Quantum Simulation of Molecular Hamiltonians on an NMR Quantum Computer

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Certificate of Examination

This is to certify that the dissertation titled **Quantum Simulation of Molecular Hamiltonians on an NMR Quantum Computer** submitted by **Rajveer Nehra** (Reg. No. MS09104) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Arvind(Supervisor) Dr. Kavita Dorai(Supervisor) Dr. Kamal P. Singh

Dated: April 25, 2014

Declaration

The work presented in this dissertation has been carried out by me under the supervision of Dr. Arvind and Dr. Kavita Dorai at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Rajveer Nehra
(Candidate)

Dated: April 25, 2014

In my capacity as the supervisor of the candidates project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Arvind   Dr. Kavita Dorai

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Rajveer Nehra

List of Figures

Notation

$\mathbb{I}$	Identity Matrix(in appropriate dimensions)
$\mathbb{H}^n$	Hilbert space, dimension n
σ_x, σ_y and σ_z	Pauli Matrices
R_x, R_y and R_z	Rotation operators for X, Y and Z axis respectively

Abstract

Quantum computer can solve certain problems which are hard for conventional computer. Due to exponential size of Hilbert space it is intractable to simulate quantum systems on a conventional computer. Exact solution of Schrodinger equation within a finite one particle basis set full configuration interaction (FCI) is very computationally hard. Its complexity scales exponentially with a size of the system. In principle, quantum computers are capable to carry out such calculations with only polynomial scaling. Situation gets much harder when we consider solutions of relativistic molecular hamiltonians, so happens due to larger hamiltonian matrix eigen value problem and symmetry has also lost due to spin-orbit interaction which causes a significant large no. of integrals to be nonzero in Hamiltonian matrix. In this work, the simulation of molecular Hamiltonian of SbH molecule in $CAS(2,2)$ is discussed. The Hamiltonian matrix is obtained from DIRAC software in Kramer restricted approach and simulation involved implementation of adiabatic state preparation, iterative phase estimation which are discussed in detail. We used digital quantum simulation where controlled-U in phase estimation algorithm is decomposed into smaller unitary operators governed by local interaction Hamiltonian.

Contents

Nature isn't classical, dammit, and if you want to make a simulation of nature,
you'd better make it quantum mechanical, and by golly it's a wonderful
problem, because it doesn't look so easy.
R.P Feynman

A good idea has a way of becoming simpler and solving problems other than
that for which it was intended.
Robert Tarjan, in the context of QFT.

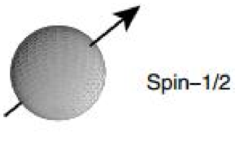
Chapter 1

Introduction of NMR Quantum Information Processing

Nuclear magnetic resonance (NMR) provides a suitable platform to explore physical implementations of quantum information processing (QIP)tasks. Firstly, D. Cory, A. Fahmy and T. Havel[2] proposed some protocols of using liquid-state NMR for quantum information.

1.1 Nuclear Magnetic Resonance

The Nuclei of all elements carry a charge and net magnetic moment when the spins of the protons and neutrons comprising these nuclei are not paired up, the overall spin of the charged nucleus generates a magnetic dipole along the spin axis, and the intrinsic magnitude of this dipole is a fundamental nuclear property called the nuclear magnetic moment denoted by μ. The symmetry of the charge distribution in the nucleus is a function of its internal structure. If charge distribution is completely spherical then whole Nucleus behave like a positive point charge is surrounded by electrons orbiting it and it is said to have a corresponding spin angular momentum number of I = $\frac{1}{2}$, of which examples are 1_H, 13_C, 19_F, etc.
A spin-$\frac{1}{2}$ nucleus is not lumpy, but behaves as a perfectly smooth, magnetic, billiard ball. Since the part of the Hamiltonian which comes from the interaction of the nucleus charge with the external electric field no longer depend on the position and momentum coordinates. Hence this part can be ignored because it does not contribute in the time evolution the of the quantum mechanical system[3].



$$H_i^{elec} = 0 \tag{1.1}$$

When the nuclear magnetic moment interacts with external magnetic field, then the nuclear magnetic energy is given as

$$\mathscr{H} = -\vec{\mu}.\vec{B}$$

and the nuclear magnetic moment can be expressed in terms of spin angular momentum as follows

$$\mu_j = \gamma_j I_j$$

Where I_J and γ_j are spin angular momentum operator and gyromagnetic ratio respectively. Similarly, the Hamiltonian of two scaler coupled spins is given by the following equation

$$H_{NMR} = \frac{\omega^p}{2}\sigma_z^p + \frac{\omega^s}{2}\sigma_z^s + \frac{\pi J_{ps}}{2}\sigma_z^p\sigma_z^s \tag{1.2}$$

Where $\frac{\omega^p}{2\pi}$ and $\frac{\omega^p}{2\pi}$ are the Larmor frequencies of probe and system nuclei, and J_{ps} is the scalar coupling between them. There are two kinds of magnetic fields used in NMR-spectroscopy to manipulate the spin states. These fields are RF-pulses as well as static homogeneous.

- The superconducting solenoid provides a very strong, very homogeneous, static magnetic field, denoted as B_0.
- The RF coils in the probe generates an radio-frequency (RF) oscillating field, denoted as $B_{RF(t)}$. Ideally, the r.f. field B_{RF} is perpendicular to the static field B_0.

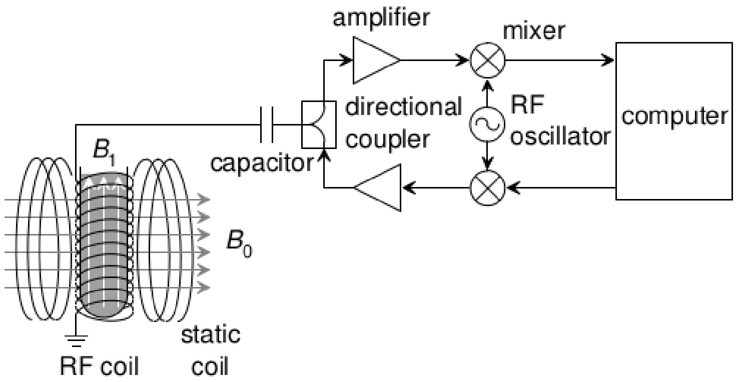


Figure 1.1: Schematic of an NMR apparatus.

The static homogeneous magnetic field is oriented along Z-axis is carefully trimmed to be uniform over the entire region. Orthogonal saddle or Helmholtz coils lying in the transverse plane allow small, oscillating RF fields to be applied along the x and y directions. These fields can be rapidly pulsed on and off to in order to rotate nuclear spin. The same coils are also part of tuned circuits which are simultaneously used to pick up the RF signal generated by the precessing nuclei which can be understood by Lenz's law. These two different magnetic fields interact with nuclear spin and system's Hamiltonian can be written as

$$
\begin{aligned}
B_{net} &= B_0\hat{z} + B_{RF}(\hat{x}cos(\omega t) + \hat{y}sin(\omega)t) \\
H_{NMR} &= \frac{\omega_0\sigma_z}{2} + g(\sigma_x cos(\omega t) + \sigma_y sin(\omega t))
\end{aligned}
$$

Where g and ω_0 determines the strength of B_{RF} and B_0 respectively. Suppose, we define $|\psi_t\rangle = e^{i\omega t\sigma_z/2}|\xi_t\rangle$, so that Schrödinger equation

$$\partial_t|\xi(t)\rangle = H|\xi(t)\rangle \tag{1.3}$$

can be re-written as

$$i\partial_t|\psi(t)\rangle = [e^{i\omega t\sigma_z/2}He^{-i\omega t\sigma_z/2} - \frac{\omega\sigma_z}{2}]|\phi(t)\rangle \tag{1.4}$$

$$e^{i\omega tZ/2}\sigma_x e^{-i\omega tZ/2} = (\sigma_x cos(\omega t) - \sigma_y sin(\omega t))$$

By using the above equality equation (1.4) can be simplified by using some commutation relations of Pauli matrices and Euler equations for spin operators

$$i\partial_t|\psi(t)\rangle = [\frac{\omega - \omega_0}{2}\sigma_z + g\sigma_x]|\psi(t)\rangle \tag{1.5}$$

In equation (1.4) the Hamiltonian in the right hand side does not have any time dependence and it can be interpreted as the Hamiltonian in the rotating frame where magnetic fields are stationary. The solution leads to

$$i\partial_t|\psi(t)\rangle = e^{i[\frac{\omega-\omega_0}{2}\sigma_z + g\sigma_x]t}|\psi(0)\rangle$$

This solution can also be thought as the rotation of single qubit about the $\hat{n}$ and by an able $|\vec{n}|$

$$\hat{n} = \frac{\hat{z} + \frac{2g}{\omega_0-\omega}}{\sqrt{1 + (\frac{2g}{\omega_0-\omega})^2}}$$

$$|\vec{n}| = t\sqrt{(\frac{\omega_0 - \omega}{2})^2 + g^2}$$

When ω is far from ω_0, the spin is negligibly affected by the B_{Rf} field, the axis of its rotation is nearly parallel to Z-axis, and its time evolution is nearly exactly due to free B_0 Hamiltonian. On the other hand, when $\omega_0 \approx \omega$, the B_0 contribution becomes negligible, and a small B_{RF} field can cause large changes in the state, corresponding to rotations about the x-axis. Thus, there can be an enormous effect a small perturbation on the spin system, when tuned to the appropriate frequency, and this phenomena is termed as resonance in nuclear magnetic resonance.

1.2 Realizing quantum bits and quantum gates

In case of liquid-state NMR QIP spin-$\frac{1}{2}$ nuclei are considered as qubits who can carry quantum information. Spin-$\frac{1}{2}$ nucleus is two states system, when put in the strong magnetic field, its state space consists of superposition of spin *up* and spin *down* state. Spin *up* is denoted as logical state $|0\rangle$ and spin down is $|1\rangle$. An analogy can be set up here between spin-$\frac{1}{2}$ nucleus and a tiny magnet which can point either up or down. Since, spin is purely quantum degree of freedom which allows it to stay in the superposition state $|\phi_0\rangle = \alpha|0\rangle + \beta|1\rangle$ with $\alpha^2 + \beta^2 = 1$. In the the presence of external magnetic field, both logical states have slightly different energies which results in the following state after time evolution has taken place

$$|\phi_t\rangle = e^{-i\omega t/2}\alpha|0\rangle + e^{i\omega t/2}\beta|1\rangle \tag{1.6}$$

Where ω is the precession frequency of nuclear spin the presence of external magnetic field which depends on energy difference $\delta = \frac{2\pi\epsilon}{\hbar}$ $\hbar$ is the Planck's constant. Using the Pauli matrix σ_z, the time evolution can be expressed as $|\phi_t\rangle = e^{i\omega\sigma_z t/2}|\psi_0\rangle$. From equation (1.2), we can see that the operator $\omega\sigma_z$ is the part of internal Hamiltonian, hence can be implement by letting the system to evolve freely. The next step in implementation is to control the qubits and change their state in the Bloch sphere according to a quantum algorithm. A unitary operator can be thought as a rotation operator in the Hilbert space of system. In modern NMR, modulated external Rf-fields are applied to realize specific unitary evolutions known as quantum gates and the evolution due to free Hamiltonian allows to implement two qubit quantum gates. Thus, Rf-fields and evolution due to free Hamiltonian provides us the universal control.

1.3 Quantum Simulations

Feynman(1982)[4] originally conjectured that Quantum computers can be programmed to simulate any quantum system Further, Lloyd (1996)[5] in his pioneered work proved that If the system is governed by Local interaction Hamiltonian, then Trotter's formula can approximate the time evolution with a large number of simpler operations acting on subspace of Hilbert Space.

Hamiltonian for a system of n particles

$$H = \sum_{k=1}^{L} H_k \tag{1.7}$$

Where each H_k acts on at most c number of systems and L is Poly(n)
As Trotter expansion suggests:

$$U = e^{-iHt} \approx [e^{-i\frac{H_1 t}{n}} e^{-i\frac{H_2 t}{n}} e^{-i\frac{H_3 t}{n}} ......e^{-i\frac{H_L t}{n}}]^n \tag{1.8}$$

Suppose each H_k acts on a local Hilbert space with dimensions m_k. Hence, the number of operations needed to simulate $e^{-i\frac{H_k t}{n}}$ is approximately m_k^2. We need to simulate each H_k, n times and there are L operations of these. So total number of operations to simulate the time evolution e^{-iHt} turns out to be $\approx n(\sum_k m_k^2) \leq nLm^2$ where m = max$\{m_k\}$. Each of these simpler operations grows polynomially with the system size and can be simulated efficiently by using Poly(n) resources. According to complexity, simulation is efficient if to simulate a system takes computer time that is Poly(n). So it can be concluded that this simulation is efficient if L scales polynomially as system size increases.

Quantum simulator which uses this approach of decomposing the whole time evolution of the system into a sequence of simple local operations are known digital quantum simulators. These kind of simulator are able to simulate a wide range of quantum system by using the correct sequence of gates. In the case where any unitary operation can be implemented, i.e. a general quantum computer, one will be able to simulate any quantum system with local interactions, this defines a universal quantum simulator.

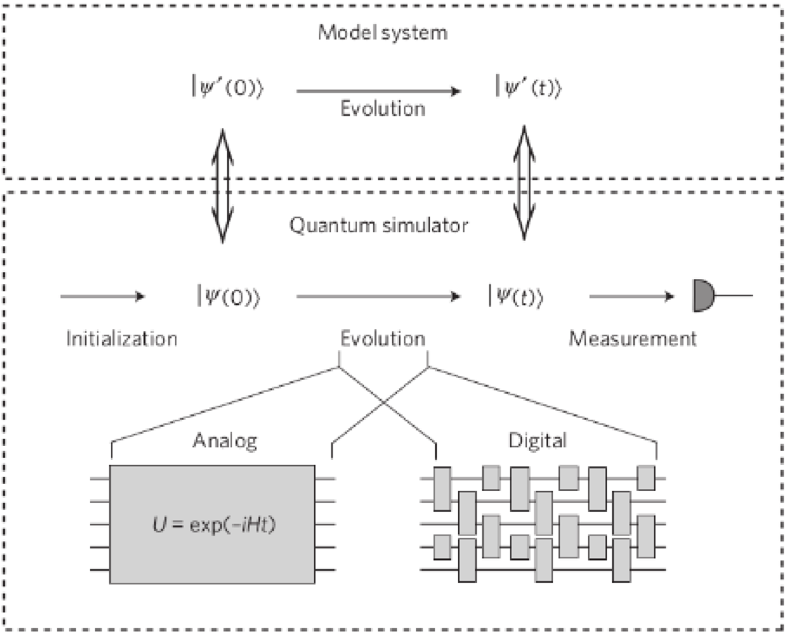


Figure 1.2: Analog and Digital quantum simulator

The second type is analog quantum simulator where the simulator is a quantum system which can be easily controlled and tuned as desired. By tuning the controlling parameters so that the Hamiltonian is equivalent to that of the model system that we want to simulate. Once we have matched both the Hamiltonians then by starting this system in a desired state and let the evolution to happen. After some time measurements are done on simulator and the obtained results can be mapped to that of the model system. Advantages of this approach is that it is easier to implement than a digital simulator because we do not have a standard approach to efficiently decompose any unitary into parts. These simulator can not act as universal simulator.

Chapter 2

Quantum Simulation of Molecular Hamiltonians

This chapter includes all the essential steps required for simulation of molecular Hamiltonians on quantum computer. We start with mapping between physical system and simulated system which is followed by starting the quantum computer with the desired state, in our case it is ground state since we are interested in calculating the ground state energy of SbH molecule. Next step is the iterative phase estimation algorithm which is necessary in the sense that it encodes the energy eigen value in the phase of probe qubits and this phase can be directly detected by phase sensitive NMR spectra.

2.1 Putting the wave function on quantum computer

Quantum simulation requires a mapping between simulating system and a physical system. There are two kinds of mapping

- Direct mapping: In this mapping Fock space of the molecule is mapped on to Hilbert space of qubits. Each spin orbital is mapped with a qubit. The qubit state $|1\rangle$ corresponds to the presence of one fermion and the qubit state $|0\rangle$ suggests that there is no fermion in the spin orbital. This mapping is less efficient as it requires large number of qubits to map the whole Fock space.

- Compact mapping: This kind of mapping requires fewer qubits because it maps the subspace of fixed electron onto Hilbert space of qubits. This kind of mapping is the most the most economical. For example, we are interested in m electrons occupying in n spin orbitals, then the dimension of the configuration space is n_{c_m} which requires n' number of qubits such that

  $$2^{n'} \geq \; n_{c_m}$$

Thus, the Hilbert space of quantum computer would be large enough to simulate the full configuration space. It was proven by Aspuru Guzik *et al*[6] that number of qubits required in both mappings scales linearly with number of basis functions.

2.1.1 First quantization method

This method was originally proposed by Zalka [13] in which the time evolution of the wave function of a quantum mechanical many particle system is simulated on quantum computer. Firstly, the wave function, here in position space, is discretized into 2^n points which can be represented by the basis set n qubits Hilbert space, ranging from $|000..00\rangle \Rightarrow |1111..11\rangle$. The discretized wave function is stored as the exponentially many amplitudes of classical basis states of the quantum computer and the time-evolution of the wave function in carried out in quantum parallelism. Hamiltonian to be simulated is

$$H = T + V = \frac{P^2}{2m} + V(x) \tag{2.1}$$

$$a_n = \psi(n \vartriangle x), \qquad a_{n+N} = a_n \tag{2.2}$$

$$|\psi\rangle = \sum_{n=1}^{N-1} a_n |n\rangle, \qquad N = 2^l \tag{2.3}$$

The next step is how to implement the time evolution in Δt. The time evolution operator is the following

$$U(\delta t) = e^{-i\hat{H}\Delta t} \tag{2.4}$$

$$U(\delta t) = e^{-i\Delta t(\frac{P^2}{2m} + V(x))} \tag{2.5}$$

Which can be approximated as:

$$U(\delta t) = e^{-i(\frac{P^2}{2m})\Delta t} e^{-iV(x)\Delta t} + O(\Delta t^2) \tag{2.6}$$

The second term $e^{-iV(x)\Delta t}$ corresponds to diagonal operator in position space and adds a phase to quantum computer state $|\psi\rangle$ and the first term is $e^{-i(\frac{P^2}{2m})\Delta t}$ diagonal in momentum space. So by applying quantum Fourier transformation between them we can implement this too. As we can see that if we use classical computer instead of quantum computer, we would have to have exponential memory and exponentially more time. The only disadvantage of this approach is that we have to choose a larger quantum register in order to obtain a better spatial resolution in representation of wave function.

2.1.2 Second quantization method

Second quantization is based on the mapping of electronic Fock space and state of M qubits, qubit **i** in 0(or 1) state indicates the spin orbital is occupied (or unoccupied)

$$|0\rangle^i = a_i^\dagger |vac\rangle \tag{2.7}$$

$$|1\rangle^i = |vac\rangle \tag{2.8}$$

where $|vac\rangle$ is vacuum state with no fermion. Hamiltonian in the second quantization form is given as:

$$H = \sum_{ij} E_{ij} a_i^\dagger a_j + \sum_{ijkl} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \tag{2.9}$$

where $E_{ij} = \langle i|T + V_N|j\rangle$ are single electron integrals and $V_{ijlk} = \langle ij|E_{ijkl}|kl\rangle$ are double electron integrals. Both are precomputed on classical computer while having a proper basis set, STO-3G for water, to define the system. The Evolution operator corresponding to Hamiltonian is:

$$U_{ij} = e^{-iE_{ij} a_i^\dagger a_j \delta t} \text{ Or } U_{ijkl} = e^{-iV_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \delta t}$$

U_{ij} can be implemented by converting $a_i^\dagger$ and a_j to spin operators which is known as Jordan-Wigner Transformation. It is basically a transformation from fermionic annihilation and creation operators to spin operators. We define two matrices as raising and lowering matrices

$$\sigma_+ = \tfrac{1}{2}(\sigma_x + i\sigma_y) \text{ and } \sigma_- = \tfrac{1}{2}(\sigma_x - i\sigma_y)$$

An analogy can be set up here in which σ_+ acts as creation operator and σ_- acts as annihilation. The mapping is given as

$$a_n^\dagger = (\textstyle\prod_{k=1}^{n-1} \sigma_z^k)\sigma_+^n \text{ and } a_n = (\textstyle\prod_{k=1}^{n-1} \sigma_z^k)\sigma_-^n$$

Here, the creation and annihilation operators on n^{th} spin orbital are of tensor product of Pauli matrices up $n-1$ and after that it is identity matrix for remaining spin orbitals. Thus, $U_{ij} = e^{-iE_{ij} a_i^\dagger a_j \delta t}$ can be expressed in Pauli matrices which can be further converted into one and two qubits operation. Here is a simple example in which single electron Hamiltonian is considered with similar value of indices i and j,

$$a_i^\dagger a_i = (\textstyle\prod_{k=1}^{i-1} \sigma_z^k)\sigma_+^i \; (\textstyle\prod_{k=1}^{i-1} \sigma_z^k)\sigma_-^i = \sigma_+^i \sigma_-^i$$

$$\sigma_+^i \sigma_-^i = \tfrac{1}{2}(1^i + \sigma_z^i)$$

Evolution operator due to this part of Hamiltonian,

$$U_{ii} = e^{-i(1^i + \sigma_z^i)E_{ii}\Delta t} = \text{Diag}(e^{-iE_{ii}\Delta t}, 1)$$

Which can be implemented by single qubit gate. Likewise, whole evolution operator is divided into elementary gates and the algorithm scales as $O(n^5)$, n = N(spin-orbitals. A comprehensive study of other part of the Hamiltonian can be found here [20].

2.2 Adiabatic Quantum Computation (AQC)

In adiabatic quantum computation, the quantum computer remains forever in the ground state of quantum system throughout the computation. The method is extensively used in optimization problems and large number of the computationally hard problems can be formulated as optimization problems.The solution of the optimization problem is encoded in the ground state energies, phases, etc. by using some unitary transformations. The Hamiltonian $H(t)$ of the computer is changed gradually from a initial simple Hamiltonian H_i whose ground state is already known, to a final Hamiltonian H_f whose ground state encodes the solutions we are looking for. The adiabatic theorem suggests that if the variation in the Hamiltonian is sufficiently slow, the initial prepared ground state will be transformed to ground state of H_f. In the following example The particle starts out in the ground state of infinite square well of width a, whose wave function is given by

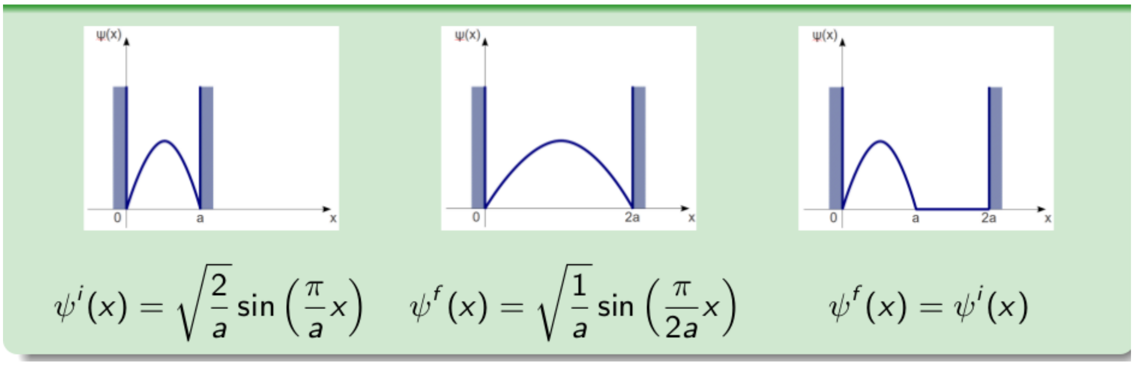


Figure 2.1: (a) Ground state of infinite square well of thickness a. (b) Ground state of infinite square well of thickness b. (c) When wall expands quickly

$$\psi_x^i = \sqrt{\frac{2}{a}} sin(\frac{\pi x}{a}) \tag{2.10}$$

If now the wall is gradually expanded to width 2a, the adiabatic theorem says that particle will end up in the ground state of the excited well which is shown in the mid of above figure.

$$\psi_x^f = \sqrt{\frac{1}{a}} sin(\frac{\pi x}{2a}) \tag{2.11}$$

Unlike the small perturbation theory, here the change in the Hamiltonian is huge, the system's energy has changed with a substantial amount. By contrast, if the width of the wall is changed suddenly, the resulting state will still be ψ_i^x, which might be linear combination of eigenstates of new Hamiltonian. Sudden change can be thought as the free expansion of a gas into the vacuum when the piston is removed, the free expansion does not require any external work done on system, hence energy is conserved. Due to limited coherence time of quantum states, it is desirable to complete the evolution as quick as possible but the rate of change is determined by the energy gap between ground state and the first excited state during the evolutions. The application of AQC in quantum simulations becomes important in the of preparation of quantum states of interest. For example, if our motive is to calculate the ground state energy of an arbitrary Hamiltonian, then the quantum computer starts with the ground state which can be efficiently prepared by using AQC.

Suppose, we start with simple Hamiltonian H_0 whose ground state is easily prepared, given by $|\psi_0\rangle$. The change in the Hamiltonian is governed by following equation

$$H_{ad} = (1-s)H_0 + sH_f; \quad s = \frac{t}{T} \tag{2.12}$$

If the variation from H_0 (t = 0) to the target Hamiltonian H_f (t = T) is slow enough such that adiabatic conditions are valid, then the final state $|\psi(t)\rangle$, satisfies the time-dependent Schrödinger equation

$$ih\frac{d|\psi(t)\rangle}{dt} = H(t)|\psi_f\rangle \tag{2.13}$$

follows the corresponding eigenstate of H(t) adiabatically. It implies that $|\psi(T)\rangle$ has a good overlap with the ground state of the target Hamiltonian H_f. A sufficient condition ensuring the process as adiabatic for a linear interpolation between two Hamiltonians for the total evolution time T is

$$T \gg \frac{||\partial_s H(s)||}{\triangle_{min}^2} \tag{2.14}$$

Where $\triangle_{min} \equiv (E_1(s) - E_0(s))$ for s ϵ[0 1] is the minimum value of energy gap between instantaneous ground state and first excited state. Boixo *et al.* [8] proposed a new general bound on T which is also valid for other non-linear interpolations if the rate of change of instantaneous eigenstate $|\partial_s\psi(s)\rangle$ is provided.

$$T > \frac{L^2}{\triangle_{min}} \tag{2.15}$$

Where L is the path integral given as

$$L = \int ||\psi(s)\rangle||ds \tag{2.16}$$

AQC becomes extremely important when we do not have enough quantum control to physically implement the unitary evolutions of Hamiltonian H(t). In this case, it is feasible to implement the adiabatic state preparation first into a quantum algorithm and simulate the adiabatic process on a digital quantum computer. Recently, developed D-wave quantum computer also works on adiabatic model of computation.

2.3 Evolution and Measurements

2.3.1 Phase Estimation Algorithm

The phase estimation algorithm (PEA) is a quantum algorithm for determining the eigenvalue of an arbitrary unitary operator. The relevance of phase estimation algorithm was originally proposed by Abrams and Lloyd *et al* for quantum simulations in their phenomenal paper [7] and further Aspuru-Guzik *et al* used it in the quantum simulation of small molecules in order to calculate the lowest energy eigen values [6]. The algorithm essentially uses quantum Fourier transformation (QFT) and opens new windows in the quantum simulations of molecular Hamiltonians. The PEA is efficient because it is mainly based on QFT whose complexity scales as $O(n^2)$ [1].

2.3.2 Quantum Fourier Transform

Quantum Fourier transform is the quantum mechanical way of classical Fourier transform and it takes the advantage of quantum superposition. The classical discrete Fourier transform drives an input which can be considered as a vector of complex numbers $(x_0, ..., x_{N1})$ and outputs the elements of another vector $(y_0, ..., y_{N1})$ according to the equation

$$y_k \equiv \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} x_j e^{2\pi ijk/N} \tag{2.17}$$

The quantum Fourier transformation on an orthogonal basis $|0\rangle$,....,$|N-1\rangle$ is a linear operator whose action is given as

$$|j\rangle \longrightarrow \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} e^{2\pi ijk/N} |k\rangle \tag{2.18}$$

Equivalently, QFT of an arbitrary quantum state is written as

$$\sum_{j=0}^{N-1} x_j |j\rangle \longrightarrow \sum_{k=0}^{N-1} y_k |k\rangle \tag{2.19}$$

Suppose, we assume N = 2^n, where n is an integer and the basis $|0\rangle$,...$|2^n - 1\rangle$ is the computation basis states for quantum computer working with n qubits. We may adopt the binary representation of basis states as j = $j_1 j_2 j_3 ... j_n$ and $0.j_l j_{l+1} ... j_m = \frac{j_l}{2} + \frac{j_{l+1}}{4} + ... + \frac{j_m}{2^{m-l+1}}$. With a little calculations Equation (2.18) can be written in the following product representation:

$$|j_1j_2...j_n\rangle \longrightarrow \frac{1}{2^{n/2}}(|0\rangle + e^{i2\pi 0.j_n}|1\rangle)(|0\rangle + e^{i2\pi 0.j_{n-1}j_n}|1\rangle)......(|0\rangle + e^{i2\pi 0.j_1j_2j_3...j_n}|1\rangle) \quad (2.20)$$

Quantum Fourier transform requires $O(n^2)$ no. of gates in order to implement it on quantum computer while the best classical algorithm for computing the discrete Fourier transform on 2^n elements requires $O(n2^n)$ gates. Thus, it requires exponentially more operations to compute Fourier transform on classical computer than it does on a quantum computer **??** Chuang.

2.3.3 Ground state energy calculation via PEA

The crucial part of evolution is the implementation of the phase estimation algorithm to generate a phase on probe qubits. Phase estimation algorithm uses two quantum registers as shown in figure.

$$|R\rangle : |t\rangle \otimes |u\rangle \quad (2.21)$$

Where the system qubit $|u\rangle$ is the eigen state of unitary operator and probe qubits $|t\rangle$ are used to encode the phase. The algorithm includes the application of unitary operator $U = e^{-iH\tau}$ which has to be efficiently implemented in order to make the algorithm efficient. Application of $U = e^{-iH\tau}$ on the ground state generates the phase $e^{i2\pi\phi}$, where $E = \frac{-2\pi\phi}{\tau}$ and τ can be an arbitrary number such that phase $\phi \epsilon 01. Suppose, proberegister$—t⟩ starts with $|0\rangle^{\otimes n}$ and eigen state $|u\rangle$ has the eigen value $e^{i2\pi\phi}$ and phase ϕ can be exactly expressed in m binary digits, as $\phi = 0.\phi_1\phi_2\phi_3...\phi_m$ Thus, Output state is

$$\tfrac{1}{2^{t/2}}\ (|0\rangle\ +\ e^{i2\pi 0.\phi_m}|1\rangle)\ (|0\rangle\ +\ e^{i2\pi 0.\phi_{m-1}\phi_m}|1\rangle)\ ......(|0\rangle\ +\ e^{i2\pi 0.\phi_1\phi_2....\phi_m}|1\rangle).$$

The output state is nothing but the quantum Fourier transform 2.20 of $|\phi_1\phi_2\phi_3...\phi_m\rangle$. An inverse QFT is applied at the end and a measurement is computational basis gives ϕ exactly.

$$|j\rangle \Longrightarrow \sum_{k=1}^{2^n-1} e^{\frac{2\pi ijk}{N}}|k\rangle \qquad O(n^2) \quad (2.22)$$

Thus PEA is efficient but it uses large number of qubits in probe register as desired accuracy increases. To overcome this, the algorithm can be modified such that it uses less resources but operates iteratively. In the circuit shown above, the upper line is used as probe qubits and initially set in $|0\rangle$ while the lower line represents the physical system to be implemented which starts with the ground state of the Hamiltonian (H_f) whose energies are being calculated. As we can see from the circuit, there is a Controlled_U operator with $U = e^{-iH_ft}$ and the eigen value of U is $e^{i2\pi\phi}$. The state before measurement is

$$|\psi_m\rangle = \frac{1}{\sqrt{2}}[(1 + e^{i2\pi\phi})|0\rangle + (1 - e^{i2\pi\phi})|1\rangle] \quad (2.23)$$

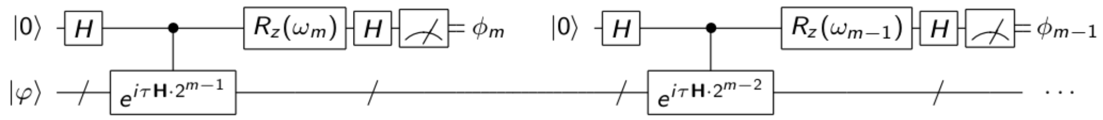


Figure 2.3: Iterative Phase Estimation algorithm

When measurements are performed, the probability of collapsing into $|0\rangle$ is $P_0 = cos^2(\pi\phi)$ and apparently, it has dependence on phase ϕ. If we repeat the procedure N times, it determines P_0 with an accuracy of $\frac{1}{\sqrt{N}}$. Hence, it has to be repeated $N \approx 2^{2m}$ in order to obtain m accurate binary digits of phase ϕ. Each cycle ends up with the measurements, consequently, we must have 2^{2m} measurements. This makes intractable to implement on a physical system.

To overcome this difficulty, Kitaev [9]proposed a modified PEA which requires less number of cycles and consequently less number of measurements, provided that we are able to implement controlled_U^{2^k} (C_U) gates. For $0 \leq k \leq m$ then, $C\_U^{2^{k-1}}$ will transform the probe qubit into

$$|\psi_{k-1}\rangle = \frac{1}{\sqrt{2}}[|0\rangle + e^{i2\pi(2^{k-1}\phi)}|1\rangle] \tag{2.24}$$

Firstly, the IPEA determines least significant bits in the binary representation of phase. Obtained bit is fed back into the algorithm by a Z-rotation gate on probe qubit as shown in the circuit. The rotation angle for m^{th} iteration is given as $\omega_m = 2\pi(0.0\phi_k\phi_{k+1}\phi_{k+2}...\phi_m)$. In the first iteration (k = m), application of $C\_U^{2^{m-1}}$ followed by a measurements gives the $|0\rangle$ with the probability $P_0 = cos^2[0.\phi_m]$ which means P_0 is zero if ϕ_m is one and P_0 is one if ϕ_m is zero. Further, In the second iteration when k = m - 1 the measurement determines m 1th bit. The phase associated with probe qubit just before Z -rotation is $2\pi(0.0\phi_{m-1}\phi_m)$ and application of Z - rotation by an angle $\omega_{m-1} = 2\pi(0.0\phi_m)$ results in the probability P_0 to be $cos^2[0.\phi_{m-1}]$. Thus, using feedback the second bit is also measured deterministically and likewise, all the remaining bits are obtained.

Chapter 3

Many electrons system

This chapter involves the basic concepts and terminologies used in quantum chemistry. We discuss structure of many electron operators and the form of wave functions which are called as Slater determinants. In subsequent sections Born-Oppenheimer approximation and schrodinger -Sock approximation are elaborated. Further, we consider relativistic effects in the case of heavy elements and introduce new approximations to overcome the difficulties coming due to larger Hamiltonian matrix. At the end, the possibility of simulating relativistic Hamiltonians on quantum computer is considered.

3.1 The electronic problem and Born-Oppenheimer approximation

The Hamiltonian for a system of nuclei and electrons is given as

$$H = -\sum_{i=1}^{N} \frac{1}{2} \triangle_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \triangle_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{3.1}$$

Where M_A is the ration of electron and nucleus masses, Z_A and Z_B are atomic numbers of nuclei A and B respectively. The first term in equation 3.1 represents the kinetic energy operator for electrons, so as the second term for nuclei while the third terms is for coulomb attaraction between electrons and nuclei; the last two terms are for electron-electron and nuclei-nuclei repulsion. Our motive is to solve the non-relativistic time independent Schrödinger equation given below

$$H|\phi\rangle = E|\phi\rangle \tag{3.2}$$

The analytical solutions are not possible for heavy molecules, not even for triatomic and demands large computational power which increases exponentially as system size grows. We employ some approximation in order to solve analytically and an approximation known as Born-Oppenheimer (BOA) simplifies the equation. BOA is based on the fact that nuclei are much heavier that electrons, hence move very slowly. Thus, to a good approximation, we can consider the motion of electrons independently in the average field of fixed nuclei. Moreover, the second term in the equation 3.1 can be considered constant and similar goes with nuclei-nuclei repulsion energy. As a result, the whole Hamiltonian can be approximated to only electronic Hamiltonian or precisely the Hamiltonian describing the motion of N free electrons in the field of M charges,

$$H_{elec} = -\sum_{i=1}^{N} \frac{1}{2}\triangle_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \tag{3.3}$$

Thus, the solution to a Schrondinger equation involving the electronic Hamiltonian

$$H_{elec}\phi_{elec} = E_{elec}\phi_{elec} \tag{3.4}$$

Hence, the electronic wavefunction,

$$\phi_{elec} = \phi_{elec}(r_i; R_A) \tag{3.5}$$

Equation (3.5) suggests that wave function depends of electronic coordinates as well as nuclear coordinates, similar is true for E_{elec} energy,

$$E_{elec} = E_{elec}(R_A) \tag{3.6}$$

As a result, the total energy for fixed nuclei includes the constant nuclear repulsion.

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

3.2 Spin-orbitals, configuration and basis functions

An orbital is defined as the wavefunction for a single particle, an electron as we are dealing with an electronic problem. A spatial orbital $\psi_i(r)$, is a function of the r vector and the spatial distribution depends of the probablity $|\psi_i(r)^2|dr$ of finding the electron in dr volume surrounding r. The spatial orbitals are considered as orthogonal set so that

$$\int dr \psi_i(r)^* \psi_j(r) = \delta_{ij}$$

Since the set of ψ_i is complete, so any arbitrary function can be written as

$$f(r) = \sum_{i=1}^{\infty} a_i \psi_i(r)$$

The set should be infinite in order to be complete but we consider only a finite set of K orbitals which span a certain region of the complete space but results can be described exact within the subspace spanned by finite set of orbitals.
Electron has an intrinsic spin degree of freedom, hence it is necessary to specify this into basis set. A complete set consists of two orthonormal functions is denoted as $\alpha\omega$ and $\beta\omega$, where α and β are for spin up and down states respectively. Now the complete wavefunction has both spin as well as spatial part and called as spin orbitals, denoted by ξ_x, where x denotes both spin and spatial cooridantes. Thus, for each spatial orbital, there would be two different spin orbitals-one corresponding to spin up and other to spin down. As a result of the whole spin orbitals is written in the vector form as

$$\begin{pmatrix} \psi(r)\alpha(\omega) \\ \psi(r)\beta(\omega) \end{pmatrix}$$

For example, K spatial orbitals would lead to 2K spin orbitals $\{\xi_i|1,2,....2K\}$ whose vector form would be

$$\begin{pmatrix} \xi_{2i-1}(x) = \psi(r)\alpha(\omega) \\ \xi_{2i}(x) = \psi(r)\beta(\omega) \end{pmatrix}$$

Where i = 1, 2,...K. Since spatial orbitals are orthogonal which implies that spin orbitals would also be orthogonal.

$$\int dr \xi_i(x)^* \xi_j(x) = \delta_{ij}$$

3.3 Hartee products, Slater determinants and Hartree-Fock approximation

So far we have discussed about single electron wave function which is one spin orbital, we now will study the wavefunction of many electrons. In the simple case, we consider a system of N noninteracting electrons whose overall Hamiltonian would be sum of the all the individual Hamiltonians of all the electrons which is given as

$$\mathscr{H} = \sum_{i=1}^{N} h(i)$$

Where $h(i)$ is the sum of kinetic and potential energy operator of i^{th} electron. The operator $h(i)$ would have eigenfunctions which are given by the set of spin orbitals ξ_j

$$h(i)\xi_j(x_i) = E_j \xi_j(x_i)$$

Now we focus on to calculate the eigenfunction of whole Hamiltonian H which would be the product of spin-orbital wavefunctions for each electron. This happens due to indenpendent nature of all the $h(i)$ Hamiltonians and H is the sum of them. Hence, the wavefunction would be

$$\psi_{HP}(x_1, x_2, ...x_n) = \xi_i(x_1)\xi_j(x_2)....\xi_k(x_N) \tag{3.7}$$

ψ^{HP} is the solution of following Schrödinger equation whose eigenvalue is just the sum of spin orbital energies of each spin orbital.

$$\begin{aligned} H\psi^{HP} &= E\psi^{HP} \\ E &= \epsilon_i + \epsilon_j + ... + \epsilon_k \end{aligned}$$

ψ^{HP} is called as Hartree product, with first electron is described by the spin orbital ξ_i and second electron is described by the ξ_j spin orbitals. The Hartree products does not consider the antisymmetry principle which does not allow to stay two fermions in one spin orbital and it is also called as Pauli exclusion principle. We can make the wavefunction antisymmetrized in the following manner. Suppose, there are two electrons occupying two spin orbitals ξ_i and ξ_j. In the first case, electron one occupies in ξ_i and eletron two occupies in ξ_j and in the second case, electron one occupies in ξ_j and eletron two occupies in ξ_i. Both of these cases are denoted by ψ_{12}^{HP} and ψ_{21}^{HP} respectively.

$$\begin{aligned} \psi_{12}^{HP} &= \xi_i(x_1)\xi_j(x_2) \\ \psi_{21}^{HP} &= \xi_j(x_1)\xi_i(x_2) \end{aligned}$$

If we consider a wave in the superposition state given below where the negative sign in the superposition ensures that there would be an overall negative sign in the wavefunction if both the eletrons are interchanged.

$$\psi(x_1, x_2) = \frac{1}{2}[\xi_i(x_1)\xi_j(x_2) - \xi_i(x_2)\xi_j(x_2)] \tag{3.8}$$

From this equation, it can also be seen as that if $i = j$, which means both the electron occupy same spin orbital then the wavefunction vanishes. Moreover, $\psi(x_1, x_2)$ can also be written in the form of determinants that is also called as Slater determinant.

$$\psi(x_1, x_2) = |\xi_1\xi_2\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \xi_i(x_1) & \xi_j(x_1) \\ \xi_i(x_2) & \xi_j(x_2) \end{vmatrix} \tag{3.9}$$

Likewise, the ground state of N-electron system is

$$\psi_0\rangle = |\xi_1\xi_2..xi_N\rangle \tag{3.10}$$

According to variation principle, the optimal wavefunction would be the one which corresponds to minimum possible energy

$$E_0 = \langle \psi_0 | H \psi_0 \rangle \tag{3.11}$$

Thus, we have the freedom to chose spin orbitals in equation3.10 and by minimizing the E_0, we obtain the optimal spin orbitals which satify the Hartree-Fock equation

$$f(i)\xi(x_i) = \epsilon\xi(x_i) \tag{3.12}$$

Where $f(i)$ is the effective one-electron operator, called Fock operator which has the form

$$f(i) = -\frac{1}{2}{}_{i}^{2} - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + V_{HF}(i) \tag{3.13}$$

Where V_{HF}^{i} is the effective potential experienced by i^{th} electrons due to presence of other electrons in the system. This approximation is termed as Hartree-Fock and the essence is to replace the complex problem by one electron problem.

3.4 Simulation of Relativistic Hamiltonians on QC

It is well understood that an accurate study of molecules with heavy elements needs consideration of electron correlation and relativistic effects. The approach to deal with is based on four component formalism which also involves no-pair approximation. Dirac-Coulomb Hamiltonian is

$$H = \sum_{i=1}^{N} [c(\alpha_i . p_i) + \beta_i' mc^2 - \phi_{nuc}] + \sum_{i<j} \frac{1}{r_{ij}} + V_{NN} \tag{3.14}$$

$$\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}, \ \beta = \begin{bmatrix} I_2 & 0 \\ 0 & -I_2 \end{bmatrix}.$$

and $\beta' = \beta - I_4$ Here, we have already considered Born-Oppenheimer approximation which allows to separate the electronic degrees of freedom from nuclei. The one electron operator of the electronic Hamiltonian has two terms, one Dirac Hamiltonian and second is electrostatic potential ϕ_{nuc} of nuclei considered at rest under BOA. Dirac-Coulomb Hamiltonian has no bound solutions due to negative energy solutions of Dirac equation. To overcome this problem we only take positive energy bi-spinors as N-particle basis of Slater determinants. This approximation is known as no-pair approximation. No-pair approximation is quite justifiable because we have already adopted BOA which has larger impact on energy levels than to neglect the negative energy bi-spinors.

The algorithm to simulate relativistic Hamiltonians start with a mapping of relativistic

quantum mechanical wave function onto register qubit. We mostly use direct mapping in non-relativistic case. With the application of no-pair approximation relativistic case turns out to be similar to non-relitivistic(NR) because we ignore negative energy solutions of Dirac equation. We could also take the advantage of time reversal symmetry of Dirac equation which makes bi-spinors to be degenerate Kramer's pair denoted as A and B which can be thought as two spin states α and β in NR approach. Kramer's pairs are the bi-spinors related with time-reversal operator and are orthogonal to each other. Thus, direct mapping is possible by assigning a qubit with one bi-spinor A and one qubit for B
Dealing with 4c relativistic formalism brings additional computational difficulties compared to non-relativistic.

non-relativistic FCI $\Longrightarrow$ Relativistic four component FCI
Relativistic Full Configuration Interaction

- Large Hamiltonian matrix eigen value problem
- One and two electron integral come out to complex, hence dealing in complex space. This does not pose difficulties because we are working in complex Hilbert space even in the NR approach.

To overcome these we adopt some approximations like,

- No pair approximation: N-particle space is build-up from determinants containing positive-energy spinors
- Loss of symmetry due to spin-orbit interaction makes many integrals nonzero in the Hamiltonian matrix but situations gets better due to time-reversal symmetry of the Dirac equation, bispinors occur in Kramers pairs $(\psi_p, \psi_{\bar{p})}$ denoted as A, B
- Direct mapping is applicable: one qubit is assigned to A bispinor, one qubit for the B bispinor.

Chapter 4

Experimental Results

In this chapter we discuss the implementation of adiabatic state preparation method (ASP), iterative phase estimation algorithm and the calculations of ground state energy from the phase of obtained spectra. We start with preparing the system into the ground state of the hamiltonian which intend to simulate using NMR quantum computer. ASP is based on the fact that the if the Hamiltonian is changed adiabatically from H_i to H_f, then the system would stay in the ground state of newer Hamiltonian (H_f) if the system was intially prepared in the ground state of H_i. Further, implementation protocol of IPEA is elaborared. IPEA is the crucial part of the whole process because it encodes the enery eigen values into the phase of probe qubit. The phase can be measured by a mature technology called using interferometry frequently used in NMR implementations[21].

Adiabatic State Preparation

Liquid state NMR consists of spin-$\frac{1}{2}$ nuclei, which act as a qubit for quantum information processing. Due to low energy gap between $|0\rangle$ and $|1\rangle$ states of nuclear spin compared to room temperature(KT), the equilibrium distribution of the ensemble in highly mixed state. In liquid state samples time taken to reach at equilibrium state is around $10s - 40s$ in the absence of any RF fields, apparently every quantum computational task starts with thermal state which is highly mixed state and far from the standard state used for quantum information processing(QIP). However, it can be used to perform some quantum computations. The method which transforms thermal state to psuedo pure state, which acts as pure state for all practical purposes is based on the fact that only the traceless part of the density matrix contributes to overall transverse magnetization detected by NMR coils. The thermal state for a single spin is given as

$$\begin{aligned} \rho_{thermal} &= \frac{\mathbb{I}}{2} + \frac{\epsilon \mathbb{Z}}{2} \\ &= \frac{1-\epsilon}{2}\mathbb{I} + \epsilon|0\rangle\langle 0| \end{aligned} \tag{4.1}$$

If we start with n spin-$\frac{1}{2}$ in a molecule whose density of state is given as ρ. The expectation value of the current magnetization would be $tr(\rho s)$, where s is the traceless spin operator. Thus the magnetization turns out to be zero for the part of ρ proportional to identity matrix $\mathbb{I}$. We define a new matrix called as deviation matrix such that δ - $\rho = \lambda\mathbb{I}$ for some λ. The expectation value of the magnetization $(tr(\rho s))$ results in zero for the identity part in equation 4.1 due to traceless observables and non-zero for $|0\rangle\langle 0|$ part of the density matrix. In case of one spin system, $\epsilon|0\rangle\langle 0|$ is the deviation matrix

$$\begin{aligned} tr(\rho s) &= tr((\rho + \lambda\mathbb{I})s) \\ &= tr(\rho s) + tr(\lambda\mathbb{I}) \\ &= tr(\rho s) \end{aligned}$$

Thus, both ρ and δ give the same magnetization and considered as equivalent. A state with the deviation matrix $\epsilon|\phi\rangle\langle\phi|$ is known as pseudopure state, because this deviation is proportional to the deviation of pure state $|\phi\rangle\langle\phi|$. A pseudopure state is similar to corresponding pure state for all NMR observations and unitaty evolutions. In general, $\epsilon\delta$ can be treated as deviation matrix for a density matrix ρ if $\epsilon\delta = \rho + \lambda\mathbb{I}$ for $\forall\ \lambda$ and ϵ. In NMR quantum information processing, we have some techniques which transform the initial thermal equilibrium state to a standard pseudopure state with deviation $|000..00\rangle\langle 000..00|$ which comes out to be $|00\rangle\langle 00|$ in case to two spin-$\frac{1}{2}$ nuclei acting as two qubits required for our protocol.

The following pulses transform the equilibrium state of two qubits to psuedo-pure state where s_z^1, s_z^2 represent the first and second spin respectively.

$$\begin{aligned} & s_z^1 + s_z^2 \\ \xrightarrow{[\frac{\pi}{3}]_x^2}\quad & s_z^1 + \frac{1}{2}s_z^2 - s_y^2\frac{\sqrt{3}}{2} \\ \xrightarrow{[grad]_z}\quad & s_z^1 + \frac{1}{2}s_z^2 \\ \xrightarrow{[\frac{\pi}{4}]_x^1}\quad & \frac{s_z^1}{\sqrt{2}} + \frac{s_z^2}{2} - \frac{s_y^1}{2} \\ \xrightarrow{[1/2J_{12}]}\quad & \frac{s_z^1}{\sqrt{2}} + \frac{s_z^2}{2} + \sqrt{2}s_x^1 s_z^2 \\ \xrightarrow{[\frac{-\pi}{4}]_y^1}\quad & \frac{s_z^1}{\sqrt{2}} + \frac{s_z^2}{2} + s_x^1 s_z^2 + s_z^1 s_z^2 \\ \xrightarrow{[grad]_z}\quad & \frac{s_z^1}{\sqrt{2}} + \frac{s_z^2}{2} + s_z^1 s_z^2 \end{aligned}$$

The final state can be written as:

$$s_z^1 + s_z^2 + 2s_z^1 s_z^2 \Longleftrightarrow 2|00\rangle\langle 00| - \frac{1}{2}\mathbb{I} \tag{4.2}$$

As we discussed earlier in our implementation protocol that we start with by preparing the system in $|00\rangle\langle 00|$ where first qubit acts as probe qubit and second acts as system qubit. Further, we represent the state as $|0^p 0^s\rangle\langle 0^p 0^s|$, where p and s stand for probe and system qubits respectively.

In adiabatic state preparation, we firstly prepare our system qubit in the ground state of simpler Hamiltonian whose ground state is easily prepared and then Hamiltonian is gradually changed so that adiabatic conditions are satisfied, as a result the final state would be the ground state of the final Hamiltonian (H_f). Suppose, the system is initially prepared in the Hamiltonian σ_x^s whose ground state is $|\psi_g^i\rangle$ is given by

$$H_0 = \sigma_x$$
$$|\psi_g^i\rangle = \frac{1}{2}(|0\rangle - |1\rangle)$$

We have already prepared the system qubit in $|0\rangle$ which can be transformed to $|\psi_g^i\rangle$ by the application of R_y^{-s} -rf pulse where the magnitude of angle is $\frac{\pi}{2}$ and the direction is antiparallel to Y axis. Thus,

$$|0\rangle \quad \xrightarrow{R_y^{-s}(\frac{\pi}{2})} \quad \frac{1}{2}(|0\rangle - |1\rangle) \tag{4.3}$$

The change in Hamiltonian is governed by an interpolation scheme given as

$$H_{ad(t)} = (1-s)H_0 + H_f; \quad s = \frac{t}{T} \tag{4.4}$$

If $H_{ad(t)}$ varies adiabatically then the system remains in the ground state($|\psi_f\rangle$) of system hamiltonian (H_f) after the whole evolution has taken place, i.e $t \longrightarrow T$ and s becomes one. The adiabatic evolution of $H_{ad(t)}$ can be approximated by $M+1$ discrete steps, where each step duration is $\delta = \frac{T}{M+1}$.

$$U = \prod U_m^{ad} = \prod_{m=0}^{M} e^{-iH_m\delta}$$

The adiabatic limit is achieved when both M and T goes to infinity which implies $\delta \to 0$. Further, we can approximate the unitary operator for adiabatic steps by using Trotter's formulla. Hence, the unitary evolution for each discrete adiabatic step is given by

$$U_m^{ad} = e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} e^{-is_m H_f \delta} e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} + O(\delta^3); \quad s_m = \frac{mT}{M+1} \tag{4.5}$$

In our case H_0 is σ_x and the ground state Hamiltonian(H_f) of SbH molecule in complete active space(2,2) can be written in Pauli basis

$$H_f = c_0\mathbb{I} + c_1\sigma_x + c_2\sigma_z = \begin{bmatrix} -0.9035364 & 0.0388220 \\ 0.0388220 & -0.8761562 \end{bmatrix}$$

After solving above equation, we obtain c_1 = 0.038820 and c_2 = -0.0137. The diagonalization of Hamiltonian matrix gives -0.9310 a.u as ground state energy. Substituting the Hamiltonian into U_m^{ad} gives

$$\begin{aligned} U_m^{ad} &= e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} e^{-i(c_1\sigma_x+c_2\sigma_z)s_m\delta} e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} + O(\delta^3) \\ &= e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} e^{-ic_1 s_m\frac{\delta}{2}\sigma_x} e^{-ic_2 s_m\delta\sigma_z} e^{-ic_1 s_m\frac{\delta}{2}\sigma_x} e^{-i(\frac{\delta}{2})(1-s_m)\sigma_x} + O(\delta^3) \end{aligned}$$

The left and right part of the U_m^{ad} can be simulated by two -RF pulses along X-axis and mid part can also be decomposed into X and Y pulses.

$$e^{-ic_2 s_m\delta\sigma_z} = e^{-i\frac{\pi}{4}\sigma_x} e^{-ic_2 s_m\delta\sigma_y} e^{i\frac{\pi}{4}\sigma_x}$$

We can substitute the mid part into U_m^{ad} and as a result adiabatic evolution for one discrete step U_m^{ad} can be realized by the pulse sequence $R^s_{-}x(\phi_1) - R^s_{-}y(\phi_2) - R^s_x(\phi_3)$ where all ϕ_i are calculated using MATLAB.

The pulse program to implement adiabatic state preparation is

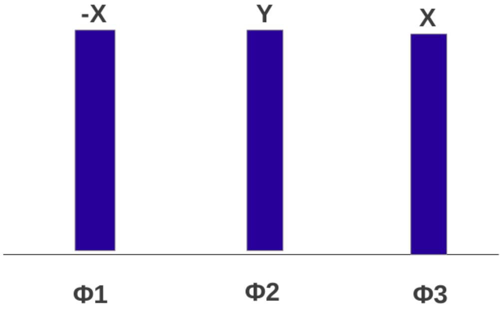


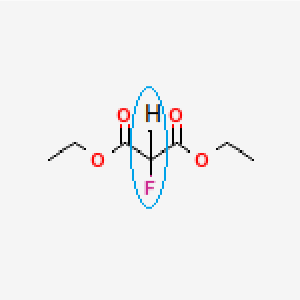
Figure 4.1: Pulse program Adiabatic State Preparation

$$\begin{aligned}\phi_1 &= \frac{\pi}{2} - \delta + 0.9612 s_m \delta \\ \phi_2 &= 0.0274 s_m \delta \\ \phi_3 &= \frac{\pi}{2} + \delta - 0.9612 s_m \delta\end{aligned}$$

For implementation, M = 10 and T = 7 were chosen and the fidelity for the ground state was obtained as 0.9759 and the evolution time was taken as $\frac{\pi}{2}$ to make the calculations simpler.

Experimental details

Diethyl fluoromalonate was used as 2-qubit quantum computer where 1_H acts as probe qubit and 19_F acts as system qubit. Measured chemical shifts, couplings, T_2 relaxation time and calibrated hard pulses are shown in table below.



	1_H	19_F
1_H	3340.725 Hz	47.50 H_z
19_F	47.50 Hz	-110922.073 H_z

To start an experiment in NMR, we have to calibrated hard pulses for $\frac{\pi}{2}$ rotations on all the nuclei. In case of 1_H, the pulse duration comes out to be 10μ s and below is the calibration curve where intensity is zero at 20μ s.

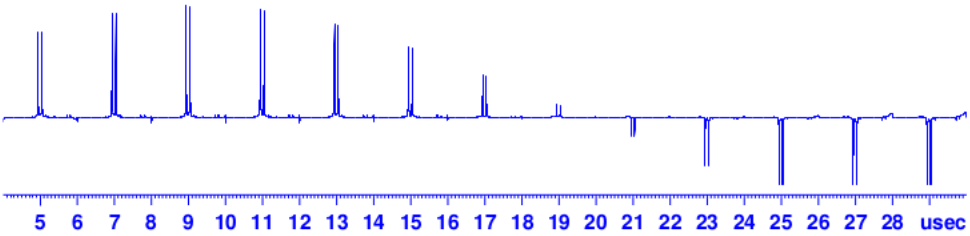


Figure 4.2: Calibration of hard pulse on 1_H nucleus

Similarly, for 19_F, the pulse duration to rotate by $\frac{\pi}{2}$ comes out to be 23.75μ s as shown in figure.

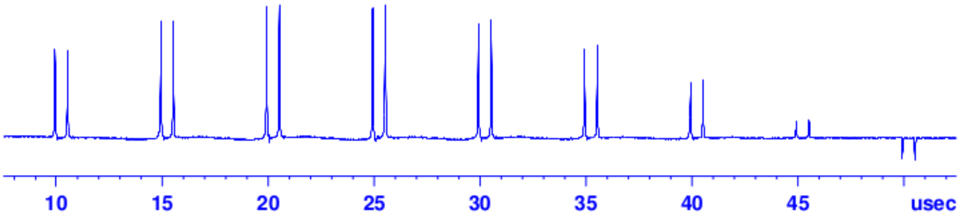


Figure 4.3: Calibration of hard pulse on 19_F nucleus

Further, the measured values of spin-spin relaxation (T_2) time for 1_H and 19_F are 4.28s and 3.87s respectively. The spin-spin relaxation is the mechanism by which transverse magnetization exponentially decays towards its equilibrium value of zero in NMR. It is given by

$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2} \tag{4.6}$$

Where $M_{xy}(0)$ is the measured transverse magnetization just after a hard pulse.

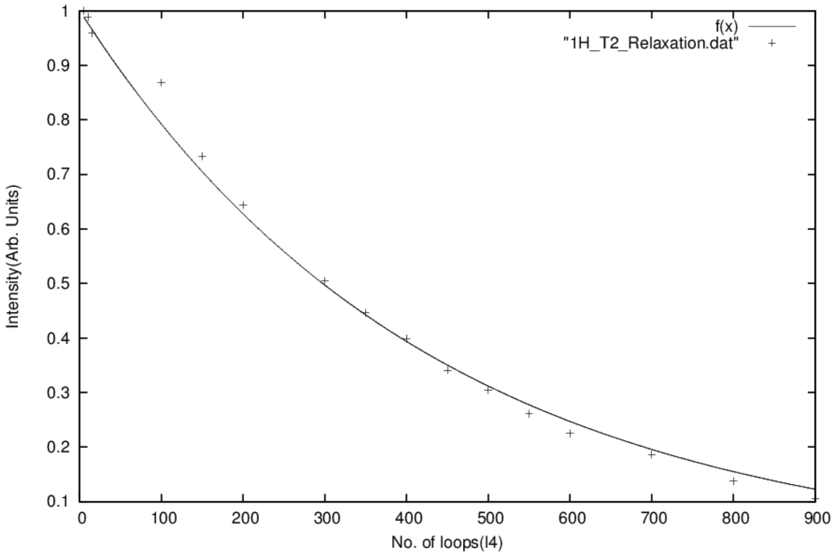


Figure 4.4: T_2 relaxation of 1_H Nucleus

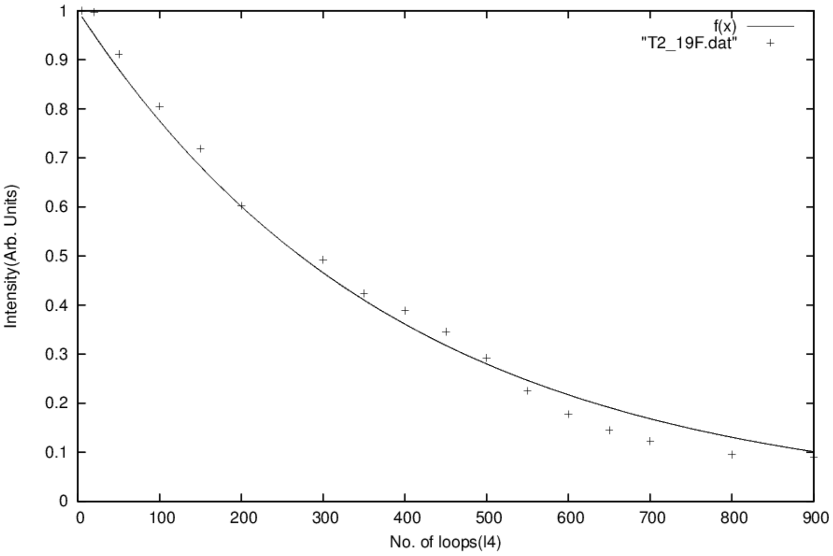


Figure 4.5: T_2 relaxation of 19_F Nucleus

Implementation of Iterative Phase Estimation Algorithm

The NMR pulse sequence to $C - U^{8^k}$ is given by following equantion and rotation along Z-axis are implemented by decomposing into X and Y-pulses similar as adiabatic state preparation

$$CU^{8^k} = e^{-i8^k\frac{\pi}{4}c_1\sigma_x^s}e^{i8^k\frac{\pi}{4}c_2\sigma_z^s}e^{i8^k\frac{\pi}{4}c_1\sigma_z^p\sigma_x^s}e^{-i8^k\frac{\pi}{4}c_2\sigma_z^p\sigma_z^s} \tag{4.7}$$

It can be further simplied using following equality into X- and Y-pulses.

$$e^{i8^k\frac{\pi}{4}c_1\sigma_z^p\sigma_x^s} = e^{-i\frac{\pi}{4}\sigma_x^s}e^{i8^k\frac{\pi}{4}c_1\sigma_z^p\sigma_z^s}e^{i\frac{\pi}{4}\sigma_x^s} \tag{4.8}$$

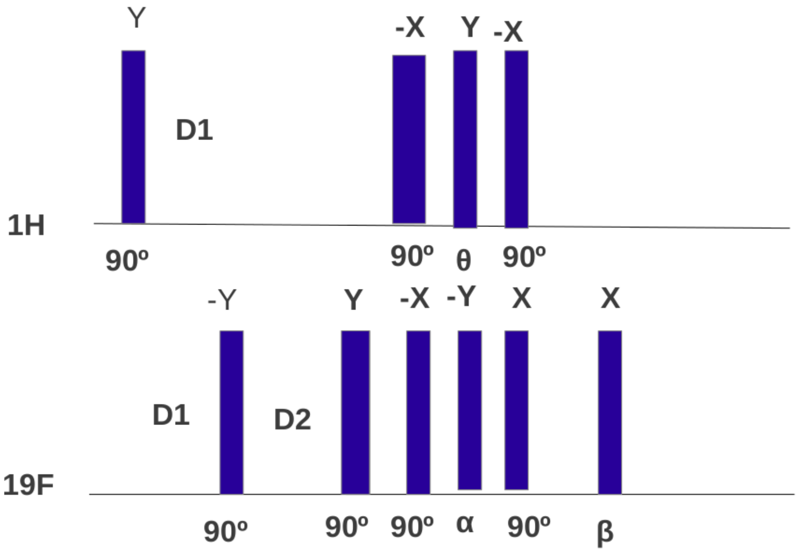


Figure 4.6: Pulse program to implement IPEA

In the pulse program shown above D1 and D2 are the delays according to equation 4.7 and values for feedback angle (θ), α and β are given as

$$\alpha = 8^k \frac{\pi c_2}{2}$$
$$\beta = 8^k \frac{\pi c_1}{2}$$
$$\theta_m = 2\pi(0.0\phi_k \phi_{k+1} \phi_{k+2} ... \phi_m)$$

The thermal state of 1_H detection is shown below

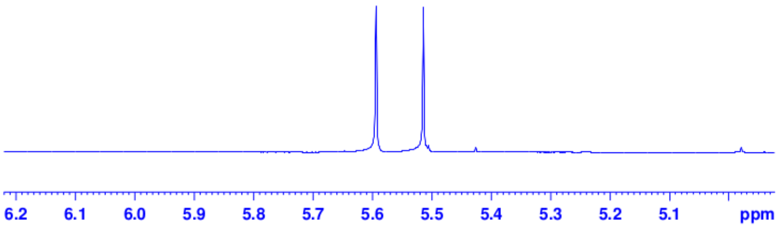


Figure 4.7: Thermal state of 1_H Nucleus

The pseudopure state when 1_H was in channel F_1

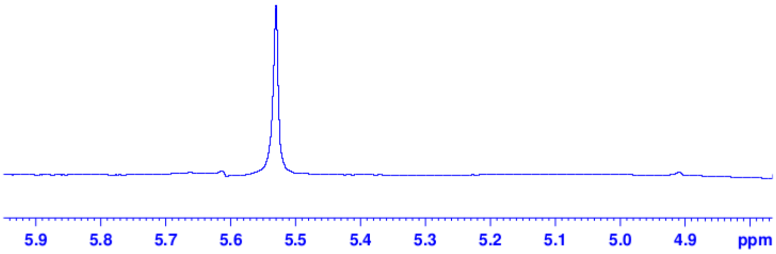


Figure 4.8: PPS of 1_H Nucleus

The acquired phase was measured by setting the phase just before IPEA as a reference. Thus, for the first iteration, k= 0 the obtained spectra is

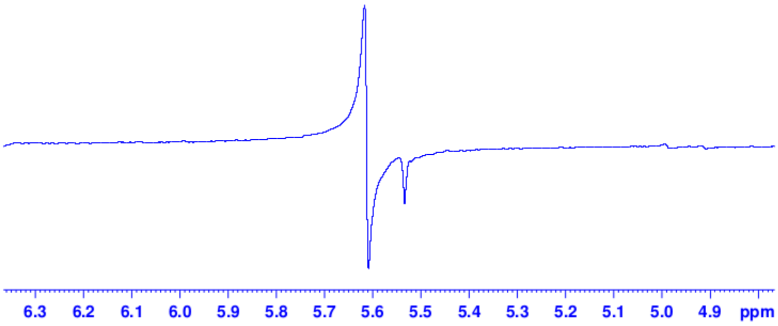


Figure 4.9: Obtained spectra after first iteration

Similarly, for the second iteration

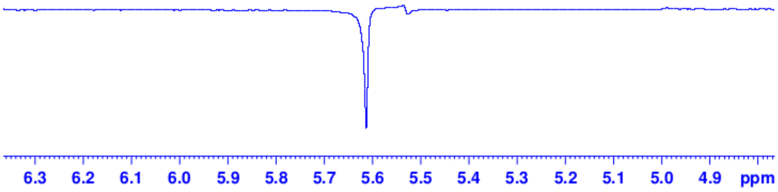


Figure 4.10: Obtained spectra after second iteration

Measured phase shifts are in the table below

Iteration	Phase Shift(deg.)	Binary Digits
1	72	0.00110011
2	178	0.01111110

For the evolution time t = $\frac{\pi}{2}$, ground state energy value can be obtained by putting the value into following equation

$$E = \frac{2\pi\phi}{t}$$

After two iterations the extracted phase is $(0.0011001101111110)_2$ corresponds to $(0.92)_{10}$ a.u energy eigen value for the ground state while the theoretical value after diagonalization of Hamiltonian matrix is 0.9310 a.u.

Chapter 5

Conclusions and future prospects

In this thesis, the quantum algorithms to simulate molecular Hamiltonians on quantum computer are reviewed. The first paper connecting quantum computation and quantum chemistry was published by Lidar and Wang [15] in which chemical dynamics is studied and an algorithm to calculate thermal rate is proposed. This work opened a new door in the field of computational chemistry. Further, Aspuru-Guzik *et al.* [6] reduced the number of qubits required in the Abrams and Lloyds algorithm [7] and calculated the molecular ground state energy. In case of heavy elements, it becomes necessary to include relativistic effects which makes quantum full configuration interaction more complicated and a detailed description is given in Libor *et. al* [10] where ground state as well as excited state energies are calculated for SbH molecule.

Recently, there have been few experimental realization in the same direction. Jiangfeng Du. *et al* [11] simulated H_2 molecule in minimal basis and calculated ground state energy on NMR quantum computer. This was followed by Deniz *et al* [16] where quantum simulation of 2p-π electronic Hamiltonian in molecular ethylene is done by using an NMR quantum computer. Simulation of H_2 molecule in minimal basis was also done on optical quantum computer by B. P. Lanyon *et al.* [18] .

In this work, simulation of SbH molecule in complete active space(2,2) was done on NMR quantum computer. The Hamiltonian matrix is obtained by using DIRAC code [22] in Kramer restricted approach while using cc-pVTZ basis set. The NMR implementation was done for ground state and it was prepared using adiabatic state preparation (ASP). In ASP, the Hamiltonian was varied through linear interpolation which is used in general to start the quantum computer. The next step was to implement iterative phase estimation algorithm(IPEA) in case of two qubits, 1_H and 19_F were used as probe and system qubits respectively. Two iterations of IPEA were implemented and the phase shift was directly measured while considering the phase before IPEA as reference in NMR phase sensitive spectra. The experimentally obtained results differ from the expected one in a very insignificant amount which is due to less iterations of IPEA which are yet to be performed. The success of ASP implies that there is gap between ground state and first excited state which is due to spin -orbit splitting and Hence, relativistic effects have impacts on energy spectrum. There are enough problems in quantum chemistry to be solved on quantum computer. For example, one can increase the size of complete active space and it would be very fascinating to implement full configuration interaction calculations on quantum computer which can not be done on a conventional computer due to requirement of exponential memory and operations. Thus, many interesting applications of quantum computer are just outside the window.

Appendix A

Matlab Codes

```
#Author: Rajveer
%%Code for adiabatic state preparation.
%%Define Hamiltonian Matrix :
T = 5.52;
M = 5;
T_sb = 7
M_sb = 10
Delta_sb = T_sb/(M_sb+1)

Delta = T/(M+1);



H11= -1.8310;
H22= -0.2537;
H12 = 0.1813;
H21 = H12;
J_HF = 52.65
%% Hamiltonian Matrix for H2 molecule.                                          %%%PLEAS
H_H2 = [-1.8310   0.1812; 0.1812  -0.2537];
H11_sb = -0.9035364;
H22_sb = -0.8761562;
H12_sb = 0.0388220;
H_sb = [H11_sb H12_sb; H12_sb H22_sb]
[V,D] = eig(H_sb)
Phi_sb_g =

[V,D] = eig(H_H2);
```

```
%Phi_g_H2 = -0.9932*s0 + 0.1127*s1; %% Ground state in S0 and S1 basis.
%E_g_H2 = Phi_g'*H_H2*Phi_g;
%% Ground State of Hydrogen Molecule. Done.
%%Define Angle Thetas for ASP and Calculate them for 7 Iterations.
%Theta_1 = zeros(7,1)

for m = 0 : M_sb
    s_m = m*T_sb/(M_sb+1)
   Th_1 = (pi/2 - Delta + 0.8187*Delta*s_m);
   Pulse_1 = 2*Th_1/pi;
   Th_sb_1 = (pi/2 - Delta_sb + s_m*Delta_sb*0.9612)
   Pulse_sb_1 = (2*Th_sb_1)/pi
   %if Th_1(Th_1 < 2*pi)
       %Th_1 = Th_1;
   %else
       %EffTh_1 = Th_1/(2*pi)
      % EffTh_1_rem = Th_1/(2*pi)-floor(Th_1/(2*pi))
   %end

   Th_2 = (pi*s_m*Delta/2);
   Pulse_2 = 2*Th_2/pi;
   Th_sb_2 = 0.0274*s_m*Delta_sb
   Pulse_sb_2 = (2*Th_sb_2)/pi
%    %if (Th_2 < 2*pi)
%        Th_2 = Th_2;
%    else
%        EffTh_2 = Th_2/(2*pi)
%        EffTh_2_rem= Th_2/(2*pi)-floor(Th_2/(2*pi))
%    end
   Th_3 = (pi/2 + Delta - 0.8187*s_m*Delta);
   Pulse_3 = 2*Th_3/pi;
   Th_sb_3 = (pi/2 + Delta_sb - 0.9612*s_m*Delta_sb)
   Pulse_sb_3 = (2*Th_sb_3)/pi
%    if(Th_3 < 2*pi)
%        Th_3 = Th_3
%    else
%        EffTh_3 = Th_3/(2*pi)
%        EffTh_3_rem = Th_3/(2*pi) - floor(Th_3/(2*pi))
%    end
```

```
end
save adiabaticangle.mat
------------------------------------------------------------------------------------
%Code for simulation of PPS with Alanine and pulse are implemented through GRAPE.
dx=[0 1
    1 0];
dy=[0 -i
    i 0];
dz=[1 0
    0 -1];
E2=eye(2,2);
E4=eye(4,4);
E8=eye(8,8);
E16=eye(16,16);
u = [1 0; 0 0;];
d = [0 0; 0 1;];
X90  = expm(-i*pi/4*dx);
Y90  = expm(-i*pi/4*dy);
ZZ = expm(-i*pi/4*kron(dz,dz));
%pini = kron(dz,E16);
pini = kron(dz, E4) + kron(E2,kron(E2,dz)) + kron(E4,dz);

for k=1:12
    ang = (k-1)*pi/3;           %X0000
    %ang = (k-1)*pi/3+pi/2;       %% for Y0000
    O = dx*cos(pi/2+ang)+dy*sin(pi/2+ang);
    R = expm(i*pi/4*O);
    R1 = kron(R,E4);
    R2 = kron(kron(E2,R),E2);
    R3 = kron(E4,R);
    ZZ12 = kron(ZZ,E2);
    ZZ23 = kron(E2,ZZ);
    U_en = R3*ZZ23*R2*ZZ12*R1;
%    U_enk(:,:,k) = U_en;
    p0=p0+(-1)^k*U_en*pini*U_en';
end
p0

%U1 = U_enk(:,:,1);  %% output for grape pulse
```

```
 U_de = kron(E2,kron(X90,E2))*ZZ12*kron(E2,kron(Y90,X90))*ZZ23*kron(E4,Y90);
 p = U_de*p0*U_de'
%p_th = kron(kron(kron(dx,kron(u,u)),u),u);         %pps X00
p_th = kron(dx,kron(u,u))        %pps Y000
ptra = trace(p)
 fid=trace(p*p_th)/sqrt(trace(p_th^2)*trace(p^2))

 %subplot(2,1,1)
 %bar3(imag(p))
 subplot(2,1,1);
 bar3(real(p))
 subplot(2,1,2);
 bar3(real(p_th))

 %%Code for Optimization of adiabatic state preparation.
clear;
clc;
close all;
%%Phase Estimation algorithm:
%% For H2 Simualation in paper:
%% Define the hamiltonian matrix:
s0 = [1;0;];
s1 = [0;1;];
%% Ground State of the Hamiltonian. \Sigma_(x)

Phio = 0.707*(s0 - s1);



dx=[0 1
    1 0];
dy=[0 -i
    i 0];
dz=[1 0
    0 -1];
E2=eye(2,2);
E4=eye(4,4);
E8 = eye(8,8);
```

```
HO = dx;
H11= -1.8310;
H22= -0.2537;
H12 = 0.1813;
H21 = H12;
J_HF = 52.65

H_H2 = [-1.8310   0.1812; 0.1812  -0.2537];
C2_H2 = (-1.8310+0.2537)*0.5
[V,D] = eig(H_H2)
%Phi_g_H2 = -0.9932*s0 + 0.1127*s1; %% Ground state in S0 and S1 basis. %%% out by JZ, Fe
Phi_g_H2 = V(:,1)                 %%% by JZ
%E_g_H2 = Phi_g'*H_H2*Phi_g;
%% Ground State of Hydrogen Molecule. Done.

%%Similarly for SbH molecule.

T_U_H = 1.941121725;
R = 2*H12/(H11-H22);
T_R = atan(R);
Th_ta = 3.14*0.5 +(T_R);
%%For SbH_Hamiltonian Matrix:
 H11_SbH = -0.9035364;
 H22_SbH = -0.8761562;
 H12_SbH = 0.0388220;
 H_sb = [H11_SbH H12_SbH; H12_SbH H22_SbH];

 %C2 = 0.5*(-0.9035364+0.8761562)

 T_SbH = pi/sqrt(4*H12_SbH*H12_SbH  + (H11_SbH - H22_SbH)*(H11_SbH-H22_SbH))


 T_H = pi/sqrt(4*H12*H12 + (H11 - H22)*(H11-H22))
 %% Ground state of H_sb hamiltonian :
 [V, D] = eig(H_sb)
 %Phi_g_sb = -0.8163*s0 + 0.5777*s1;
 Phi_g_sb = V(:,1)
 Rho_g_sb = Phi_g_sb*Phi_g_sb'
 Rho_exp = [0.5065 0.2346+i*0.0721; 0.2346 + i*0.0721 0.4935]
```

```
  Fid_SbH = sqrt((Phi_g_sb'*Rho_exp*Phi_g_sb))
  R_SbH = 2*H12_SbH/(H11_SbH -H22_SbH);
 T_R_SbH = atan(R_SbH);
 Th_ta_sb = 0.50*3.14 + T_R_SbH;


%%This is gamma defined in the pulse programme.
%%Beta -Bko
for k = 1:10
  B_T_H_0_eff(k) =  (-8^(k-1) * 0.5* T_U_H *(H11+H22))/(2*pi) - floor((-8^(k-1) * 0.5* T_U_

  B_T_H_0_eff(k) =  (-8^(k-1) * 0.5* T_U_H *(H11+H22))/(2*pi) - floor((-8^(k-1) * 0.5* T_U_

   end

 for k = 1:10
  A_T_H(k) =  (8^(k-1)*0.5*T_U_H*sqrt(4*H12*H12 + (H11-H22)*(H11-H22))) - floor((8^(k-1)*0.
%% Alpha defined in the paper.
   D_T_H(k) = A_T_H(k)/(3.14*J_HF);;
    end

%% Matrix is defined.
%Fid = zeros(40,40);
%F = []
%Uadtotal = zeros(10,10);
M = 10;
T = 7;
delta = T/(M+1);
s = 0:delta:T;
% for T = 1:1;
      Uadtotal= eye(2,2);
  l = length(s)

  H1 = (1-delta)*H0 + delta*H_sb
  H2 = (1-2*delta)*H0 + 2*delta*H_sb
  H3 = (1-3*delta)*H0 + 3*delta*H_sb
  U0 = expm(-i*delta*H0)
  U1 = expm(-i*H1*delta);
  U2 = expm(-i*H2*delta)
```

```
  U3 = expm(-i*H3*delta)

  U = U3*U2*U1*U0
  Ph2 = U0*U1*Phio

 for m = 1: length(s)
   Hm = (1-s(m))*H0 + s(m)*H_sb
    Uadtotal = expm(-i*delta*Hm)*Uadtotal
   Phiasp = Uadtotal*Phio
   Norm = Phiasp'*Phiasp
   Fid(m) = abs((Phi_g_sb'*Phiasp))^2
  % plot(Fid(m))
 end
save(Orig_JZ.mat)
```

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