtual tunneling between quantum dots and S_j is spin of the electric charge quanta of the j th dot.

1.4.3 Superconducting circuits

There are many ways in which one can encode quantum information in superconducting circuits: number of superconducting electrons on a small island, direction of current around a loop or in oscillatory states of the circuit. The circuit can be manipulated by applied voltages and currents. These have an advantage over real atoms since one can tailor characteristic frequencies, interaction strengths and so on much easily. Hamiltonian for N charge (flux) qubits biased at their symmetry points (optimal for quantum coherence) coupled capacitively is

$$H = - \sum_{i=1}^N \frac{\Delta_i}{2} \sigma_i^z - \sum_{i,j} J_{ij} \sigma_i^z \sigma_j^z \quad (7)$$

Where Δ_i is level splitting and the J_{ij} is for coupling strength between i and j qubits. It must be noted that these are not two level systems however these additional levels could possibly be utilized for AQS for spin greater than $1/2$.

1.4.4 Photons

Photons can carry quantum information over long distances and would hardly be affected by noise and decoherence and can encode qubits using polarization. One qubit gates can easily be realized using linear optical components

however implementing two qubit gates for photonic systems are much more difficult. These have been used for many impressive tasks however like to calculate the possible fractional statistics of anyons using a six photon graph state, calculate the energy spectrum of hydrogen to 10 bits of precision and even simulate frustrated spin systems. These do have issues in flexibility and scalability so have a long way to go.

2 Hartree-Fock Theory

2.1 The formulae

The main aim here is calculations involving many electron systems in a pairwise potential. Using the Born-Oppenheimer approximation one can find the exact solutions for a hydrogen atom (or any one electron atom) however exact solutions cannot be found once we have more than one electron. The idea of the approximation is to consider that nuclei are relatively stationary since electron movement is much faster. Let's first write the for an N electron system with N_{nucl} nuclei each with some Z_j atomic number at \vec{R}_j .

$$H^{el} = \sum_{i=1}^N \frac{p_i^2}{2m} - \sum_{i=1}^N \sum_{j=1}^{N_{nucl}} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} + \sum_{i>j=1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (8)$$

Our aim is to solve $H |\psi(1, 2, \dots, N)\rangle = E |\psi(1, 2, \dots, N)\rangle$. We must note that this will be anti symmetric since it describes fermions. We will adopt the mean field approach where we assume particle's dynamics are decided by a mean field created by particles at rest. Another assumption is that each electron is described by a single electron wavefunction called the spin orbital which we represent as $\phi_i(x)$ which has both a spatial and spin component. The final solution is represented as a determinant called the slater determinant

$$\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \quad (9)$$

The electrostatic potential felt by an electron occupying orbital $\phi_i(\vec{r})$ due to the mean field of remaining $N - 1$ electrons would be

$$V_i(\vec{r}) = \sum_{j=1, j \neq i}^N \langle \phi_j | \frac{e^2}{|\vec{r} - \vec{r}'|} | \phi_j \rangle \quad (10)$$

We also will define $V_{nucl}(\vec{r})$ which is the nuclear attraction potential felt by an electron at \vec{r} then we have

$$V_{nucl}(\vec{r}) = \sum_{i=1}^{N_{nucl}} \frac{Z_i e^2}{|\vec{r} - \vec{R}_i|} \quad (11)$$

From this we get the Hartree equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{nucl}(\vec{r}) + V_i(\vec{r}) \right) \cdot \phi_i(\vec{x}) = \varepsilon_i \phi_i(\vec{x}) \quad (12)$$

Clearly the nuclear attraction potential is a one electron operator and the electrostatic potential is a two electron operator. The following equation shows the expectation values for one electron and two electron operators.

$$\langle \Phi | O_1 | \Phi \rangle = \sum_i \langle \phi_i | f | \phi_i \rangle = f_{ii}, O_1 = \sum_i f(\vec{r}_i) \quad (13)$$

$$\langle \Phi | O_2 | \Phi \rangle = \frac{1}{2} \sum_j \sum_i (\langle \phi_i \phi_j | g | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | g | \phi_j \phi_i \rangle), O_2 = \sum_{i,j} g(\vec{r}_i) \quad (14)$$

So the whole thing is reduced into an eigenvalue problem. We define the operators $h(\vec{r}_i) = \frac{p_i^2}{2m} + V_{nucl}(\vec{r}_i)$, $V_H |\phi_i\rangle =$

$\sum_{j=1}^N \langle \phi_j | \frac{e^2}{r_{12}} | \phi_j \rangle | \phi_i \rangle$, $V_{ex} |\phi_i\rangle = \sum_{j=1}^N \langle \phi_j | \frac{e^2}{r_{12}} | \phi_i \rangle | \phi_j \rangle$ and the problem reduces to the following eigenvalue problem

$$(h + V_H + V_{ex}) |\phi_i\rangle = \varepsilon_i |\phi_i\rangle \quad (15)$$

The total energy however is not simply the sum of all the orbital energies for the system and is actually $E_{HF} = \frac{1}{2} \sum_{i=1}^N (\varepsilon_i + h_{ii})$. We call the fock operator as $F = h + V_H + V_{ex}$.

2.2 Canonical transformations

This part is made with reference to supplementary materials provided in [1]. For solving the hartree fock equations and arriving at the assymetric state the state is variationally solved such that energy is stationary with respect to first order changes in the wavefunction and we start from an arbitrary orthogonal basis $\{\phi_i\}$. So we solve $\langle \delta\psi | H | \psi \rangle = 0$. We assume the solution is represented as

$$\langle r | \psi \rangle = \langle r | \prod_{i=1}^n a_i^\dagger | vac \rangle = \frac{1}{\sqrt{n!}} \det \begin{bmatrix} \chi_1(r_1) & \dots & \chi_1(r_n) \\ \vdots & \ddots & \vdots \\ \chi_n(r_1) & \dots & \chi_n(r_n) \end{bmatrix} \quad (16)$$

We will now index the states which are in the product wavefunction by i and those which aren't by a . We then can write the first order variation as $\langle \delta\psi | = \langle \psi | a_i^\dagger a_a \zeta$ where ζ is the first order variation in χ_i so we get the expression for the stationarity of the state as

$$\langle \psi | a_i^\dagger a_a H | \psi \rangle = 0 \quad (17)$$

We also have the one-body fermionic generators form a closed lie-algebra

$$[a_p^\dagger a_q, a_r^\dagger a_s] = \delta_{q,r} a_p^\dagger a_s - \delta_{p,s} a_r^\dagger a_s \quad (18)$$

The adjoint representation of an element of the algebra would be $\kappa = \sum_{p,q} \kappa_{p,q} a_p^\dagger a_q$ and it's commutators can be represented as $[\kappa, a_p^\dagger] = a_p^\dagger \kappa_{p,q}$ and $[\kappa, a_p] = a_p \kappa_{p,q}^*$. We then define similarity transformations on the ladder operators: $e^K a_p^\dagger e^{-K} = \sum_q a_q^\dagger u_{q,p}$, $e^K a_p e^{-K} = \sum_q a_q u_{q,p}^*$ and here u is the matrix given by the exponentiation of the coefficient matrix for the generator operator κ so it is $u = e^\kappa$.

Any rotation of the underlying basis can now be written with the similarity transform as

$$|\phi(\kappa)\rangle = e^K a_1^\dagger e^{-K} \dots e^K a_n^\dagger e^{-K} = e^K |\psi\rangle \quad (19)$$

Now before we proceed we must note that the 2-RDM (reduced density matrix) can be obtained from the 1-RDM since

$${}^1D_i^j = \langle \phi | a_j^\dagger a_i | \phi \rangle \quad (20)$$

$${}^2D_{ij}^{pq} = \langle \phi | a_p^\dagger a_q^\dagger a_j a_i | \phi \rangle = {}^1D_i^{p1} {}^1D_j^{q1} - {}^1D_i^{q1} {}^1D_j^{p1} \quad (21)$$

Using expression of energy we get that we can express energy in terms of the 1-RDM purely since we can write the 2-RDM in terms of 1-RDM.

$$E(\kappa) = \sum_{ij} h_{ij} \langle \phi(\kappa) | a_i^\dagger a_j | \phi(\kappa) \rangle + \sum_{ijkl} V_{ijkl} \langle \phi | a_i^\dagger a_j^\dagger a_k a_l | \phi \rangle \quad (22)$$

$$= \sum_{ij} h_{ij} {}^1D_i^j + \sum_{ijkl} V_{ijkl} {}^2D_{lk}^{ij} \quad (23)$$

3 Simulation of H₂ molecule using chloroform

This section is essentially a summary of the ideas discussed in [2]. The paper shows results of calculation of ground state of a hydrogen molecule which as done to 45 bits of accuracy in 15 iterations. The main idea of the calculation is that the ground state is prepared using adiabatic state preparation and then phase estimation of eigen value is done but instead of using the inverse fourier transform method, an iterative NMR interferometer is used. It must be noted that to obtain a 45 bit accuracy in the phase value one would require 45 qubits in the register that is used for phase measurement using the inverse QFT method if one wants to extract the whole information with one circuit.

3.1 Phase estimation using QFT

This is just a description of how phase estimation is done using the quantum fourier transform normally taken from [5]. Suppose we have unitary operator U with an eigen vector $|u\rangle$ with an eigenvalue $e^{2\pi\phi}$ where ϕ is unknown and we wish to estimate its value. We us two registers, one which has t qubits and the other which is initialized in state $|u\rangle$. Now lets say that the binary representation of ϕ is $0.\phi_1\phi_2\dots\phi_t$ accurate to t places after the radix point.

The state of the first register will now be

$$\frac{(|0\rangle + e^{2\pi i 0.\phi_t} |1\rangle)(|0\rangle + e^{2\pi i 0.\phi_{n-1}\phi_n} |1\rangle)\dots(|0\rangle + e^{2\pi i 0.\phi_1\phi_2\dots\phi_n} |1\rangle)}{2^{n/2}}$$

Clearly doing an inverse Fourier transform over this will give us the state $|\phi_1\phi_2\dots\phi_t\rangle$ hence on measurement we will be able to estimate this phase.

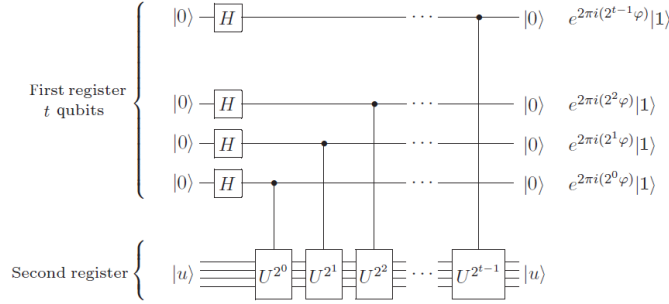


Figure 1: Circuit for phase estimation. Note that we perform inverse Fourier transform on the first register and then a measurement on the first register

3.2 Description of the system

The hamiltonian of the hydrogen molecule can be described by the following equation

$$H = \sum_{i=1}^2 (T_i + \sum_{j=1}^2 V_{ij}) + \sum_{i,j=1, i>j}^2 O_{ij} \quad (24)$$

Here T_i is the kinetic energy of the i th electron and V_{ij} is the Coulomb potential energy between the i th electron and the j th nucleus and O_{ij} is the Coulomb potential energy between the i th and j th electron. This is under the Born Oppenheimer approximation where the nuclei are assumed at rest.

This molecule has two nuclei and two electrons and the two 1s orbitals can combine to form a gerade bonding orbital and an ungerade antibonding orbital 4 spin orbitals which can be occupied hence giving 6 possible configurations (4 choose 2). The only two states we will be concerned with are the ground state $|\Psi_0\rangle$ and the double excited state $|\Psi_{11}^{22}\rangle$ giving us the following hamiltonian matrix which has a theoretical eigen value of -1.851 570 929 351 19 a.u.

$$\mathcal{H} = \begin{pmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_{11}^{22} \rangle \\ \langle \Psi_{11}^{22} | H | \Psi_0 \rangle & \langle \Psi_{11}^{22} | H | \Psi_{11}^{22} \rangle \end{pmatrix} = \begin{pmatrix} -1.8310 & 0.1813 \\ 0.1813 & -0.2537 \end{pmatrix}$$

When doing the experimental implementation chloroform (CHCl_3) with carbon-13 dissolved in d_6 acetone as a two qubit computer where ^{13}C nucleus is used for the system qubit and the H atom is used for probe qubit. The natural hamiltonian of the system is the following

$$\mathcal{H}_{\text{NMR}} = \frac{\omega_p}{2} \sigma_z^p + \frac{\omega_s}{2} \sigma_z^s + \frac{\pi J_{ps}}{2} \sigma_z^p \sigma_z^s$$

Here J_{ps} represents the coupling constant and is typically 214.6 Hz in value. The $\omega_s/2\pi$ and $\omega_p/2\pi$ are the Larmor frequencies.

3.3 Calculation of the ground state energy

The first step is creation of ground state of \mathcal{H} in the system qubit. It is essentially done by applying three pulses of rotations $R_x(\theta_3)R_y(\theta_2)R_x(\theta_1)$ in multiple steps. In the ASP process we start with an initial hamiltonian of $H_0 = \sigma_x$ and is prepared at it's ground state of $|-\rangle$. This is then driven to the actual system hamiltonian \mathcal{H} using linear interpolation $H_{ad} = (1 - \frac{t}{T})H_0 + \frac{t}{T}\mathcal{H}$ and the t goes from 0 to T and so $|\Psi\rangle$ the ground state is approached as time passes. The total evolution time is taken as $T = 5.52$ a.u. to ensure success of ASP

The probe qubit is kept at the $|+\rangle$ state initially and is used as a controlled qubit for applying the U_k operator which starts as $U_0 = U$. The iterative process is done as $U_{k+1} = [e^{-i2\pi\phi'_k} U_k]^{2^n}$, $\phi'_k = \max\{\phi_k - \phi_{\text{errbd}}, 0\}$ where ϕ_k is the phase shift measured in the k th iteration. In each iteration the phase shift caused by U_k is measured and here n is the number of bits extracted in each iteration and we have $2^{-n} \geq 2\phi_{\text{errbd}}$. Essentially each iteration for the given setup increases the accuracy by 3 bits.

The controlled U_k is essentially the operation $\mathcal{U}_k = |\uparrow\rangle\langle\uparrow| \otimes I + |\downarrow\rangle\langle\downarrow| \otimes U_k$. Applying this on $|+\rangle |\Psi_{asp}\rangle$ gives us $\frac{1}{\sqrt{2}}(|\uparrow\rangle + e^{i2\pi\phi} |\downarrow\rangle) |\Psi_{asp}\rangle$. In an interferometer this phase shift will be seen as a relative phase between "two paths" of the $|0\rangle$ and $|1\rangle$ states hence is read out directly in NMR. Here $\phi = -E\tau/2\pi$ essentially and since one can choose any τ it is taken as $\tau = \pi/\sqrt{(2H(1,2))^2 + (H(1,1) - H(2,2))^2}$ for convenience since there is a constant α which

is length of one of the pulses used in implementing the U_k operation which becomes $8^{k-1}\pi/2$ with this choice of τ . For measurement one can measure the NMR signal of the probe qubit which is essentially just phase detection and gives us the fourier transformed spectrum of relative phase information. Each iteration would have some phase measurement and to get the actual phase value the iterative equations are used. $\phi_{i-1}^c = \phi_i^c / \phi_{\text{errbd}} + \phi_{i-1}'$ is the recursive relation and we use $\phi_k^c = \phi_k$ where ϕ_k is the measured phase of the k th iteration and we get the result that $\phi_{\text{exp}} = \phi_0^c$

3.4 Conclusions

The main takeaway from this paper was that without using the traditional setup for a phase measurement using inverse fourier transform, an iterative setup which uses NMR interferometer readings can provide a highly accurate answer with a much smaller setup. A thing to note however which is a problem here is that implementation of the U_k gates is possible using a pulse sequence for this small scale but in general for U^j where j is fairly large would be done by j successive U implementations instead of finding a suitable pulse sequence hence resulting in cascading of errors. One possible work around which can be slightly favorable is to find pulse sequences for a good number of U^{2^n} (possibly by an algorithm specifically for this) and then for U^j we just use the binary implementation which puts a cap of $\mathcal{O}(\log_2(j))$ in size but finding the sequences should be efficient.

4 Hardware efficient VQE for small molecules and quantum magnets

This section is a summary of the ideas discussed in [4] which discusses a hardware efficient variational quantum eigensolver for finding ground states of some systems such as molecules as large as BeH_2 and for an antiferromagnetic Heisenberg model in an external magnetic field and does so using a stochastic optimization routine to create ground states.

4.1 Variational Quantum Eigensolver

Variational quantum eigensolvers are used for minimization of eigenvalue obtained from a certain state which would in fact be it's ground state. The circuit is usually set to a certain depth say d with n qubits (See figures below). RyRz has $n \times (d+1) \times 2$ parameters, Ry with linear entanglement has $2n \times (d + \frac{1}{2})$ parameters, and Ry with full entanglement has $d \times n \times \frac{(n+1)}{2} + n$ parameters. Over a certain number of iterations, these parameters are varied so as to minimize

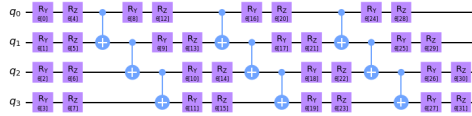


Figure 2: Circuit for linear entanglement

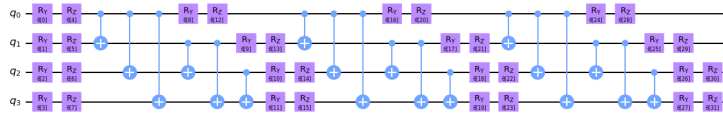


Figure 3: Circuit for full entanglement

the expectation value of the Hamiltonian $\langle \psi | H | \psi \rangle$. One can argue that this approach need not be universal since one makes a different circuit as per value of depth and that would be true since arbitrary state preparation would require a calculated approach most of the times and are proven to be efficient for some select cases (discussed in [3]).

The circuit used in [4] essentially makes the state as the following

$$|\Phi(\theta)\rangle = \prod_{q=1}^N [U^{q,d}(\theta)] \times U_{ENT} \times \prod_{q=1}^N [U^{q,d-1}(\theta)] \times \dots \times U_{ENT} \times \prod_{q=1}^N [U^{q,0}(\theta)] |00\dots 0\rangle \quad (25)$$

Here $U^{q,i}(\theta)$ is a single qubit Euler rotation of $Z - X - Z$ applied on the q qubit at a depth of i . Here U_{ENT} is used to give entanglement and can be seen as the sequence of CNOT gates on the above figures for linear and full entanglement respectively but in case of this paper it was chosen as cross resonance gates. Z rotations were implemented as

frame changes and X rotations were implemented by appropriately scaling of calibrated X_π pulses using a fixed total time of 100 ns for every single qubit rotation.

The algorithm can be written as follows:

```

1: Map the quantum Hamiltonian to a qubit Hamiltonian  $H$ 
2: Set  $d$  as depth of circuit for trial state preparation
3: Choose a set of  $\theta_i$  as parameters which are for rotations applied
4: Choose a number of samples  $S$  for the feedback loop and one  $S_f$  for final estimation
5: Choose the maximal number of control updates  $k_L$ 
6: while  $E_f$  has not converged, do:
7:   procedure Quantum feedback loop:
8:     for  $k = 1$  to  $k_L$ , do:
9:       Prepare trial states using  $\theta_k$  and evaluate  $\langle H \rangle$  with  $S$  samples
10:      Update and store the controls  $\theta_k$ 
11:    end for
12:    Evaluate  $E_f = \langle H \rangle$  with  $S_f$  samples using the best controls
13:  end procedure
14:  Increase  $d, k_L, S, S_f$ 
15: end while
16: return  $E_f$ 
    
```

In line 9: and 10: the

choice used for getting values of the new θ_k is done using optimization by gradient descent. The paper uses a simultaneous perturbation stochastic approximation (SPSA) which has also been used in context of quantum control and quantum tomography recently. In the SPSA approach at every step k , p symmetrical Bernoulli distributions Δ_k are sampled and c_k and a_k are chosen from already decided sequences that converge to zero. The gradient is evaluated as $g_k(\theta_k)$ using this

$$g_k(\theta_k) = \frac{\langle \Phi(\theta_k^+) | H | \Phi(\theta_k^+) \rangle - \langle \Phi(\theta_k^-) | H | \Phi(\theta_k^-) \rangle}{2c_k} \Delta_k \quad (26)$$

Here $\theta_k^\pm = \theta_k \pm c_k \Delta_k$. We then update $\theta_{k+1} = \theta_k - a_k g_k(\theta_k)$. The convergence to the optimal solution can be proven if the starting point lies in the domain of attraction however if not then convergence is not guaranteed and also in case of multiple attraction points there would be issues. The sequences chosen in this paper were

$$c_k = \frac{c}{k^\gamma}, \quad a_k = \frac{a}{k^\alpha}$$

with parameters $\{\alpha, \gamma\} = \{0.602, 0.101\}$ to ensure a smooth descent. The choice for c is decided based on magnitude of energy fluctuations with the θ_k since larger energy fluctuations require a larger c_k so that they do not affect gradient approximations as much. For this $c = 0.1$ is chosen for realistic simulations and $c = 0.01$ is chosen for numerical optimizations where energy is evaluated without fluctuations. The value for a is chosen so that there is a reasonable angle update in the first step since it's essentially like learning rate and so it is chosen so that the angle update is at least $2\pi/10$ and hence

$$a = \frac{2\pi}{5} \frac{c}{\langle |\langle \Phi(\theta_k^+) | H | \Phi(\theta_k^+) \rangle - \langle \Phi(\theta_k^-) | H | \Phi(\theta_k^-) \rangle| \rangle_{\Delta_1}}$$

And here the $\langle \rangle_{\Delta_1}$ means averaging over the Δ_1 distribution.

4.2 Finding the ground state energy for certain molecules

For the fermionic systems of molecules the hamiltonian can be written as

$$H = H_1 + H_2 = \sum_{\alpha, \beta=1}^M t_{\alpha\beta} a_\alpha^\dagger a_\beta + \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta=1}^M u_{\alpha\beta\gamma\delta} a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta \quad (27)$$

$$t_{\alpha\beta} = \int dx_1 \Psi_\alpha(x_1) \left(-\frac{\nabla_1^2}{2} + \sum_i \frac{Z_i}{r_{1i}} \right) \Psi_\beta(x_1) \quad (28)$$

$$u_{\alpha\beta\gamma\delta} = \int \int dx_1 dx_2 \Psi_\alpha^*(x_1) \Psi_\beta(x_1) \frac{1}{|r_{12}|} \Psi_\gamma^*(x_2) \Psi_\delta(x_2) \quad (29)$$

For LiH and BeH₂ perfect filling of the 1s orbitals in the basis where H_1 is diagonalized and using a transformation on the annihilation and creation operators we can write $H_1^d = \sum_{\alpha=1}^M \omega'_\alpha a_\alpha^\dagger a'_\alpha$ and since the 1s states are effectively

filled one can approximate them to not interact with the higher orbitals and so this effectively reduces the number of qubits required for mapping to 6 or 8 for LiH and BeH₂ respectively.

Due to these two orbitals being filled all those terms in the hamiltonian would essentially contribute to an energy shift for single fermionic terms and also modifies the two fermionic terms since any terms with $a'_\alpha a'_\alpha$ with $\alpha \in \{1s \uparrow, 1s \downarrow\}$. We now map the H_2 hamiltonian is mapped first onto 4 qubits using a binary tree mapping. The M spin orbitals are listed by first listing $M/2$ spin up ones and $M/2$ spin down ones. Then Z Pauli operators are assigned on the basis of the total number of electrons where if Z_M has even parity of electrons it is assigned +1 and otherwise -1 and based on the value of $\text{mod}(m,4)$ we can decide what parity to assign to $Z_{M/2}$ and if m is odd then this parity can be either +1 or -1 and it would not really affect anything and so we get a degeneracy. Using all this we can effectively map this for H₂, LiH and BeH₂ as effectively 2,4 and 6 qubits each with 2, 25 and 44 tensor product basis sets and 4,99, 164 Pauli terms respectively.

Now we have described the method of gradient descent however the measurements of expectation value of the hamiltonian is not done directly by measurement. We represent the hamiltonian as a weighted sum of T Pauli terms on N qubits once mapping is done

$$H = \sum_{\alpha=1}^T h_\alpha P_\alpha \quad (30)$$

Where each $P_\alpha \in \{X, Y, Z, I\}^{\otimes N}$ and so we write the following by measuring each α -th Pauli operator.

$$\langle H \rangle = \sum_{\alpha=1}^T h_\alpha \langle P_\alpha \rangle \quad (31)$$

$$\text{Var}[H] = \sum_{\alpha=1}^T h_\alpha^2 \langle \Delta P_\alpha^2 \rangle \quad (32)$$

These individual Pauli operators are measured by correlating measurement outcomes of single qubit disperse readouts in the Z basis. The issue however is that if one samples a large number of trial states there can be a significant overload in measurement.

To minimize these sampling overheads the Pauli operators are grouped in sets s_1, s_2, \dots, s_A which have terms that are diagonal in the same tensor product basis. It is shown (in [4]) using numerical simulations that making use of this grouping can offer better results without as much overhead as opposed to not grouping. Also in the experiments done assignment errors which would occur at readout were taken into account by running readout calibrations at every angle update and then correcting the sampling account using the calibrations. It must be noted that there would be an exponential loss by weight of a certain Pauli operator and so binary tree encoding for representation of H as in equation 30 is important to prevent exponential scaling.

4.3 Applying on Quantum Magnets

To demonstrate how the advantage of greater circuit depths is crucially dependent on the target Hamiltonian, the paper explores a four qubit Heisenberg model in the presence of an external magnetic field. The Hamiltonian is described for it as follows

$$H = J \sum_{\langle ij \rangle} (X_i X_j + Y_i Y_j + Z_i Z_j) + B \sum_i Z_i \quad (33)$$

Here $\langle ij \rangle$ indicates the nearest neighbour pairs, J is the strength of spin-spin interaction and B is the magnetic field along the Z direction. The VQE technique is used to solve for the ground state energy. At $J = 0$ the ground state is completely separable and one can obtain the best estimate for a circuit with $d = 0$ as depth since the state can be characterized purely by rotations. However as J is increased, the ground states start getting more entangled and one would require a $d = 2$ depth with some U_{ENT} in the circuit to get the best estimate.

4.4 Conclusion

The main motivation of this algorithm is that given a Hamiltonian mapping it will produce the state which would have the minimum energy. The impressive feat I believe is that they were able to work this out for BeH₂ which is a fairly large molecule. It must be noted that as per the results obtained, the convergence of the energy happens at a value which is at an error of around 0.015 hartree. Also the gradient descent approach brings a big issue if one were to try to descent in functions where there are multiple minimas which one can only hope to avoid by choosing good parameter sets since this would be dependent on whether the Hamiltonian can be mapped in such a way that uniform convergence is guaranteed. One can also draw various similarities to Hamiltonians and cost functions for machine learning due to the gradient descent approach and is in fact used in a quantum machine learning algorithm.

References

- [1] Frank Arute et al. “Hartree-Fock on a superconducting qubit quantum computer”. In: *Science* 369.6507 (2020), pp. 1084–1089. ISSN: 0036-8075. DOI: [10 . 1126 / science . abb9811](https://doi.org/10.1126/science.abb9811). eprint: [https : / / science . sciencemag . org / content / 369 / 6507 / 1084 . full . pdf](https://science.sciencemag.org/content/369/6507/1084.full.pdf). URL: <https://science.sciencemag.org/content/369/6507/1084>.
- [2] Jiangfeng Du et al. “NMR Implementation of a Molecular Hydrogen Quantum Simulation with Adiabatic State Preparation”. In: *Phys. Rev. Lett.* 104 (3 Jan. 2010), p. 030502. DOI: [10 . 1103 / PhysRevLett . 104 . 030502](https://doi.org/10.1103/PhysRevLett.104.030502). URL: <https://link.aps.org/doi/10.1103/PhysRevLett.104.030502>.
- [3] I. M. Georgescu, S. Ashhab, and Franco Nori. “Quantum simulation”. In: *Rev. Mod. Phys.* 86 (1 Mar. 2014), pp. 153–185. DOI: [10 . 1103 / RevModPhys . 86 . 153](https://doi.org/10.1103/RevModPhys.86.153). URL: [https : / / link . aps . org / doi / 10 . 1103 / RevModPhys . 86 . 153](https://link.aps.org/doi/10.1103/RevModPhys.86.153).
- [4] Abhinav Kandala et al. “Hardware-efficient variational quantum eigensolver for small molecules and quantum magnets”. In: *Nature* 549.7671 (Sept. 2017), pp. 242–246. ISSN: 1476-4687. DOI: [10 . 1038 / nature23879](https://doi.org/10.1038/nature23879). URL: <http://dx.doi.org/10.1038/nature23879>.
- [5] Michael A. Nielsen and Isaac L. Chuang. *Quantum Computation and Quantum Information: 10th Anniversary Edition*. 10th. USA: Cambridge University Press, 2011. ISBN: 1107002176.