Filipe do Vale Melo

Quantum Simulation of the Two-Site Hubbard Hamiltonian

Brasil 2020

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Dissertação apresentada ao Centro Brasileiro de Pesquisas Físicas, como requisito parcial para a obtenção do Grau de Mestre em Física.

Centro Brasileiro de Pesquisas Físicas

Supervisor: Roberto S. Sarthour

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"QUANTUM SIMULATION OF THE TWO-SITE HUBBARD HAMILTONIAN"

FILIPE DO VALE MELO

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"I think I can safely say that nobody understands quantum mechanics." Richard Feynman

Resumo

Na presente dissertação, apresentamos um estudo experimental sobre a simulação quântica do modelo de Hubbard. Implementando um sistema de Ressonância Magnética Nuclear (RMN) como um computador quântico de 2 qubits, realizamos a simulação quântica da dinâmica gerada pelo Hamiltoniano de Hubbard em uma rede de dois sítios ocupada por dois férmions. Variando-se parâmetros como a razão entre a interação coulombiana U e a energia cinética J_h (U/J_h) , foi possível observar mudanças no comportamento do sistema que demonstram que a simulação carrega a física do modelo de Hubbard, como a ocorrência de uma transição metal-isolante de Mott no limite em que $U >> J_h$. Os resultados experimentais foram comparados com as previsões teóricas, e concluímos que a simulação quântica do modelo de Hubbard foi muito bem sucedida. O problema é de grande relevância para as áreas de Computação Quântica e Física do Estado Sólido, e estabelece uma possível nova abordagem para tratar o modelo.

Palavras chave: Simulação Quântica, Modelo de Hubbard, RMN.

Abstract

In this dissertation, we present an experimental study on the quantum simulation of the Hubbard model. Implementing a Nuclear Magnetic Resonance (NMR) system as a 2-qubit quantum computer, we performed the quantum simulation of the dynamics generated by the Hubbard Hamiltonian in a two site lattice occupied by 2 fermions. By varying parameters such as the ratio between the Coulomb interaction U and the kinetic energy J_h (U/J_h) , it was possible to observe changes in the behavior of the system, showing that the simulation carries the physics of the Hubbard model, such as the occurrence of a metal-Mott insulator transition in the limit $U >> J_h$. The experimental results were compared with the theoretic predictions, and we concluded that the quantum simulation of the Hubbard model was successful. The problem is of great relevance to the areas of Quantum Computation and Solid State Physics, and establishes a possible new approach to treat the model.

Keywords: Quantum Simulation, Hubbard Model, NMR.

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1 Introduction

Solid State Physics is concerned with the properties of rigid matter. It has been successful in explaining and predicting phenomena that occur in many types of materials, with important applications in technology and industry. One of its greatest triumphs was the description of electrical conductivity. The first model, proposed by Paul Drude in 1900, tried to describe classically the transport properties of electrons in metals, supposing that they travel through the material bouncing off the ions, which are heavier and considered to be static. The Drude model was successful in explaining AC and DC conductivity, magnetoresistance and the Hall effect (1). But other properties could only be explained with a quantum treatment of the theory, which was proposed by Arnold Sommerfeld 28 years later, with the free electron model (2). Sommerfeld combined the Drude model with the Fermi-Dirac statistics (3), considering the electrons as free particles in a box of finite volume, a *fermion gas* where the ions play almost no role (1, 3). It was able to explain inconsistencies in the Drude model such as the shape of density of states and thermal properties like the temperature dependence of the specific heat of materials.

But although the Drude and Sommerfeld models provided good results on the properties of metals, they could not explain the differences between conductors, insulators and semiconductor materials. These properties can be understood when one considers how the electrons are arranged in a crystal. Their ranges of energies are organized into *energy bands*, separated by regions where no electron can be found, the *energy gaps*. These form the *electronic band structure* of the crystal. It behaves like a conductor when the bands are partly filled, so that the electrons can move to the higher energy levels when an electric field is applied. When the bands are completely full or empty, the electrons cannot move and the material is an insulator. Semiconductors occur when the lattice is slightly full or empty. The energy gaps are a consequence of the interaction of the electrons with the periodic potential generated by the lattice, which was not taken into account in Drude and Sommerfeld models. The study of this band structure of the crystals is known as the *band theory*, and has Felix Bloch as one of its pioneers, who found the solution for the Schrödinger equation in periodic potentials, known as Bloch theorem (4). Bloch said:

"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal [...]. By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation."

The effort of Bloch and others to understand band theory was very profitable to science, as it helped to understand not only how materials conduct electricity, but why

they do so. Many technological applications followed in the next years, semiconductor devices being one of the most important for modern society. But despite its success, band theory still could not explain the properties of some materials, that should, under the prediction of the theory, conduct electricity, but were insulators instead. Nowadays, such insulators are known as Mott insulators, and their properties are due to electron-electron interactions, which are not considered in band theory.

The first model which tried to explain the conductivity of materials taking electron correlations into account was the Hubbard model. It was proposed independently by Martin Gutzwiller (5), Junjiro Kanamori (6) and John Hubbard (7), all in 1963. The model simplifies the physics of many body quantum systems, as it discretizes the motion of the particles considering that the electrons can hop between the sites of a lattice, with kinetic energy given by $-J_h$. In its simplest form, only hopping between adjacent sites is allowed. An additional term was introduced: the interaction term U, which accounts for the Coulomb repulsion between electrons occupying the same site. With these assumptions, the Hubbard model was successful in explaining several situations of physical interest that the band theory failed to describe, being the description of the Mott insulator and its transition from a metal to an insulator one of the most prominent (8). Although originally imagined for electrons, it can be apllied to the study of fermions in general, even in the attractive case (9).

But even though the Hubbard model has became a paradigm in solid state physics, it has not been completely solved yet: only the one dimensional case has an exact solution. With the development of the cold-atom optical trapping technique in the early 2000s, experimental realizations of the Hubbard model have been achieved, the first one by Greiner *et al*, where a bosonic lattice showed a transition from a superfluid to a Mott insulator (10). A fermionic version, such as the original proposal of the model, was performed by Jördens *et al* (11).

Numerical studies of higher-dimensional cases of the Hubbard model have already been performed, but they are limited to a low number of sites in the lattice (12). Due to these difficulties, a good physical approach of the problem is to use quantum computers as simulators of the model, in a process known as *quantum simulation*. Although numerical simulations have always been important for areas of science such as chemistry, biology and physics, it is impossible to efficiently simulate quantum systems with large numbers of particles, since there are phenomena such as the superposition of states and the entanglement that are intrinsic to Quantum Mechanics. The first discussion about this problem was made 1982 by Richard Feynman, in his paper *Simulating Physics with Computers* (13). Feynman argued that a good simulator of a physical system would require a number of computer elements proportional to the space-time volume of that physical system. He wrote: "The rule of simulation that I would like to have is that the number of computer elements required to simulate a large physical system is only to be proportional to the space-time volume of the physical system. [...] If doubling the volume of space and time means I'll need an exponentially larger computer, I consider that against the rules."

The mathematical description of a quantum system occurs in Hilbert space, which grows exponentially with the number of particles (14). Therefore, to efficiently simulate a quantum system with a large number of particles using the Feynman rules, a classical computer would not be suited to the task, and it would be necessary to use another quantum system.

This idea gave rise to the area of Quantum Computation and Quantum Information, which studies how to store, process and use information contained in these types of systems. The smallest unit of storage is the quantum bit (qubit), which can be represented by any two-level quantum system, and may have the values zero, one or a superposition of both (15). Besides, two qubits can be linked through quantum entanglement. These properties brought a whole new paradigm for computation theory, and the idea of using a quantum computer as a simulator for quantum systems was discussed in the next years by several researchers like Lloyd (16) and Zalka (17).

In 1999, Somaroo *et al.* (18) managed to perform the first physical realization of a quantum simulation: the dynamics of a truncated quantum harmonic oscillator was simulated using a Nuclear Magnetic Resonance (NMR) system. NMR is a well known technique that has been developed for decades, which facilitates its implementation, using the nuclear spins of a given molecule as the qubits. Actually, one of the first papers reporting experimental implementations of operations on qubits (known as quantum gates), published by Chuang *et al.* in 1997 (19), used an NMR system.

Nuclear Magnetic Resonance was first observed by Isidor Rabi in 1938 (20), in an experiment in which a beam of hydrogen molecules was subjected to an inhomogoneous magnetic field and then to a homogeneous field, while radiofrequency (RF) radiation was applied. Rabi noticed that when the RF field had a frequency specific to the nuclei and was oscillating in a certain direction with respect to the homogeneous field, the resonance effect occurred. For this work, Rabi received the Nobel Prize of Physics in 1944. In 1946, two research groups working separately, leaded respectively by Edward Purcell and Felix Bloch (the same scientist from the band theory), improved the NMR technique by observing the phenomenon on solid and liquid states of matter (21). That was a remarkable discovery, as until that point atomic nuclei could only be observed in exotic states such as those found on particle beams. Bloch and Purcell shared a Nobel Prize of Physics in 1952 for their discovery.

It was in 1950 that Erwin Hahn proposed another method for the detection of nuclear spins, the *pulsed* NMR (22). In contrast to the technique developed by Bloch and Purcell, in which the sample is always subjected to the radiofrequency radiation (known as *continuous-wave* NMR), the pulsed NMR method consisted on the RF excitation being applied to the sample in short time periods, known as pulses. This allows one to rotate the nuclear magnetization (that is, the ensemble of nuclear spins in a sample) through well defined angles. This way, one can use a variety of pulse sequences to measure properties of a molecule or to compensate for the effects of field inhomogeneity during experiments.

The precise manipulation of the nuclear spins brought by the pulsed NMR method is essential for the use of NMR in quantum computation. It allows to apply arbitrary rotations on the qubits, which can be translated into quantum gates. Also, the coupling between nuclear spins on the same molecule enables the implementation of multi-qubit quantum gates, providing a universal set of quantum gates to NMR quantum computers (23).

In this dissertation, the proposal is to use a quantum computer to simulate the dynamics of the two site Hubbard model. The experimental quantum simulation was performed on a two-qubit quantum computer, from the well-established technique of NMR. By varying the magnitude of interactions between the fermions during evolution, some properties inherent to a system described by the Hubbard model could be observed, like the transition from a metal to a Mott insulating phase and the formation of charge-density-waves (24).

This dissertation is organized as follows: in Chapter 2, the fundamentals of the NMR technique will be exposed. In Chapter 3, basic concepts of Quantum Computation will be presented, together with its implementation on NMR systems. Chapter 4 treats the Hubbard model, introducing some of its concepts that were useful in the experiments. Finally, Chapter 5 gives the theoretical background of quantum simulations, details the experimental setup and presents the results obtained. The conclusions are given in Chapter 6.

2 Nuclear Magnetic Resonance

Resonance is a phenomenon which occurs whenever a physical system is excited periodically by an external perturbation whose frequency is close to that of the system, resulting in an increase in the amplitude of vibration. When a particle possessing magnetic moment is placed in a static magnetic field, and perturbed by an oscillating electromagnetic field with a certain frequency, the phenomenon of *magnetic resonance* can occur. Particularly, if this particle is the nucleus of an atom, this phenomenon is called *nuclear magnetic resonance* (NMR).

2.1 Nuclear Spin

The phenomenon of nuclear magnetic resonance occurs for nuclei that have non-zero total angular momentum, which is called *nuclear spin*. In NMR, it is represented by the angular momentum $\hbar \mathbf{I}$, being \hbar the Planck's constant divided by 2π . It has the same properties as any other angular momentum operator and is characterized by the eigenvalues and eigenvectors of its square modulus \mathbf{I}^2 and usually its z-component I_z :

$$\mathbf{I}^{2} | I, m \rangle = I(I+1) | I, m \rangle
I_{z} | I, m \rangle = m | I, m \rangle,$$
(2.1)

where $|I, m\rangle$ denotes the common eigenvectors of \mathbf{I}^2 and I_z , with m = -I, -I + 1, ..., I - 1, I. Other important spin operators in the magnetic resonance study are the raising and lowering operators (or ladder operators), which can be written in terms of the I_x and I_y components of \mathbf{I} as

$$I_{+} = I_{x} + iI_{y}$$

$$I_{-} = I_{x} - iI_{y},$$
(2.2)

and act in the $|I, m\rangle$ vectors as (14)

$$I_{+} |I, m\rangle = \sqrt{I(I+1) - m(m+1)} |I, m+1\rangle$$

$$I_{-} |I, m\rangle = \sqrt{I(I+1) - m(m-1)} |I, m-1\rangle.$$
(2.3)

In most usual NMR experiments, the energies involved are not sufficient to excite the nucleus to higher energy levels. Therefore, it is a good approximation to consider that the nucleus will always be in the ground state with I fixed, that is, in a state of well-defined total angular momentum. Then the quantum state is represented only by $|m\rangle$, and the energy is characterized by the quantum number m. The total angular momentum of a nucleus is given by the contribution of the angular momentum of all the *nucleons* (protons and neutrons). Nuclear physics provides some general rules to predict nuclear spin values (25). For example, nuclei with even number of nucleons have zero spin, while nuclei with odd numbers have non-zero spin, suggesting a compensation mechanism. These rules are sufficient to explain the nuclear spin value of commonly used nuclei in NMR, such as ¹H and ¹³C (both with I = 1/2).

The concept of spin is important in NMR as all nuclei with non-zero nuclear spin possess a magnetic dipole moment, given by (26)

$$\boldsymbol{\mu} = \gamma \hbar \mathbf{I} \tag{2.4}$$

where γ is the *gyromagnetic ratio* of the nucleus, and is characteristic of each nuclear species.

2.2 Static magnetic fields

Atomic nuclei with I = 1/2 interact with near electromagnetic fields through the nuclear magnetic dipole moment. This interaction is called Zeeman interaction (23), and gives rise to two distinct energy levels, associated with the orientation of the magnetic dipole with respect to the axis defined by the applied magnetic field. The absorption and emission of radiation due to transitions between these levels is what characterizes the magnetic resonance phenomenon. In this section, details about this magnetic interaction are going to be discussed, in both semiclassical and quantum approaches.

2.2.1 Semiclassical picture

When a magnetic dipole $\boldsymbol{\mu}$ is placed in an external magnetic field \mathbf{B}_0 , their interaction is described by a potential energy $U = -\boldsymbol{\mu} \cdot \mathbf{B}_0$, and the dipole experiences a torque $\boldsymbol{\tau}$ given by

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B}_{\mathbf{0}}.\tag{2.5}$$

As the torque in a rigid body is proportional to the time derivative of its angular momentum

$$\boldsymbol{\tau} = \frac{\mathrm{d}\mathbf{L}}{\mathrm{d}t} \tag{2.6}$$

(where $L = \hbar \mathbf{I}$) and the nuclear magnetic dipole is proportional to the nuclear spin via the gyromagnetic ratio (Equation (2.4)), then the motion equation for this system is given by

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \boldsymbol{\mu} \times (\gamma \mathbf{B}_0). \tag{2.7}$$

Equation 2.7 shows that the variation of the magnetic dipole must be always perpendicular to it and to the magnetic field. Therefore, the movement is a *precession* of

the dipole around the applied magnetic field. For a field $\mathbf{B}_0 = B_0 \hat{z}$, the solutions of (2.7) are

$$\mu_x = \mu_{xy}(0) \sin \omega_0 t$$

$$\mu_y = \mu_{xy}(0) \cos \omega_0 t$$

$$\mu_z = \mu_z(0),$$

(2.8)

where

$$\omega_0 = \gamma B_0 \tag{2.9}$$

is the *Larmor frequency* of the nuclear spin. The component parallel to \mathbf{B}_0 is constant, while the components in the *xy*-plane oscillate in time with frequency ω_0 . This precession movement is called *Larmor precession*, and is analogous to that of a spinning top under the action of a gravitational field, as shown in Figure 1.



Figure 1 – The movement of a magnetic moment in a magnetic field (right) is analogous to that of a spinning top in a gravitational field (left).

As the solutions of (2.7) denote a precession movement, it is more convenient to work in a rotating frame, with rotation frequency Ω . From classical mechanics, it is possible to rewrite the time derivative of a vector in terms of a coordinate system rotating with an arbitrary angular frequency Ω as (27)

$$\frac{\mathrm{d}\mathbf{F}}{\mathrm{d}t} = \frac{\delta\mathbf{F}}{\delta t} + \mathbf{\Omega} \times \mathbf{F} \tag{2.10}$$

where $\delta \mathbf{F}/\delta t$ denotes the time derivative of \mathbf{F} relative to the rotating frame.

So, the equation of motion (2.7) for μ can be written as

$$\boldsymbol{\mu} \times (\gamma \mathbf{B}_0) = \frac{\delta \boldsymbol{\mu}}{\delta t} + \boldsymbol{\Omega} \times \boldsymbol{\mu}$$
(2.11)

or

$$\frac{\delta \boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times (\gamma \mathbf{B}_0 + \boldsymbol{\Omega}) \tag{2.12}$$

Equation (2.12) shows that, in the rotating frame, the spin obeys the same motion law as in the laboratory frame, replacing the field \mathbf{B}_0 with an *effective field* \mathbf{B}_{eff}

$$\mathbf{B}_{\mathbf{eff}} = \mathbf{B}_{\mathbf{0}} + \frac{\mathbf{\Omega}}{\gamma} \tag{2.13}$$

For the static field $\mathbf{B}_0 = B_0 \hat{z}$, the solution for the motion of μ can be readily solved by choosing $\boldsymbol{\Omega}$ such that $\mathbf{B}_{\text{eff}} = 0$, that is, $\boldsymbol{\Omega} = -\gamma \mathbf{B}_0$. In this reference frame, which rotates with the Larmor frequency, $\delta \boldsymbol{\mu} / \delta t = 0$, and $\boldsymbol{\mu}$ remains fixed with respect to \hat{x} , \hat{y} and \hat{z} .

2.2.2 Quantum picture

The quantum mechanical description of a spin $\boldsymbol{\mu}$ in a static field $\mathbf{B}_{\mathbf{0}} = B_0 \hat{z}$ starts with the following interaction Hamiltonian:

$$\mathcal{H}_Z = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\mu_z B_0 = -\gamma \hbar B_0 I_z = -\hbar \omega_0 I_z$$
(2.14)

where the quantum operator I_z acts on the subspace spanned by $|m\rangle$, with m = -I, -I + 1, ..., I - 1, I. The Hamiltonian (2.14) is know as Zeeman Hamiltonian. Its eigenvalues are easy to calculate, as they are proportional to the eigenvalues -1 and 1 of the I_z operator:

$$E_m = -m\hbar\omega_0, \tag{2.15}$$

which indicates that a nucleus with spin I will have 2I + 1 energy levels, each one equally spaced by

$$\Delta E = E_{m+1} - E_m = -(m+1)\hbar\omega_0 - (-m\hbar\omega_0) = \hbar\omega_0.$$
(2.16)

Due to the minus symbol, the higher positive m represent the lower energy values, and the ground state corresponds to m = I, that is, when the spin is completely aligned with the direction of \mathbf{B}_{0} .

An example of the energy levels for the I = 3/2 case is shown in Figure 2.



Figure 2 – Energy levels for I = 3/2.

2.3 Time dependent magnetic field

The application of oscillating magnetic fields with the appropriate Larmor frequency may induce transitions between the energy levels (2.15), turning it possible to manipulate

the spin states. For static fields of the order of a few Tesla, the Larmor frequencies of most nuclear spins are of the order of MHz, and so the level transitions are possible with radiofrequency (RF) excitations.

The effect of these alternating magnetic fields can be overviewed from a semiclassical and a quantum picture, each one giving different insights about the phenomenon. They are going to be discussed in the next two sessions.

2.3.1 Semiclassical picture

The semiclassical picture is better understood by breaking the alternating field $\mathbf{B}_1(t)$ into two rotating components, both with the same amplitude $B_1 \ll B_0$, rotating with the same frequencies Ω around the z-axis, but in opposite directions:

$$\mathbf{B_1}(t) = \mathbf{B_1}^+(t) + \mathbf{B_1}^-(t)$$

$$\mathbf{B_1}^+(t) = B_1[\cos\left(\Omega t\right)\hat{x} + \sin\left(\Omega t\right)\hat{y}]$$

$$\mathbf{B_1}^-(t) = B_1[\cos\left(\Omega t\right)\hat{x} - \sin\left(\Omega t\right)\hat{y}].$$

(2.17)

For $\Omega = \omega_0$ (that is, on resonance), $\mathbf{B}_1^-(t)$ rotates in the same sense as the precession of the nuclear spin, whereas $\mathbf{B}_1^+(t)$ rotates in the opposite sense. In a reference frame that rotates with the Larmor frequency ω_0 , the nuclear spin and the field $\mathbf{B}_1^-(t)$ are stationary, while $\mathbf{B}_1^+(t)$ rotates with frequency $2\omega_0$. Therefore, as long as the amplitude B_1 of the RF field is small compared to B_0 , it is possible to neglect the action of $\mathbf{B}_1^+(t)$ and assume that only $\mathbf{B}_1^-(t)$ will have a considerable influence on the spin (26). In this case, $\mathbf{B}_1(t) = \mathbf{B}_1^-(t)$ and the motion equation in the laboratory frame (2.7) can be written as

$$\frac{\delta \boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times \gamma \left(\mathbf{B}_{\mathbf{0}} + \mathbf{B}_{\mathbf{1}}^{-}(t) \right)$$
(2.18)

In the rotating frame of frequency $\mathbf{\Omega} = -\Omega \hat{z}$, the RF field is time independent $(\mathbf{B}_{1}^{-}(t) = B_{1})$, and the equation of motion becomes

$$\frac{\delta \boldsymbol{\mu}}{\delta t} = \boldsymbol{\mu} \times \gamma \left(\mathbf{B}_{\mathbf{0}} + \mathbf{B}_{\mathbf{1}}^{-} + \frac{\boldsymbol{\Omega}}{\gamma} \right) = \boldsymbol{\mu} \times \left[\gamma \left(B_{0} - \frac{\boldsymbol{\Omega}}{\gamma} \right) \hat{z} + B_{1} \hat{x} \right]$$
(2.19)

with the effective field \mathbf{B}_{eff} given by

$$\mathbf{B}_{eff} = \left(B_0 - \frac{\Omega}{\gamma}\right)\hat{z} + B_1\hat{x},\tag{2.20}$$

whose vectorial representation is shown in Figure 3

Notice that when $\Omega = \omega_0 = \gamma B_0$, that is, when the resonance condition is fulfilled, the effective field is simply $B_1 \hat{x}$. Therefore, in the rotating frame, a magnetic moment initially parallel with $\mathbf{B_0}$ would experience a torque $\boldsymbol{\mu} \times \mathbf{B_1}$, precessing around the yz-plane, with frequency $\omega = \gamma B_1$. Eventually, it would become anti-parallel to $\mathbf{B_0}$. This suggests that if the field \mathbf{B}_1 is turned on for a certain time period t_p (that is, a pulse), the moment would precess through an angle $\theta = \gamma B_1 t_p$. Controlling the amplitude B_1 and the pulse time, it is possible to rotate the moment through well-defined angles. For example, if $\theta = \pi/2$, a magnetic moment initially along the z-direction will be rotated to the y-direction. After the RF field is turned off, it will lie in the xy-plane, fixed along the y-direction. In the laboratory frame, however, it will precess around the direction of the \mathbf{B}_0 field (z-direction) with the Larmor frequency $\omega_0 = \gamma B_0$.



Figure 3 – Effective field after the application of an RF pulse in the \hat{x} -direction.

2.3.2 Quantum picture

A quantum approach of the effect of magnetic fields in the nuclear spins starts with the definition of the Hamiltonian operator associated to the perpendicular magnetic field $\mathbf{B_1}(t)$, named *RF Hamiltonian*, which is obtained in a similar way as the Zeeman Hamiltonian:

$$\mathcal{H}_{RF} = -\boldsymbol{\mu} \cdot \mathbf{B}_{1}(t) = \gamma \hbar I_{x} [2B_{1} \cos\left(\Omega t\right)]$$
(2.21)

where $\mathbf{B}_1(t) = 2B_1 \cos{(\Omega t)}\hat{x}$. As stated in the previous session, $B_1 << B_0$, and therefore \mathcal{H}_{RF} can be treated as a perturbation to the Zeeman Hamiltonian. This way, the problem can be treated using time-dependent perturbation theory (28), which attests that, when the resonance condition is fulfilled ($\Omega \approx \omega_0$), the probability ratio of transitions between the eigenstates $|m\rangle$ and $|n\rangle$ of \mathcal{H}_z are given by the *Fermi golden rule*:

$$P_{m \to n} = P_{n \to m} \propto \gamma^2 \hbar^2 B_1^2 |\langle m | I_x | n \rangle |^2.$$

$$(2.22)$$

Equation (2.22) shows that the transition rate is proportional to the matrix element $\langle m | \mathcal{H}_{\mathcal{RF}} | n \rangle = \gamma \hbar B_1 \langle m | I_x | n \rangle$ of the perturbation \mathcal{H}_{RF} , therefore growing with the gyromagnetic factor and the magnitude B_1 of the applied field. This way, only RF fields perpendicular to B_0 could cause a transition, as parallel ones would cancel the matrix element between the states $|m\rangle$ and $|n\rangle$:

$$\langle m | I_z | n \rangle = \langle m | n | n \rangle = n \langle m | n \rangle = 0.$$
(2.23)

This happens because the eigenstates of observables (that is, quantum operators which represent measurable physical quantities) are orthogonal (14).

Not all transitions between any levels are available, though. A selection rule can be obtained from the properties of operators I_x and I_y . Following equation (2.2), writing the x-component of the spin operator as $I_x = (I_+ + I_-)/2$ and using the property of the ladder operators (2.3), the matrix element $\langle m | I_x | n \rangle$ is (remember that $|m\rangle \equiv |I,m\rangle$)

$$\langle m | I_x | n \rangle = \langle m | \frac{1}{2} (I_+ + I_-) | n \rangle = \frac{1}{2} (\langle I, m | I_+ | I, n \rangle + \langle I, m | I_- | I, n \rangle)$$

$$= \frac{1}{2} \Big(\langle I, m | \sqrt{I(I+1) - n(n+1)} | I, n+1 \rangle + \langle I, m | \sqrt{I(I+1) - n(n-1)} | I, n-1 \rangle \Big)$$

$$= \frac{1}{2} \Big(\sqrt{I(I+1) - n(n+1)} \langle I, m | I, n+1 \rangle + \sqrt{I(I+1) - n(n-1)} \langle I, m | I, n-1 \rangle \Big)$$

$$= \frac{1}{2} \Big(\sqrt{I(I+1) - n(n+1)} \delta_{m,n+1} + \sqrt{I(I+1) - n(n-1)} \delta_{m,n-1} \Big)$$

$$(2.24)$$

where the last statement is non-zero only if $m = n \pm 1$. So, only transitions between levels which obey the selection rule $\Delta m = \pm 1$ are allowed. This calculation is analogous for the I_y component.

2.4 Relaxation phenomenon

When working with real experiments, one does not deal with a single nuclear spin, but with an ensemble of identical nuclei. The number of particles (nuclei) that is found in the same energy levels will depend on the temperature of the system. The nuclear spins of these particles interact with each other and with the environment, returning the system to an equilibrium position after the perturbation by the RF fields, a phenomenon known as *relaxation*. This phenomenon is divided into two processes that occur simultaneously and (in general) independently: the *transverse relaxation* and the *longitudinal relaxation*. In this section, these processes are going to be discussed, and the *Bloch equations* will be presented.

2.4.1 Nuclear magnetization

It was stated in section 2.2.2 that a nucleus of spin I in a constant and uniform magnetic field \mathbf{B}_0 will have 2I + 1 equally spaced energy levels. When dealing with an ensemble of identical nuclei, the population of the energy levels is given by the Boltzmann distribution:

$$p_m \propto e^{-\frac{E_m}{k_b T}} \tag{2.25}$$

where p_m denotes the probability that the level is occupied, E_m is the energy of that state, T its temperature and k_b the Boltzmann constant (3). In a two-level system, like an ensemble of spins I = 1/2 with populations n_{-} (m = -1/2) and n_{+} (m = 1/2), the population ratio between the levels is given by the Boltzmann factor, which in thermal equilibrium is written as:

$$\frac{n_{-}}{n_{+}} = e^{-\frac{\hbar\omega}{k_{b}T}}.$$
(2.26)

As this exponential is less than 1, the ratio (2.26) shows that more spins will be aligned in the same direction of the field (ground state) than against it (excited state). Therefore, a net *magnetization* will arise along the direction of the field \mathbf{B}_0 . The magnetization can be defined as the density of magnetic moments:

$$\mathbf{M} = \frac{1}{V} \sum_{k} \boldsymbol{\mu}_{k} \tag{2.27}$$

For protons in a field of 5 T at room temperature, the Boltzmann factor between the populations n_{-} and n_{+} is of the order of 10^{-5} . Therefore, in most NMR experiments the magnetization is very low, showing that this technique requires very sensitive detection instruments.

2.4.2 Transverse relaxation

In section 2.3.1, it was shown that an RF pulse along a direction perpendicular to a nuclear spin causes it to precess around the direction of that pulse (in the rotating frame). The same is true for the magnetization. After a $\pi/2$ pulse, for example, the magnetization, initially along the z-direction, is rotated and now lies in the xy-plane (the transverse plane), and precesses in the laboratory frame around \mathbf{B}_0 with the Larmor frequency. This is a non-equilibrium situation, as the magnetization is not in the same direction as the field \mathbf{B}_{0} . Ideally, in the case where the spins are completely isolated and do not interact with each other and the environment, this state would persist forever, and the magnetization would continuously precess around \mathbf{B}_0 . However, this is not the case: the nuclear spins do interact with one another, which results in each spin having a different magnetic neighborhood. As stated in section 2.2.1, the Larmor frequency of a spin depends on the external field \mathbf{B}_0 , and in the case of an ensemble of spins, also on the fields generated by the neighboring magnetic moments. Therefore, each spin will have slightly different Larmor frequencies, which will cause a dephasing in their precession, leading eventually to a completely random distribution of the magnetization on the transverse plane, resulting in zero magnetization on that plane. This process is known as transverse relaxation (23), or spin-spin relaxation, as it is due to the spin-spin interactions inside the system. The different mechanisms that cause the transverse relaxation are going to be explained in section 2.5.4.

This decaying of the nuclear magnetization can be described phenomenologically, in the rotating frame, by a differential equation of the form

$$\frac{\mathrm{d}M_{xy}}{\mathrm{d}t} = -\frac{M_{xy}}{T_2} \tag{2.28}$$

where T_2 is a time parameter known as *transverse relaxation time*. The solution of this equation is given by

$$M_{xy} = M_0 e^{-t/T_2} \tag{2.29}$$

where M_0 is the initial magnetization value after application of the RF pulse. Notice that $t = T_2$ gives the time instant when $M = 0.37 \times M_0$, that is, the magnetization has lost around 63% of its value. A plot of equation (2.29) is shown in Figure 4, for the ¹H nuclear spin.



Figure 4 – Plot of M_{xy} components of magnetization versus time, for $T_2 = 0.62$ s.

2.4.3 Longitudinal relaxation

As the transverse magnetization decays, the magnetization along the direction of \mathbf{B}_0 tends to be recovered, as the system returns to the equilibrium state. This is a process distinct from the transverse relaxation and happens due to transitions between energy levels to reestablish the equilibrium. In a spin I = 1/2 system, for example, a $\pi/2$ pulse would cause the populations to be distributed equally in both levels m = 1/2 and m = -1/2, and a π pulse would cause the initial population in the ground state to be reversed to the excited level, as shown in Figure 5. The return of the populations to the ground state is the reason for the recovery of the magnetization in the z-direction, in a process known as *longitudinal relaxation*. This process is caused by the interaction of the spins with the environment (or the lattice), and therefore is named *spin-lattice relaxation*.

The longitudinal relaxation can also be described by a phenomenological differential equation in the rotating frame:

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = \frac{M_0 - M_z}{T_1} \tag{2.30}$$



Figure 5 – Effect of RF pulses on the populations of an I = 1/2 system. Ideally, after a $\pi/2$ pulse the populations are equally distributed in each energy level. After a π pulse, the initial population is reversed.

which has the solution

$$M_z(t) = M_0 \left(1 - e^{-t/T_1} \right) \tag{2.31}$$

where T_1 is the *longitudinal relaxation time*, the time instant when the M_z has recovered around 63% of its value. A plot of equation (2.31) is shown in Figure 6 for the ¹H nuclear spin.



Figure 6 – Plot of M_z component of magnetization versus time for $T_1 = 7$ s.

The whole process of relaxation is depicted in Figure 7.

2.4.4 Bloch equations

The behavior of relaxation as shown in Equations (2.28) and (2.30) was proposed phenomenologically by Felix Bloch in 1946 (29), and are known as *Bloch equations*. They give the magnetization dynamics in the rotating frame. In the laboratory frame, they are


Figure 7 – Relaxation process, in a frame that rotates with the Larmor frequency of the nucleus. (a) The magnetization, initially at M_0 , is rotated to the y-axis after an RF pulse and begins to rotate with the Larmor frequency ω_0 in the xy-plane. (b) to (d) Time evolution of the transverse and longitudinal magnetization. Notice that in (d) the M_z component is not equal to M_0 yet, as $T_1 > T_2$, and so the process is finally concluded in (e).

written as

$$\frac{dM_x}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_x - \frac{M_x}{T_2}
\frac{dM_y}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_y - \frac{M_y}{T_2}
\frac{dM_z}{dt} = \gamma (\mathbf{M} \times \mathbf{B})_z - \frac{M_z - M_0}{T_1}.$$
(2.32)

The values of T_1 and T_2 are intrinsic to each particular system and depend on the physical state of matter (solid or liquid), temperature, molecular mobility, etc (26). Generally, $T_1 \ge T_2$, with the equality occurring in some liquids. Experimentally, T_1 is used to decide how long to wait until the relaxation is complete and a new experiment can be performed, typically in a period of $t > 10 \times T_1$. From T_2 the period during which it is possible to perform operations in a quantum state without losing coherence is obtained. If an experiment time is near T_2 , the relaxation effects must be taken into account. Therefore, a good characterization of T_1 and T_2 values is an essential preliminary step in an NMR experiment.

2.5 Free Induction Decay and spectrum

The precession of the magnetization in the xy-plane after the application of an RF pulse suggests a method for observing nuclear magnetic resonance. Oscillating magnetic moments produce oscillating magnetic fields, which are associated with an electric field through the Faraday's Induction Law

$$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},\tag{2.33}$$

that generates an oscillating electromotive force (emf) in a coil placed next to the sample, transverse to the precession plane. In this section, this technique and the NMR spectrum are going to be discussed.

2.5.1 Free Induction Decay

As stated in section 2.4, relaxation processes are responsible for a decay in the xy components of the magnetization (M_{xy}) , that is, the transverse relaxation. Therefore, the signal coming from the sample is an oscillation with decaying amplitude (Figure 8). It is referred to as *free induction decay* (FID), as it is detected in the absence of the RF field.



Figure 8 – Free induction decay, as observed from the laboratory frame.

The NMR FID signal has the form (21)

$$s(t) = A e^{-\lambda t} e^{i\omega t} \tag{2.34}$$

where A is the amplitude and $\lambda = 1/T_2$ is the damping factor due to relaxation. The amplitude A is usually a complex quantity given by

$$A = |A|e^{i\phi} \tag{2.35}$$

where |A| is the signal intensity, and ϕ is the signal phase.

2.5.2 Fourier transform

The FID signal is detected on the time domain, but the useful information is about the frequencies of the magnetization precession. A mathematical operation capable of transforming a time signal in a frequency signal (and vice-versa) is the *Fourier transform*.

The Fourier transform of a function f(t) defined on the time domain is given by (30)

$$F(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt.$$
 (2.36)

In short, this operation decomposes a signal in its constituent frequencies. For example, a signal with a sampling frequency of 1 kHz and a duration of 1 second, composed of a 50 Hz sinusoid wave of amplitude 0.7 and a 120 Hz sinusoid wave of amplitude 1, can be Fourier transformed to show each frequency component, as shown in Figure 9.



Figure 9 – Fourier transform of a signal $S(t) = 0.7 \sin(2\pi \times 50t) + \sin(2\pi \times 120t)$.

2.5.3 NMR spectrum

NMR experiments deal with the Larmor frequencies of different nuclei, thus a technique such as the Fourier transform is quite useful. The FID signal observed is commonly Fourier transformed, generating what is called the *NMR spectrum*.

Equation (2.34) reffers to a spectrum with just one peak. In most cases, more peaks are present in the spectrum, and a more general representation is

$$s(t) = \sum_{p} A_{p} e^{-\lambda_{p} t} e^{i\omega_{p} t}$$
(2.37)

which describes a superposition of different signals $s_n(t)$, with each component having a particular amplitude A_p , frequency ω_p and damping factor λ_p .

The Fourier transform of the FID signal (for one component) is a *complex Lorentzian* (21)

$$\mathcal{L}(\omega;\lambda_p,\omega_n) = \frac{1}{\lambda_p + i(\omega - \omega_p)}$$
(2.38)

where ω is the argument of the function, λ_p and ω_p are the peakwidth and center frequency of the peak, respectively. The complete spectrum is a superposition of Lorentzian spectral components

$$S_n(\omega) = \sum_p A_p \mathcal{L}(\omega; \lambda_p, \omega_n).$$
(2.39)

The real part of the Lorentzian is called the *absorption Lorentzian*

$$\mathcal{A}(\omega;\lambda_p,\omega_n) = Re\{\mathcal{L}(\omega;\lambda_p,\omega_n)\} = \frac{\lambda_p}{\lambda_p^2 + (\omega - \omega_p)^2}.$$
(2.40)

The imaginary part is the dispersion Lorentzian

$$\mathcal{D}(\omega;\lambda_p,\omega_n) = Im\{\mathcal{L}(\omega;\lambda_p,\omega_n)\} = -\frac{\omega - \omega_p}{\lambda_p^2 + (\omega - \omega_p)^2}.$$
(2.41)

Equations (2.38), (2.40) and (2.41) are related by

$$\mathcal{L} = \mathcal{A} + i\mathcal{D} \tag{2.42}$$

and they are shown in Figure 10.



Figure 10 – Absorption and dispersion Lorentzians.

2.5.4 Spin echoes and T_2^*

In 1950, Erwin Hahn discovered a pulse sequence that could reverse the effect of the transverse relaxation, recovering part of the NMR signal even after it had been extinguished. This effect was named *spin echo* (22), and was used by Hahn to measure relaxation times of several molecules. The sequence proposed by Hahn was improved by Carr and Purcell in the next years (31), and nowadays it is widely used to study diffusion effects in liquid samples and to perform relaxation time measurements.

The sequence proposed by Carr and Purcell is as follows: first, a $\pi/2$ pulse along the y-direction is applied, placing the initial magnetization $\mathbf{M}_0 = M_0 \hat{z}$ along the x-axis. Then, as explained in section 2.4.2, each spin will precess at slightly different Larmor frequencies, causing the magnetization to lose coherence on the xy-plane. This means that, in the rotating frame, the spins will rotate away from the x-axis with different velocities. After a time interval τ , a pulse of π along the y-direction is applied, causing the magnetization to rotate around the y-axis. Now, the groups of spins that were moving away from the x-axis will rotate towards the negative x-axis, regrouping there after a time interval τ and recovering the NMR signal.

However, the spin echo cannot revert all the effects of transverse relaxation, as the amplitude of the magnetization measured after the spin echo sequence is smaller than the initial value M_0 , denoting that even though the signal was recovered, part of it was lost. Therefore, the transverse relaxation occurs due to two different effects: those that are caused by macroscopic inhomogeneities of the magnetic fields, which can be refocalized after a spin echo sequence; and those that are caused by fluctuations in the microscopic magnetic fields, and which cannot be refocalized (21). Hahn designated a constant known as T_2^* for the characteristic time of the second effect.

2.6 Nuclear spin interactions

The interactions in NMR are classified as external, due to the magnetic fields applied on the nuclear spins, and internal, due to magnetic and electrical fields generated inside the molecule.

From the NMR spectrum it is possible to obtain the values of the internal interactions between the spins. Therefore, NMR technique can be used in many interesting applications, such as analysis of chemical structures and implementation of logical gates in quantum computation experiments (23), a very important part of this work that will be described later.

The internal and external interactions are both described by the *nuclear spin* Hamiltonian $\mathcal{H}_{nuclear}$, which can be written in the basis $\{|m\rangle\}$ of the eigenstates of the Zeeman Hamiltonian $\mathcal{H}_{\mathcal{Z}}$. $\mathcal{H}_{nuclear}$ is then

$$\mathcal{H}_{nuclear} = \mathcal{H}_{ext} + \mathcal{H}_{int} \tag{2.43}$$

where \mathcal{H}_{ext} and \mathcal{H}_{int} represent the external and internal interactions, respectively. As discussed in sections 2.2.2 and 2.3.2, \mathcal{H}_{ext} is given by

$$\mathcal{H}_{ext} = \mathcal{H}_Z + \mathcal{H}_{RF}.$$
 (2.44)

The internal Hamiltonian has several contributions. In the case of liquids, these contributions come from the *chemical-shift* (\mathcal{H}_{CS}), the *dipolar coupling* (\mathcal{H}_D), the *scalar coupling*, also known as *J-coupling* (\mathcal{H}_J) and the quadrupolar coupling (\mathcal{H}_Q) for a nucleus with spin I > 1/2. In the general case, this leads to:

$$\mathcal{H}_{int} = \mathcal{H}_{CS} + \mathcal{H}_D + \mathcal{H}_J + \mathcal{H}_Q. \tag{2.45}$$

The first three terms will be presented after a brief discussion about the *secular approxi*mation. In this work, only nuclei with spins I = 1/2 were used, therefore the quadrupolar term did not play any role and will not be discussed.

2.6.1 Secular approximation

The secular approximation concerns the case where the Hamiltonian is composed of a *strong* and a *weak* term:

$$\mathcal{H} = \mathcal{H}_{strong} + \mathcal{H}_{weak} \tag{2.46}$$

Suppose that \mathcal{H} has a set $\{E_n\}$ of eigenvalues, which can be degenerate or nondegenerate. If \mathcal{H}_{strong} does not commute with \mathcal{H}_{weak} , then the matrix of \mathcal{H}_{weak} may have non-zero elements anywhere when written in the basis where \mathcal{H}_{strong} is diagonal. The secular approximation consists of writing \mathcal{H}_{weak} as a block-diagonal matrix.

Without the secular approximation, \mathcal{H}_{weak} can be written as

$$\mathcal{H}_{weak} = \sum_{n} r_{nn} \left| n \right\rangle \left\langle n \right| + \sum_{n \neq m} r_{mn} \left| m \right\rangle \left\langle n \right|, \qquad (2.47)$$

in the basis of eigenstates $\{|n\rangle\}$ of \mathcal{H}_{strong} (14), with eigenvalues g_n . The matrix elements r_{mn} of \mathcal{H}_{weak} are given by $\langle m | \mathcal{H}_{weak} | n \rangle$. With the secular approximation, the terms r_{mn} that obey the condition

$$|r_{mn}| << |g_m - g_n| \tag{2.48}$$

can be considered zero. This way, only when the eigenvalues of \mathcal{H}_{strong} are degenerate or almost degenerate, the matrix elements r_{mn} of \mathcal{H}_{weak} are non-zero, implying that the matrix representation of \mathcal{H}_{weak} will acquire a block-diagonal structure.

2.6.2 Chemical shift

The magnetic field experienced by the nuclei is not equal to the external field, due to the electronic cloud surrounding each nucleus. The chemical shift is a process that changes the local magnetic field and occurs in two steps: first, the external field causes disturbances in the orbital motions of the electrons surrounding the nucleus. Second, the disturbed motion of the electrons induces magnetic fields that lead to a *local* magnetic field:

$$\mathbf{B}_{\mathbf{loc}} = \mathbf{B}_{\mathbf{0}} - \tilde{\sigma} \mathbf{B}_{\mathbf{0}} = (1 - \tilde{\sigma}) \mathbf{B}_{\mathbf{0}}$$
(2.49)

where $\tilde{\sigma}$ is the *chemical shielding tensor* (21), associated with the nuclear position where \mathbf{B}_{loc} is being evaluated. As a tensor, $\tilde{\sigma}$ implies that the direction of \mathbf{B}_{loc} is in general different from that of \mathbf{B}_0 , which reflects the anisotropy of the molecular environment of the considered nucleus. The Hamiltonian \mathcal{H}_{CS} of the chemical shift is given by

$$\mathcal{H}_{CS} = -\mu \cdot (-\tilde{\sigma} \mathbf{B}_0) \approx \gamma \hbar \sigma_{zz} B_0 I_z, \qquad (2.50)$$

where the secular approximation was used in the last step, as the magnitude of the interaction between the nuclear spins and \mathbf{B}_0 is much greater than that of the nuclear spins and the field generated by the chemical shift. The term σ_{zz} depends on the orientation of the electron clouds with respect to the external field. For isotropic liquids, the average of all possible molecular orientations leads to the *isotropical chemical shift* (σ_{iso}) (26):

$$\mathcal{H}_{CS} = \gamma \hbar \sigma_{iso} B_0 I_z; \tag{2.51}$$

The parameter σ_{iso} is an average of the orientation of the electron clouds, calculated over all molecules, and related to the trace of the tensor σ in a reference frame known as *principal axis system* (21):

$$\sigma_{iso} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3}.$$
(2.52)

Therefore, the effect of the chemical shift is to cause a deviation of the Larmor frequency of each nucleus, which depends on its chemical environment

$$\omega = \omega_L (1 - \sigma_{iso}) \tag{2.53}$$

In homonuclear molecules, this can be used to identify each nucleus of a same element with different chemical environments.

2.6.3 Dipolar coupling

Magnetic dipoles generate their own magnetic fields. From electromagnetic theory, they can be written as

$$\mathbf{B}_{\mathbf{dip}} = \frac{\mu_0}{4\pi} \frac{3(\boldsymbol{\mu} \cdot \mathbf{e})\mathbf{e} - \boldsymbol{\mu}}{r^3},\tag{2.54}$$

where $\boldsymbol{\mu}$ is the magnetic dipole moment, r and \mathbf{e} are, respectively, the magnitude of the vector \mathbf{r} and the unit vector along its direction, and μ_0 is the magnetic permeability of free space.

If this field is generated by a dipole μ_2 (denoted by $\mathbf{B}_{dip}^{(2)}$, another dipole μ_1 will interact with it through Zeeman interaction: $\mu_1 \cdot \mathbf{B}_{dip}^{(2)}$. The Hamiltonian describing the interaction between two dipoles is

$$\mathcal{H}_{dip} = \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r_{12}^3} [\mathbf{I_1} \cdot \mathbf{I_2} - 3(\mathbf{I_1} \cdot \mathbf{e_{12}})(\mathbf{I_2} \cdot \mathbf{e_{12}})], \qquad (2.55)$$

where $\mathbf{e_{12}}$ is the unit vector which points from $\boldsymbol{\mu}_1$ to $\boldsymbol{\mu}_2$. Expression (2.55) can be rewritten for the heteronuclear case ($\gamma_1 \neq \gamma_2$) using the secular approximation (21):

$$\mathcal{H}_{dip} = -\frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar^2}{r_{12}^3} I_{1z} I_{2z} (3\cos^2\theta_{12} - 1), \qquad (2.56)$$

where θ_{12} is the angle between the vector $\mathbf{e_{12}}$ and the external magnetic field $\mathbf{B_0}$.

In the case of an isotropic liquid, the Hamiltonian (2.56) has no contribution, as the term $3\cos^2\theta_{12} - 1$ averages to zero, due to the direct dipolar interaction for the NMR spectrum (23).

2.6.4 Scalar coupling

The scalar coupling (also called *indirect* or *J*-coupling) is the other relevant interaction between the nuclear magnetic dipole moments of neighbour nuclei. In this case, however, the interaction is mediated by the electrons responsible for the chemical bonds connecting the atoms.

In general, the Hamiltonian describing the scalar coupling is given by

$$\mathcal{H}_J = 2\pi\hbar\mathbf{I}_1\cdot\hat{J}\cdot\mathbf{I}_2 \tag{2.57}$$

where \tilde{J} is a tensor which has non-vanishing trace. In isotropic liquids, it can be simplified due to the symmetry and the motion of the molecules of the sample as

$$J = \frac{J_{xx} + J_{yy} + J_{zz}}{3}$$
(2.58)

which leads to the simplified form, due to the secular approximation

$$\mathcal{H}_J = 2\pi\hbar J I_{1z} I_{2z}.\tag{2.59}$$

The secular approximation can be used when $|\pi J_{nk}| \ll |\omega_n - \omega_k|$, where ω_n and ω_k are the Larmor frequencies of the two coupled nucleus. In this work, the molecules used during experiments obey this condition and therefore the form of \mathcal{H}_J in equation (2.59) could be adopted.

The scalar coupling creates a split in the lines of an NMR spectrum. For two distinct nuclear spins 1/2, for example, the lines of each nuclei are split into two other lines, separated by an interval equal to J (in frequency units). In the chloroform molecule used in the experiments of this work, the scalar coupling is J = 215 Hz.

2.6.5 Two coupled spin-1/2

Taking into consideration all the themes discussed in the sections above, the Hamiltonian for a molecule containing two spin-1/2 coupled through scalar coupling is given by

$$\mathcal{H} = -\hbar\omega_1 I_z \otimes \mathbb{1} - \hbar\omega_2 \mathbb{1} \otimes I_z + 2\pi\hbar J_{12} I_z \otimes I_z.$$
(2.60)

The eigenstates of (2.60) are denoted by $|m_1, m_2\rangle$, where $m_1 = \pm 1$ and $m_2 = \pm 1$, which are the orientations of the first and second spins, respectively, with respect to the field $\mathbf{B}_0 = B_0 \hat{z}$. The energy levels of this system are then

$$|+1/2, +1/2\rangle : E_{++} = \hbar \left(-\frac{\omega_1}{2} - \frac{\omega_2}{2} + \frac{\pi J_{12}}{2} \right)$$

$$|+1/2, +1/2\rangle : E_{+-} = \hbar \left(-\frac{\omega_1}{2} + \frac{\omega_2}{2} - \frac{\pi J_{12}}{2} \right)$$

$$|+1/2, +1/2\rangle : E_{-+} = \hbar \left(\frac{\omega_1}{2} - \frac{\omega_2}{2} - \frac{\pi J_{12}}{2} \right)$$

$$|+1/2, +1/2\rangle : E_{--} = \hbar \left(\frac{\omega_1}{2} + \frac{\omega_2}{2} + \frac{\pi J_{12}}{2} \right)$$

(2.61)

If J_{12} is positive and $\omega_1 > \omega_2$, these energies are crescent from the top to the bottom, and the transitions are allowed by the selection rule $\Delta m_{1,2} = \pm 1$. Therefore, four transitions are possible and the NMR spectrum will have four peaks, in the positions $\omega_1 \pm \pi J_{12}$ and $\omega_2 \pm \pi J_{12}$ (Figure 11).



Figure 11 – The full spectrum of a molecule with two J-coupled spins 1/2. Due to the coupling, the lines of each spin are split into two, which are separated by a distance equal to $2\pi J_{12}$ and centered at the Larmor frequency of each nucleus.

2.7 Experimental setup

Experiments involving NMR require sophisticated equipment. The NMR signal, as stated in section 2.4.1, is very weak, and the Larmor frequencies must be measured with high accuracy, of at least 1 part in 10^9 (21).

In this section, the experimental aspects of the NMR technique, which is performed in an NMR spectrometer, will be discussed. This kind of device generally is composed of a magnet to generate the \mathbf{B}_0 field, a probe where the sample will be placed, and a system of coils that applies radiofrequency excitations on the system, also receiving the signal generated by the nuclear magnetization precessing around the main field (Figure 12). In modern spectrometers, this apparatus is controlled by a computer interface that allows the automatic recording and processing of the data.

2.7.1 Magnet

As discussed in section 2.2, for the NMR phenomenon to occur a static and *homogeneous* (i.e independent of position) magnetic field is required. This field is responsible for the high resolution required in the experiments in this work.

In almost every NMR spectrometer this field is generated by a *superconducting* magnet. Superconductors are materials capable of maintaining a current with zero resistance (4). Once charged, the current would run indefinitely, thus a superconducting magnet should sustain a static magnetic field for a long time.

To achieve the superconductivity, the magnet is placed in a cryostat composed of liquid He around the temperature of 4 K (the boiling point of He is 4.18 K), a vacuum layer and a large reservoir of liquid N_2 around 77 K. Both reservoirs are separated from the environment by evacuated barriers in order to avoid thermal leakage.

The NMR spectrometer used in the present work was a Varian 500 MHz, with a field of 11.7 T.

2.7.2 Probe

Through the center of the superconducting coil, there is a cylindrical hole called *bore*. Inside it goes the *probe*, a cylindrical device where the sample is allocated after being introduced inside the bore. The probe is a complex piece of apparatus that in general has the following functions:

- 1. It places the sample in the region of the homogeneous magnetic field;
- 2. It has an RF system composed of coils that irradiate the sample with RF pulses, and subsequently detect the RF emissions from the resultant magnetization in the

plane perpendicular to \mathbf{B}_{0} ;

- 3. It usually has some device to stabilize the sample temperature (notice that, during an experiment, the sample is not at the same temperature as the superconducting magnet);
- 4. In some cases, it may have a device to spin the sample, in order to reduce the width of NMR peaks.



Figure 12 – Schematic picture of an NMR spectrometer. The liquid He and liquid N_2 are separated by a vacuum layer. The probe is inserted through the bottom of the bore.

The probe is the only part of the NMR spectrometer that is changed depending on the experiment to be done. Solid-state NMR and liquid-state NMR demand different probes, for example. In the experiments developed during this work, only probes for liquid-state NMR were used.

The liquid sample is placed inside the probe in a tube made of a special type of glass, which is insensitive to magnetic fields and therefore does not disturb the signal measurement. Coils transverse to the sample are responsible for generating the RF pulses, which are perpendicular to \mathbf{B}_{0} .

Two capacitors are present in the probe, called *matching* and *tuning* capacitors. The first is responsible for tuning the frequency of the resonant electronic circuit, and the second matches its impedance. It is known from electromagnetic theory (32) that a circuit composed a capacitor of capacitance C and a coil of inductance L generates an electromagnetic oscillator of natural frequency given by

$$\omega_{LC} = \frac{1}{\sqrt{LC}},\tag{2.62}$$

in radians per second for L in henries [H] and C in faradays [F]. The energy is stored in this circuit in the form of electric fields in the capacitors and magnetic fields in the coils. If an electromagnetic field with frequency matching ω_{LC} sets up oscillations in this circuit, more energy is accumulated, in an effect similar to a child's swing being pushed periodically by an external person. This way, it is possible to increase the power of the pulsed RF fields. Conversely, when detecting the NMR signal, this LC-circuit may build up energy if ω_{LC} is near the Larmor frequency of the nuclear spin being analyzed.

As each nuclear spin has specific Larmor frequencies, the matching and tuning capacitors must be adjusted every time a sample with a different molecule is used, in a process called *probe tuning*.

2.7.3 RF transmitter

The radiofrequency transmitter is the NMR spectrometer section dedicated to produce the RF pulses to be applied to the system. Some spectrometers have several transmission circuits, often called *channels*, each working separately and responsible for pulsing in a particular frequency closest to the Larmor frequency of each nucleus in the sample. The scheme of a single channel is presented in Figure 13.



Figure 13 – Scheme of the transmitter circuit.

The RF synthesizer (1) is responsible for generating an oscillating signal with a well-defined frequency. The phase shifter (2) controls the phase of this signal, and the pulse gate (3) is a switch that opens and closes rapidly to cut a "slice" of the signal coming from (1), generating the pulse. The time interval the gate remains closed determines the

duration of the pulse, which is called *pulse width*, and is from the order of μs . Both (2) and (3) are controlled by a pulse programmer (4). Everything is finally sent into an amplifier (5), then to the coil.

2.7.4 Duplexer

The same coils that send the RF pulse to the sample are responsible for the detection. Therefore, first the coils receive a high RF pulse, and then they need to detect the weak signal coming from the magnetization. This task is performed by a device called *duplexer*. It selects the signal coming from the amplifier and does not let it into the sensitive receiver device. When the tiny NMR signal comes from the probe to the duplexer (that is, in the opposite direction), it is directed to the receiver and not to the amplifier.

2.7.5 RF receiver

Figure 14 shows the scheme of the receiver circuit. After a pulse sequence, the signal from the nuclear spins is detected by the coils and sent down to the duplexer (6), directed to a *signal preamplifier* (7) which increases the voltage levels without increasing the noise, and arrives at a *quadrature receiver* (8). The signal that gets to the receiver will be sent to an *analog-to-digital converter (ADC)*. This device transforms a voltage induced from an input signal into a sequence of zeros and ones - a digital signal. The digitized NMR signal is obtained by repeating the measurement during well defined time intervals and storing the results in the computer as a set of values.



Figure 14 – Scheme of the receiver circuit.

The signal generated from the nuclear magnetization, although weak in amplitude, has a high frequency, oscillating at megahertz. This is too fast for the ADC to compute, so a *down conversion* is necessary. This is achieved through a reference signal of frequency ω_{ref} sent by the RF synthesizer (1) to the receiver, that combines it with the NMR signal that oscillates with the Larmor frequency ω_0 to generate a new signal oscillating at the *relative Larmor frequency*

$$\Omega = \omega_0 - \omega_{ref},\tag{2.63}$$

also known as offset frequency.

2.7.6 Shim coils

For the NMR experiment to work properly, the magnetic field \mathbf{B}_0 must be as homogeneous as possible, as stated in section 2.7.1. For this purpose, two additional sets of coils, called *shims*, are set near the sample. One is the *superconducting shim*, which is made of superconducting material and immersed in the liquid He, and gives a primary correction to the inhomogeneity of the field. As the coil that generates the \mathbf{B}_0 field, the superconducting shim is charged when the magnet is installed. The second set of shim coils which gives secondary corrections is inserted in a tube into the magnet bore and is composed of the *room-temperature shims*. These shims are capable of generating currents that correct little inhomogeneities in the field and can be operated semi-automatically. This process is known as "shimming the magnet", since it is a preliminary task to every NMR experiment.

2.7.7 Magnetic field gradients

Modern spectrometers are capable of applying magnetic field gradients on the sample. This type of field depends on the position along a given direction, which in this case is the same direction of \mathbf{B}_{0} :

$$\mathbf{B}_{\mathbf{G}} = B_G \hat{z} \tag{2.64}$$

The set of coils used to create a magnetic field gradient is shown in Figure 15. Currents are passed through two coils, with different directions in each one. This way, the magnetic field near the upper coil enhances \mathbf{B}_0 , and that in the lower coils opposes \mathbf{B}_0 . If this set of coils is designed carefully, linear gradients as that of equation (2.64) can be applied with reasonably good accuracy.

When a gradient is applied in a sample, each molecule will experience different magnetic fields, precessing with different Larmor frequencies. This leads to an inhomogeneous distribution of the transverse magnetization, accelerating the relaxation process in the xy-plane. This behavior is shown in Figure 16.



Figure 15 – Coil and current configuration used to generate a gradient field in the sample. The bar in the right indicates the field intensity, which is higher in the darker region.



Figure 16 – Effect of a gradient field applied along the \hat{z} -direction on the magnetization of a sample. In the first step, the gradient is inactive. Then, after the gradient is turned on, the spins on the top will feel a more intense field and will precess faster than spins located at the bottom of the sample. The result of this process, shown in the final step, is the acceleration of the transverse relaxation process. The figures take into account only the effect of the field gradient.

3 Quantum computation

Quantum computation is the study of computation performed in quantum systems, establishing a model of computation that carries properties inherent to quantum mechanics. It introduces the notion of quantum bits, or qubits, that may have the values zero, one or a superposition of both, differently from the classical bits that have definite values. Quantum bits can also be connected through quantum entanglement, a property that has no analogous in classical computation.

Two of the first mentions of quantum computation were made by Richard Feynman in 1982 (13), arguing that a quantum computer would be a good simulator of quantum systems; and by David Deutsch in 1985 (33), proposing a universal quantum computer. Both works suggested that quantum computers could exceed the computational power of their classical versions. In the following years, many improvements in this idea were made with the proposition of quantum algorithms, like the Quantum Search by Lov Grover and the Quantum Teleportation by Charles Bennett and collaborators (23). But the most remarkable one was the 1994 Peter Shor's algorithm for factoring integer numbers in polynomial time (15). As the current cryptography protocols are based on the computational difficulty of finding the prime factors of a huge integer number (34), the Shor's algorithm showed that the safety of classical computers is vulnerable to someone with a quantum computer.

The end of the 1990 decade and the beginning of the 21st century were marked by the experimental implementation of several quantum algorithms. In this work, an NMR system was used as a quantum computer. Due to its great precision in the individual control of each nuclear spin, which are used as qubits, the NMR is a robust technique for this kind of experiment.

In this chapter, the basic principles of quantum computation will be presented. For a more detailed approach to the topic, references (15) and (34) are recommended.

3.1 Quantum bits and Bloch sphere

A classical bit is the fundamental unit of information and can have the values of 0 and 1. A quantum bit (qubit) is a two-level quantum system, which is set in a two dimensional Hilbert space and can be found in the orthogonal and normalized states $|0\rangle$ or $|1\rangle$, represented as

$$|0\rangle = \begin{bmatrix} 1\\0 \end{bmatrix}, \ |1\rangle = \begin{bmatrix} 0\\1 \end{bmatrix}. \tag{3.1}$$

Due to the properties of quantum mechanics, a qubit may also be found in a superposition of these two states:

$$|\psi\rangle = \alpha \left|0\right\rangle + \beta \left|1\right\rangle \tag{3.2}$$

with the complex coefficients α and β obeying the normalization condition

$$|\alpha|^2 + |\beta|^2 = 1. \tag{3.3}$$

This is one advantage of the quantum computation over the classical computation. As a quantum state is defined up to a global phase, it is always possible to write the general state of a quantum bit as

$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$
(3.4)

where the angles θ and ϕ are

$$0 \le \theta \le \pi, \ 0 \le \phi \le 2\pi. \tag{3.5}$$

When describing the quantum state in the form (3.4), it may be represented as laying in the surface of a sphere of radius 1, called the *Bloch sphere*. Some of the most common states are shown in Table 1.

θ	ϕ	State	Observation
0	-	$ 0\rangle$	North pole
π	-	$ 1\rangle$	South pole
$\pi/2$	0 or π	$(0\rangle \pm 1\rangle)/\sqrt{2}$	Equator line on the x-axis
$\pi/2$	$\pi/2 \text{ or } -\pi/2$	$(0\rangle \pm i 1\rangle)/\sqrt{2}$	Equator line on the y axis

Table 1 – Some states of the Bloch sphere.

3.1.1 Multiple qubits

In general, a quantum computer will be composed of a collection of N qubits instead of only one, and therefore its wave function will reside in a 2^N -dimensional complex Hilbert space, and its time-evolution dynamics will be ruled by the Schrödinger equation, as long as interactions with the environment can be neglected (14).

The most generic state of an N qubit quantum computer is represented by the tensor product of N 2-dimensional Hilbert spaces:

$$|\psi\rangle = \sum_{j=1}^{2^{N}-1} c_{j} |j\rangle$$

$$= \sum_{j_{n-1}=0}^{1} \cdots \sum_{j_{1}=0}^{1} \sum_{j_{0}=0}^{1} c_{j_{n-1},\dots,j_{1},j_{0}} |j_{n-1}\rangle \otimes \cdots \otimes |j_{1}\rangle |j_{0}\rangle$$
(3.6)

with $j_0, j_1, ..., j_n \in [0, 1]$ and the normalization constraint

$$\sum_{j=0}^{2^{N}-1} |c_j|^2 = 1 \tag{3.7}$$

over the complex coefficients. A two qubit state, according to equation (3.6), would be represented as

$$\begin{aligned} |\psi\rangle = c_0 |0\rangle + c_1 |1\rangle + c_2 |2\rangle + c_3 |3\rangle \\ = c_{00} |0\rangle \otimes |0\rangle + c_{01} |0\rangle \otimes |1\rangle + c_{10} |1\rangle \otimes |0\rangle + c_{11} |1\rangle \otimes |1\rangle \\ = c_{00} |00\rangle + c_{01} |01\rangle + c_{10} |10\rangle + c_{11} |11\rangle. \end{aligned}$$

$$(3.8)$$

Equation (3.6) shows that the number of states of a system grows exponentially with the number of qubits.

3.1.2 Spin 1/2 as quantum bits

In quantum mechanics, a nuclear spin system is described in a complex vectorial state called Hilbert space. In the case of a system with I = 1/2, a bidimensional Hilbert space is sufficient (14). Systems of spin-1/2 subjected to a magnetic field may be used as qubits, since they are two level systems.

As stated in section 2.2.2, when a spin 1/2 is placed in an external magnetic field the energy is separated in two different levels, $E_0 = -\hbar\omega_0/2$ and $E_1 = \hbar\omega_0/2$, associated with the spin up and spin down states, respectively, and are represented in the computation basis by $|0\rangle$ and $|1\rangle$.

For a system with n qubits, a molecule with n I = 1/2 spins, each with different Larmor frequencies, is used. In the 2 qubit case, for example, a molecule with two J-coupled spins with I = 1/2 is chosen. In that case, the computational basis is given by (see section 2.6.5)

$$|+1/2, +1/2\rangle = |00\rangle |+1/2, -1/2\rangle = |01\rangle |-1/2, +1/2\rangle = |10\rangle |-1/2, -1/2\rangle = |11\rangle.$$
(3.9)

3.2 Quantum logic gates

Quantum logic gates are linear operations acting on qubits. They must preserve the normalization condition (3.7) and therefore must be unitary. In a system of N qubits, they are represented by $2^N \times 2^N$ matrices, which can be decomposed into a product of unitary matrices acting on one or more qubits. In this chapter, some of the most important quantum logic gates are going to be presented, together with the *quantum circuit* language, which is a powerful tool to describe quantum computation processes.

3.2.1 Single qubit gates

A single qubit lives on a 2-dimensional Hilbert space, thus any single qubit quantum logic gate will be represented by a 2×2 matrix. The first example is the Pauli matrices:

$$X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad Y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (3.10)$$

which act on the generic state $|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$ as

$$X |\psi\rangle = \alpha |1\rangle + \beta |0\rangle, \qquad (3.11)$$

$$Y |\psi\rangle = i\alpha |1\rangle - i\beta |0\rangle, \qquad (3.12)$$

$$Z |\psi\rangle = \alpha |0\rangle - \beta |1\rangle.$$
(3.13)

The X gate is also known as NOT gate, as its action on the computational basis is similar to the NOT gate from classical computation, although it does not invert a generic quantum state of a single qubit. Operators 3.10 are also denoted by σ_x , σ_y and σ_z .

Other important single qubit gates are the Hadamard gate H, the phase gate S and the $\pi/8$ gate T:

$$H = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1\\ 1 & -1 \end{bmatrix}, \ S = \begin{bmatrix} 1 & 0\\ 0 & i \end{bmatrix}, \ T = \begin{bmatrix} 1 & 0\\ 0 & e^{i\pi/4} \end{bmatrix},$$
(3.14)

which act on the qubits as

$$H|0\rangle = \frac{|0\rangle + |1\rangle}{\sqrt{2}}, \quad H|1\rangle = \frac{|0\rangle - |1\rangle}{\sqrt{2}}$$
 (3.15)

$$S |\psi\rangle = \alpha |0\rangle + i\beta |1\rangle \tag{3.16}$$

$$T |\psi\rangle = \alpha |0\rangle + e^{i\pi/4}\beta |1\rangle$$
(3.17)

The self-reversibility of H is an important property: $H^2 = \mathbb{1}$. The S and T gates create relative phases between the components of a qubit.

3.2.2 Rotations on the Bloch sphere

An important class of unitary transformations is the *rotation operators* around the \hat{x} , \hat{y} and \hat{z} axis. They arise from the exponentiation of the Pauli matrices X, Y and Z. For a given linear operator A, such that $A^2 = \mathbb{1}$,

$$e^{-iA\theta} = \left[1 - \frac{1}{2!}\theta + ...\right] \mathbb{1} - i\left[\theta - \frac{1}{3!}\theta^3 + ...\right] A = \cos\theta \mathbb{1} - i\sin\theta A.$$
(3.18)

Since the Pauli operators satisfy $X^2 = Y^2 = Z^2 = 1$, one can use equation (3.18) to write

$$R_x(\theta) = e^{-i\theta X/2} = \cos\frac{\theta}{2}\mathbb{1} - i\sin\frac{\theta}{2}X = \begin{bmatrix} \cos\frac{\theta}{2} & -i\sin\frac{\theta}{2} \\ -i\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{bmatrix}$$
(3.19)

$$R_y(\theta) = e^{-i\theta Y/2} = \cos\frac{\theta}{2}\mathbb{1} - i\sin\frac{\theta}{2}Y = \begin{bmatrix} \cos\frac{\theta}{2} & -\sin\frac{\theta}{2} \\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{bmatrix}$$
(3.20)

$$R_z(\theta) = e^{-i\theta Z/2} = \cos\frac{\theta}{2}\mathbb{1} - i\sin\frac{\theta}{2}Z = \begin{bmatrix} e^{-i\theta/2} & 0\\ 0 & e^{i\theta/2} \end{bmatrix}$$
(3.21)

Defining a unit vector $\hat{n} = (n_x, n_y, n_z)$, a rotation around an arbitrary axis in the \hat{n} -direction can be written as

$$R_{\hat{n}}(\theta) = e^{-i\theta(\hat{n}\cdot\boldsymbol{\sigma})} = \cos\frac{\theta}{2} - i\sin\frac{\theta}{2}(\hat{n}\cdot\boldsymbol{\sigma})$$
(3.22)

where $\boldsymbol{\sigma} = (X, Y, Z)$ is a vector of the Pauli matrices.

Operations (3.19), (3.20) and (3.21) are called rotations as they represent an actual rotation of the state $|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$ on the Bloch sphere of an angle θ around the given axis \hat{n} (34).

Any quantum logic gate may be decomposed into a certain number of rotations and global phase shifts. For an arbitrary unitary operation U on a single qubit, there are real numbers α , β , γ and δ such that (15)

$$U = e^{i\alpha} R_z(\beta) R_y(\gamma) R_z(\delta).$$
(3.23)

As all operations in NMR are rotations in the magnetization vector, equation (3.23) shows that it is possible to implement any quantum logic gate using an NMR system. Since these rotations are in the x and y directions, in the context of NMR it is more useful to write equation (3.23) as

$$U = e^{i\alpha} R_x(\beta) R_y(\gamma) R_x(\delta). \tag{3.24}$$

3.2.3 Multi-qubit gates and controlled operations

Using the postulates of quantum mechanics, it is possible to construct the Hilbert space for systems containing two or more qubits. For example, an operator U acting on a single qubit in a system which contains two qubits is obtained through the tensor product:

$$U_a = U \otimes \mathbb{1}, \quad U_b = \mathbb{1} \otimes U \tag{3.25}$$

where a and b indicate the first and second qubit, adopting the convention $|a\rangle \otimes |b\rangle$. For more qubits, these expressions are analogous.

Conditional statements such as "If A then B" are useful in both classical and quantum computation, and are performed through *controlled operations*. These operations act under a *target* qubit (t) if a *control* qubit (c) is in a certain state. The first example is the controlled-NOT gate, also know as CNOT. It acts on a 2 qubit state as $|c\rangle \otimes |t\rangle \rightarrow$ $|c\rangle \otimes |c \oplus t\rangle$, where the symbol \oplus denotes the sum modulo 2 operation, given by:

$$0 \oplus 0 = 0$$

$$0 \oplus 1 = 1$$

$$1 \oplus 0 = 1$$

$$1 \oplus 1 = 0$$

(3.26)

In other words, it applies the NOT operation on the second qubit if the first qubit is $|1\rangle$.

$$CNOT = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$
(3.27)

$$|00\rangle \rightarrow |00\rangle, |01\rangle \rightarrow |01\rangle, |10\rangle \rightarrow |11\rangle, |11\rangle \rightarrow |10\rangle.$$
 (3.28)

It is also possible to have the first qubit as the target and the second qubit as the control, in which case $|t\rangle \otimes |c\rangle \rightarrow |c \oplus t\rangle \otimes |c\rangle$. This operation is denoted as CNOT_{ba} , in contrast to CNOT_{ab} to describe the conventional CNOT.

Controlled operations may be more general, implementing an arbitrary unitary operation U to the target qubit if the control qubit satisfies a given condition. Also, there could be multiple qubits in target and control.

3.2.4 Quantum circuits

Quantum circuits are widely used representations of quantum operations. These are diagrams that illustrate a quantum algorithm or process. In addition to the clean visualization, it universalizes the language in a way that the same algorithm may be implemented in any quantum system capable of performing quantum computation or the operations described in the circuit. An example of a quantum circuit is shown in Figure 17. It reads from left to right. Each line represents a qubit, and the boxes are the quantum logic gates applied to a single qubit. The big box is a multi-qubit gate applied to both qubits. The box with a pointer indicates a measurement made in the corresponding qubit.



Figure 17 – Representation of a quantum circuit.

The principal quantum gate representations in quantum circuits are shown in Figure 18.



Figure 18 – Principal quantum gates.

Controlled gates are shown in Figure 19. The dot is used to represent the control qubit, and is black if the control is $|1\rangle$ and white if it is $|0\rangle$. The \oplus symbol represents the target qubit.



Figure 19 – From left to right: $CNOT_{ab}^1$, $CNOT_{ba}^1$, $CNOT_{ab}^0$ and $CNOT_{ba}^0$

3.3 Quantum state tomography

At the end of a quantum algorithm, the final state of the system has to be known, which is done through a measurement performed on the qubits. In some systems, however, the state vector of the system cannot be determined, and only a set of outcomes $\{|\psi_i\rangle\}$ with probability $\{p_i\}$ of occurring is known. One way to characterize a quantum state in such cases is to determine its density matrix (15), which carries all the information regarding the system at a given instant of time. A process to obtain all the elements of the density matrix and reconstruct it is quantum state tomography (QST). The first method for the implementation of quantum state tomography in NMR systems was described by Gershenfeld et. al (19) for systems of coupled spin 1/2. In this chapter, the QST technique in the context of NMR systems is going to be presented, after a brief explanation of the density matrix formalism.

3.3.1 Density matrix

The set $\{ |\psi_i\rangle, p_i \}$ is a statistical ensemble. The density matrix ρ is a mathematical tool to treat such situations:

$$\rho = \sum_{i} p_i \left| \psi_i \right\rangle \!\! \left\langle \psi_i \right| \tag{3.29}$$

where $p_i > 0$ and $\sum_i p_i = 1$. If the state vector $|\psi\rangle$ is known, then the system is said to be in a *pure state*, and equation (3.29) is simply $\rho = |\psi\rangle\langle\psi|$. Otherwise, the system is in a *mixed state*, that is, a mixture of the pure states $|\psi_i\rangle$ that compose the statistical ensemble. Important properties of the density operator are:

- The eigenvalues of ρ are real and non-negative, that is, ρ is a positive operator (which implies that it is Hermitian (15)).
- $\text{Tr}\rho = 1$ due to conservation of probabilities.
- $\operatorname{Tr}\rho^2 \leq 1$, with the equality occurring only for pure states.

An operator that does not have all of these properties cannot represent a density matrix.

The diagonal terms ρ_{mm} of the density matrix are real numbers known as *populations*, which are associated with the probability of finding a member of the ensemble in the energy level associated with the quantum number m. The off-diagonal terms are complex numbers known as *coherences*, which in the NMR context are related to the existence of transversal magnetization in the system (21).

For a system of spins 1/2, the difference between populations of different levels denotes the existence of a net magnetization in the longitudinal direction. Therefore, if all the energy levels have the same populations, the system has no longitudinal magnetization.

The existence of coherences denotes not only that the spins have transverse components, but also that these components are aligned along a given direction. As the coherences are complex numbers, they have a phase besides their amplitude, which is interpreted, in NMR, as the direction of the transverse magnetization in the xy-plane.

If a system with probability p_i of being in a state $|\psi_i\rangle$ is under the action of a Hamiltonian \mathcal{H} during a time interval Δt , then after the evolution it will have probability p_i of being on the state $|\psi'_i\rangle = U |\psi_i\rangle$, where U is a unitary operator called the *evolution operator* of the system (14). Therefore, the evolution of the density matrix ρ is given by

$$\rho' = \sum_{i} p_i |\psi'_i\rangle\langle\psi'_i| = \sum_{i} p_i U |\psi_i\rangle\langle\psi_i| U^{\dagger} = U\rho U^{\dagger}$$
(3.30)

If \mathcal{H} is time independent then one can obtain U from the Schrödinger equation (14)

$$U = e^{-i\mathcal{H}\Delta t/\hbar} \tag{3.31}$$

so that equation (3.30) is written as

$$\rho' = e^{-i\mathcal{H}\Delta t/\hbar}\rho e^{i\mathcal{H}\Delta t/\hbar} \tag{3.32}$$

Alternatively, if \mathcal{H} is time dependent, it can be more appropriate to work with the Liouville-von Neumann equation, which can be obtained from the Schrödinger equation (14, 26):

$$i\hbar \frac{\mathrm{d}\rho}{\mathrm{d}t} = [\mathcal{H}, \rho].$$
 (3.33)

If a system is composed of n subsystems, each one described by a density matrix ρ_i (i = 1,...,n), then the density matrix of the whole system is given by

$$\rho = \rho_1 \otimes \rho_2 \otimes \dots \otimes \rho_n. \tag{3.34}$$

If only ρ is known, the density matrices ρ_i of each subsystem can be obtained through the *partial trace*, which is a sum over all the possible states of one subsystem. For a system composed of two subsystems A and B,

$$\rho_a = \operatorname{Tr}_a(\rho_{ab}), \quad \rho_b = \operatorname{Tr}_b(\rho_{ab}) \tag{3.35}$$

where Tr_a (Tr_b) is a partial trace operation, a sum over all the possible states of A (B)(15). It is important to remark that if the system is in an entangled state, equation (3.34) is not valid (35).

3.3.2 Density matrix in the NMR context

In NMR systems one deals with an ensemble of particles and does not have access to the state of each spin, which suggests that the density matrix formalism is a good approach to treat the NMR phenomenon. The vector model used in section 2.4.1 is oversimplified, and cannot describe all the NMR features. The components of the magnetization in NMR experiments are the observables, which are proportional to the ensemble average of the nuclear spins operators $\langle I_x \rangle$, $\langle I_y \rangle$ and $\langle I_z \rangle$ (23). If the density matrix of the spin ensemble is given by ρ , then

$$M_x \propto \text{Tr}(\rho I_x), \quad M_y \propto \text{Tr}(\rho I_y), \quad M_z \propto \text{Tr}(\rho I_z).$$
 (3.36)

In thermal equilibrium, the NMR system is often described by an ensemble of non-interacting molecules, which is a good approximation for liquid samples. In this case, the density matrix for a system with N molecules $(N \approx 10^{23})$ is given by equation (3.34) (19):

$$\rho_{sys} = \rho_{\text{molecule 1}} \otimes \rho_{\text{molecule 2}} \otimes \cdots \otimes \rho_{\text{molecule N}}.$$
(3.37)

As these matrix are identical in thermal equilibrium and the molecules do not interact during the evolution, it is sufficient to use the density matrix of only one molecule to represent the whole system. This way, a quantum computer built from an NMR sample is an ensemble of N quantum computers, each one represented by a single molecule in the sample.

In thermal equilibrium with temperature T, the density matrix is written as (26)

$$\rho_{sys} = \frac{e^{-\mathcal{H}_{sys}/k_b T}}{\mathcal{Z}}.$$
(3.38)

where k_b is the Boltzmann constant, \mathcal{H}_{sys} is the NMR Hamiltonian which includes the Zeeman and any other nuclear interactions that may appear in the system, and \mathcal{Z} the partition function (35):

$$\mathcal{Z} = \sum_{j} e^{-E_j/k_b T}.$$
(3.39)

3.3.3 Pseudo-pure states

A great part of quantum computation experiments requires the preparation of pure states, that is, states that obey the following properties:

- 1. $\rho^m = \rho$
- 2. $Tr\rho^2 = 1$

For the NMR thermal equilibrium density matrix given by equation (3.38), $\rho_{sys}^m \neq \rho_{sys}$ and $Tr(\rho_{sys}^2) \neq 1$, and ρ_{sys} represents a mixed state. It is not possible to obtain a pure state from a mixed state using only unitary operations (23). Currently, a true pure state in an NMR system cannot be constructed. However, one can build a quantum state

that for all important effects behaves like a pure one, which is called a *pseudo-pure state*, and is described by

$$\rho_{pps} = \frac{(1-\epsilon)}{2^n} \mathbb{1} + \epsilon \bigotimes_{i=1}^n |\psi\rangle\!\langle\psi|.$$
(3.40)

where n is the number of qubits in the system, and ϵ is of the order of 10^{-5} (23). Notice that the term proportional to the identity is not affected by the operations done in the NMR experiment, as they are almost unitary. Also, it is not detected during the measurements, and equation 3.40 gives the same results that would be obtained from a pure state (which justifies the pseudo-pure state nomenclature).

3.3.4 Reconstructing ρ

If a quantum state ρ is given, it is possible to calculate the mean value $\langle A \rangle$ of an arbitrary observable A, using the property (15)

$$\langle A \rangle = \operatorname{Tr}\{\rho A\}. \tag{3.41}$$

Conversely, one can determine the density matrix ρ if the mean values of a set of operators are known. Such a set is called a *quorum* (36). This is how the quantum state tomography is done: for a system of 1 qubit, the quorum is given by the identity and the Pauli matrices, that enable one to write ρ as

$$\rho = \frac{1}{2} (\mathbb{1} + \langle \sigma_x \rangle \sigma_x + \langle \sigma_y \rangle \sigma_y + \langle \sigma_z \rangle \sigma_z).$$
(3.42)

To obtain the mean value of these observables, the same measurement must be performed several times before a statistics of the results can be constructed. As in NMR one deals with an ensemble of spins instead of a single one, only a single measurement is necessary to obtain such statistics (23). Therefore, performing measurements of observables which are the products of the Pauli matrices, one can reconstruct the density matrix ρ for a one qubit state.

This procedure can be generalized for a system of n qubits. In such case, equation (3.42) will be given by

$$\sum_{\boldsymbol{v}} \frac{1}{2^n} (\langle \sigma_{v_1} \otimes \sigma_{v_2} \otimes \cdots \otimes \sigma_{v_n} \rangle \sigma_{v_1} \otimes \sigma_{v_2} \otimes \cdots \otimes \sigma_{v_n})$$
(3.43)

where the sum runs over the vectors $(\boldsymbol{v} = v_1, ..., v_n)$, whose components are chosen from the set $\{1, \sigma_x, \sigma_y, \sigma_z\}$, formed by the Pauli matrices plus the identity.

3.3.5 Quantum State Tomography in an NMR system

As stated in equation (3.36), by measuring the magnetization one has access to the averages $\langle I_x \rangle$, $\langle I_y \rangle$ and $\langle I_z \rangle$, and therefore the density matrix ρ can be reconstructed. However, in an NMR experiment only the components M_x and M_y are measured, which can be seen from the NMR signal S(t):

$$S(t) \propto \operatorname{Tr}\left[e^{-i\mathcal{H}t/\hbar}\rho e^{i\mathcal{H}t/\hbar}\sum_{k}(I_{kx}+iI_{ky})\right] = \operatorname{Tr}\left[\rho e^{i\mathcal{H}t/\hbar}\sum_{k}(I_{kx}+iI_{ky})e^{-i\mathcal{H}t/\hbar}\right], \quad (3.44)$$

where the sum is carried over the k qubits of the system. In the last equality, the Tr(AB) = Tr(BA) property of the trace operation was used. Equation (3.44) denotes that it is possible to interpret operator $\sum_{k} (I_{kx} + iI_{ky})$ as $e^{i\mathcal{H}t/\hbar} \sum_{k} (I_{kx} + iI_{ky})$, which is time-dependent and more easy to calculate than $e^{-i\mathcal{H}t/\hbar}\rho e^{i\mathcal{H}t/\hbar}$, as ρ is unknown.

To obtain $\langle I_z \rangle$, a set of pulse rotations must be applied in the final state, which depends on the number of qubits of the system.

In the 1 qubit case, \mathcal{H}_{sys} is given by

$$\mathcal{H}_{sys} = \hbar\omega_0 I_z \tag{3.45}$$

where ω_0 is the Larmor frequency of the spin, and equation (3.44) is written as (37)

$$S(t) \propto [\operatorname{Tr}(\rho I_x) + i \operatorname{Tr}(\rho I_y)] e^{i\omega t}.$$
(3.46)

A rotation of $R_y(\pi/2)$ transforms (3.46) into

$$S^{Y}(t) \propto [\text{Tr}(\rho I_z) + i \,\text{Tr}(\rho I_y)]e^{i\omega t}, \qquad (3.47)$$

from which the M_z component of the magnetization can be measured. As the value of $\langle \mathbb{1} \rangle$ is given by

$$\langle \mathbb{1} \rangle = \operatorname{Tr}(\rho \mathbb{1}) = \operatorname{Tr}(\rho) = 1, \qquad (3.48)$$

these 2 measurements are sufficient to determine the quorum of observables and reconstruct ρ using equation (3.42).

For 2 qubits, using the notation $I_j \otimes \mathbb{1} = I_{1j}$ and $\mathbb{1} \otimes I_j = I_{2j}$ for $j = \{x, y, z\}$, the Hamiltonian \mathcal{H}_{sys} is given by

$$\mathcal{H}_{sys} = -\hbar\omega_1 I_{1z} - \omega_2 I_{2z} + 2\pi\hbar J_{12} I_{1z} I_{2z}.$$
(3.49)

where ω_1 and ω_2 are the Larmor frequency of spins 1 and 2. Equation (3.44) reads (37)

$$S(t) \propto \{ [\operatorname{Tr}(\rho I_{1x}) + \operatorname{Tr}(\rho I_{1x} I_{2z})] + i [\operatorname{Tr}(\rho I_{1y}) + \operatorname{Tr}(\rho I_{1y} I_{2z})] \} e^{i(-\omega_1 + \pi J_{12})t} + \{ [\operatorname{Tr}(\rho I_{1x}) - \operatorname{Tr}(\rho I_{1x} I_{2z})] + i [\operatorname{Tr}(\rho I_{1y}) - \operatorname{Tr}(\rho I_{1y} I_{2z})] \} e^{i(-\omega_1 - \pi J_{12})t} + \{ [\operatorname{Tr}(\rho I_{2x}) + \operatorname{Tr}(\rho I_{1z} I_{2x})] + i [\operatorname{Tr}(\rho I_{2y}) + \operatorname{Tr}(\rho I_{1z} I_{2y})] \} e^{i(-\omega_2 + \pi J_{12})t} + \{ [\operatorname{Tr}(\rho I_{2x}) - \operatorname{Tr}(\rho I_{1z} I_{2x})] + i [\operatorname{Tr}(\rho I_{2y}) - \operatorname{Tr}(\rho I_{1z} I_{2y})] \} e^{i(-\omega_2 - \pi J_{12})t} .$$

$$(3.50)$$

As the coupling term J_{12} splits the spectral lines, it makes $I_{1x}I_{2z}$, $I_{1y}I_{2z}$, $I_{1z}I_{2x}$ and $I_{1z}I_{2y}$ observable. The quorum of observables is given by

$$\{1, I_x, I_y, I_z\} \otimes \{1, I_x, I_y, I_z\}$$
(3.51)

and therefore 16 ensemble averages are needed for obtaining the density matrix. To obtain all of them from the measurements, a set of nine operations must be performed on the qubits (23):

$$11, X1, Y1, 1X, 1Y, XX, XY, YX, YY$$
 (3.52)

where the letters X and Y represent rotations of $\pi/2$, with the first and second letters representing the operation acting in the first or second qubit. Actually, during these 9 experiments, some observables are measured several times, and only four experiments are sufficient to determine all the density matrix terms, say 11, 1X, 1Y and XX (37).

4 The Hubbard model

The Hubbard model is paradigmatic in solid state physics, and it is used to study the dynamics of interacting electrons on a lattice. It was proposed independently by Martin Gutzwiller (5), Junjiro Kanamori (6) and John Hubbard (7), all in 1963. It has been studied over the years in theoretical and experimental approaches, successfully describing metallic and insulating properties of materials which could not be explained with the band theory (8). Despite its usefulness, it has been completely solved only in some special cases, such as the one-dimensional model (38). In this chapter, the Hubbard model and some of its properties are going to be presented, beginning with a description of the second quantization operators, that are used to describe the Hubbard Hamiltonian, followed by the derivation of the Hamiltonian and the study of some special cases.

4.1 Creation and annihilation operators

The creation and annihilation operators (a and a^{\dagger} , respectively) for the treatment of the quantum harmonic oscillator are defined in terms of the position and momentum operators X and P (14):

$$a = \sqrt{\frac{m\omega}{2\hbar}} X + i\sqrt{\frac{1}{2m\omega\hbar}}P$$

$$a^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}} X - i\sqrt{\frac{1}{2m\omega\hbar}}P.$$
(4.1)

From the commutator $[X, P] = -i\hbar$, the commutation relation of a and a^{\dagger} can be established:

$$[a, a^{\dagger}] = 1 \tag{4.2}$$

and so the Hamiltonian for the quantum harmonic oscillator can be written as

$$\mathcal{H}_{QO} = \frac{1}{2m}P^2 + \frac{1}{2}m\omega^2 X^2 = \hbar\omega \left(a^{\dagger}a + \frac{1}{2}\right).$$
(4.3)

The ground state of (4.3) is denoted as $|0\rangle$ and has the properties (14)

$$a|0\rangle = 0 \text{ and } \mathcal{H}_{QO}|0\rangle = \frac{\hbar\omega}{2}|0\rangle.$$
 (4.4)

Then, it is possible to define the action of the a and a^{\dagger} operators on the eigenstates of the quantum harmonic oscillator:

$$a^{\dagger} |n\rangle = \sqrt{n+1} |n+1\rangle$$

$$a |n\rangle = \sqrt{n} |n-1\rangle$$
(4.5)

which is a way to obtain the excited states of the Hamiltonian (4.3).

From equation (4.5) one define the number operator as $N = a^{\dagger}a$, which act on the $|n\rangle$ states as

$$N |n\rangle = a^{\dagger} a |n\rangle = n |n\rangle.$$
(4.6)

The Hamiltonian can thus be written as

$$\mathcal{H}_{QO} = \hbar\omega \left(N + \frac{1}{2} \right), \tag{4.7}$$

whose eigenenergies are given by

$$E_n = \hbar \omega \left(n + \frac{1}{2} \right). \tag{4.8}$$

This way, the states $a^{\dagger} |n\rangle$ and $a |n\rangle$ are eigenstates of \mathcal{H}_{QO} with eigenvalues given by

$$\begin{aligned}
\mathcal{H}_{QO}(a^{\dagger} | n \rangle) &= (E_n + \hbar \omega)(a^{\dagger} | n \rangle) \\
\mathcal{H}_{QO}(a | n \rangle) &= (E_n - \hbar \omega)(a | n \rangle),
\end{aligned} \tag{4.9}$$

so that the operators a^{\dagger} and a are responsible for *creating* or *annihilating* one quanta of energy $\hbar\omega$. These operators are called *bosonic* creation and annihilation operators, as the occupation number $\langle N \rangle$ is given by the Bose-Einstein distribution (3):

$$\langle N \rangle = \frac{1}{1 + e^{\hbar\omega/k_b T}}.$$
(4.10)

The Hubbard Hamiltonian is written in terms of the *fermionic* creation and annihilation operators. Differently of the bosonic ones, these are not defined in terms of the position and momentum operators. Besides, in the Hubbard model these fermionic operators are labeled by indexes \mathbf{j} and σ , which specify the lattice site and the spin value the operator is acting on. This way, they can be defined as

 $c_{j\sigma}^{\dagger}$: creates a fermion of spin σ on the site j; $c_{j\sigma}$: destroys a fermion of spin σ on the site j.

These operators obey anticommutation relations (a anticommutator is defined as $\{A, B\} = AB + BA$):

$$\{c_{j\sigma}, c_{l\sigma'}^{\dagger}\} = \delta_{j,l}\delta_{\sigma\sigma'}, \quad \{c_{j\sigma}^{\dagger}, c_{l\sigma'}^{\dagger}\} = 0, \quad \{c_{j\sigma}, c_{l\sigma'}\} = 0.$$
(4.11)

Relations (4.11) bring some consequences. Like in the bosonic case, $c_{j\sigma}^{\dagger} |0\rangle = |1\rangle$, but sequential applications lead to

$$c_{j\sigma}^{\dagger}|1\rangle = c_{j\sigma}^{\dagger}c_{j\sigma}^{\dagger}|0\rangle = 0 \tag{4.12}$$

which is in accordance with the *Pauli exclusion principle*, that is, two identical fermions cannot occupy the same quantum state *simultaneously* in a given quantum system (3).

This principle, together with the definition (4.1), results in the fermionic states being labeled by a collection of numbers $n_{j\sigma} = 0$ or 1, instead of a single number n that could assume any natural value as in the bosonic case. Such states could be represented as

$$|n_{\mathbf{1}\uparrow}n_{\mathbf{1}\downarrow}, n_{\mathbf{2}\uparrow}n_{\mathbf{2}\downarrow}, n_{\mathbf{3}\uparrow}n_{\mathbf{3}\downarrow}, \dots\rangle.$$

$$(4.13)$$

The anticommutation relations also ensure the fermionic behavior of the quantum state, as the wave function changes sign when two fermions with different labels are exchanged: $c_{j\sigma}^{\dagger}c_{l\sigma'}^{\dagger} = -c_{l\sigma'}^{\dagger}c_{j\sigma}^{\dagger}$.

4.2 The Hubbard Hamiltonian

With the formalism presented in the last section, it is possible to begin the construction of the Hubbard Hamiltonian. As stated before, it describes the dynamics of fermions in a regular lattice. In this section, the Hubbard Hamiltonian will be derived and some of its properties in limiting cases are going to be discussed.

4.2.1 Derivation

To derive the Hubbard Hamiltonian, a first approach can be done thinking about the motion of electrons in a solid. The lattice is considered to be composed of atoms with fixed nuclear positions, the sites. The electrons may transit between the sites. If each atom consists of a single level (orbital), the Pauli exclusion principle guarantees that each site may have four possible configurations (4): zero electrons, one electron with spin up, one electron with spin down, or a pair of spin up and down electrons.

For the hopping of electrons from one site to another, one includes in the Hamiltonian a term proportional to $c_{j\sigma}$, which destroys an electron of spin σ in a site j, and $c_{l\sigma}^{\dagger}$, which creates an electron of spin σ in a site l. The energy scale is governed by a constant $-J_h$ which is related to the kinetic energy of the electrons. As the wave function of an electron located on a specific site vanishes in the neighboring sites, it is reasonable to allow hopping only between adjacent sites (7). Such a term can be written as

$$-J_h \sum_{\langle \mathbf{j}, \mathbf{l} \rangle} \sum_{\sigma=\uparrow,\downarrow} (c^{\dagger}_{\mathbf{j}\sigma} c_{\mathbf{l}\sigma} + c^{\dagger}_{\mathbf{l}\sigma} c_{\mathbf{j}\sigma})$$
(4.14)

where $\langle \mathbf{j}, \mathbf{l} \rangle$ indicates that the sum is only over the neighboring sites.

Different from the traditional electron gas, in the Hubbard model the electronelectron interactions are not neglected (4). As the interactions of electrons in different sites may be screened by the periodic potential, one can consider only the interaction between electrons on the same site, to a first approximation (7). This situation can be denoted with the inclusion of a term

$$U\sum_{\mathbf{j}} n_{\mathbf{j\uparrow}} n_{\mathbf{j\downarrow}} \tag{4.15}$$

in the Hamiltonian, which is non-zero only in the double occupancy case, in which it will assume a value of U equal to the Coulomb interaction between the electrons.

Finally, as the number of particles in a site is variable, a term to control the filling of each site is included

$$-\mu \sum_{\mathbf{j}} (n_{\mathbf{j\uparrow}} + n_{\mathbf{j\downarrow}}). \tag{4.16}$$

Putting all together, the Hubbard Hamiltonian is finally presented

$$\mathcal{H}_{H} = -J_{h} \sum_{\langle \mathbf{j}, \mathbf{l} \rangle} \sum_{\sigma=\uparrow,\downarrow} (c^{\dagger}_{\mathbf{j}\sigma} c_{\mathbf{l}\sigma} + c^{\dagger}_{\mathbf{l}\sigma} c_{\mathbf{j}\sigma}) + U \sum_{\mathbf{j}} n_{\mathbf{j}\uparrow} n_{\mathbf{j}\downarrow} - \mu \sum_{\mathbf{j}} (n_{\mathbf{j}\uparrow} + n_{\mathbf{j}\downarrow}).$$
(4.17)

The case when the number of particles is equal to the number of sites is referred to as *half-filling*, since this is half the maximum capacity of the lattice, that supports two fermions per site. The half-filling case shows some interesting properties which are going to be discussed later.

4.2.2 Single-site limit

The simplest particular case to understand some of the Hubbard Hamiltonian properties is the *single-site limit*. This limit is equivalent to consider $J_h = 0$ in (4.17). In this case, $[\mathcal{H}_H, n_{\mathbf{j}\sigma}] = 0$, and \mathcal{H}_H will have the same eigenstates as each individual number operator $n_{\mathbf{j}\sigma}$ (14). As all number operators commute with each other, it is possible to treat each sector of \mathcal{H}_H individually. Therefore, the Hamiltonian to be analyzed is

$$\mathcal{H}_H = U n_{\uparrow} n_{\downarrow} - \mu (n_{\uparrow} + n_{\downarrow}). \tag{4.18}$$

The four possible configurations for each individual site are $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$ and $|\uparrow\downarrow\rangle$, which happen to be the eigenstates of \mathcal{H}_H , with eigenvalues 0, $-\mu$, $-\mu$ and $U - 2\mu$, respectively. In the basis of these eigenstates, the matrix of \mathcal{H}_H is diagonal:

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & -\mu & 0 & 0 \\ 0 & 0 & -\mu & 0 \\ 0 & 0 & 0 & U - 2\mu \end{bmatrix}$$
(4.19)

and therefore the partition function is given by (3)

$$\mathcal{Z} = Tr\{e^{-\beta \mathcal{H}_H}\} = 1 + e^{\beta \mu} + e^{\beta \mu} + e^{\beta (U-2\mu)}, \qquad (4.20)$$

where $\beta = 1/k_bT$, k_b being the Boltzmann constant. From the partition function of a system, its thermodynamics properties may be derived (3). In particular, the mean value of the total number operator $\langle (n_{\uparrow} + n_{\downarrow}) \rangle$, the *occupation number*, is

$$\langle (n_{\uparrow} + n_{\downarrow}) \rangle = Tr\{(n_{\uparrow} + n_{\downarrow})\rho\} = \frac{Tr\{(n_{\uparrow} + n_{\downarrow})e^{-\beta\mathcal{H}_{H}}\}}{\mathcal{Z}}$$

$$= \frac{e^{\beta\mu} + e^{2\beta\mu - \beta U}}{1 + e^{\beta\mu} + e^{\beta(U - 2\mu)}}.$$
(4.21)

Figure 20 shows a plot of the occupation number (4.21) versus the chemical potential, for U = 4 (in units such that $k_b = 1$). For high temperatures, they have a linear relation in the range shown. As the temperature approaches zero, increasing the chemical potential μ increases the occupation number from zero to one, but a 'plateau' arises in $\langle n \rangle = \langle (n_{\uparrow} + n_{\downarrow}) \rangle = 1$ in the range between $\mu = 0$ and $\mu = U$, returning to increase to two after that. This indicates that, to add a second fermion to the site, the chemical potential must be increased by an amount $\Delta \mu = U$. This phenomena is a property of the Hubbard Hamiltonian known as *Mott insulating gap*, which shows that a fermion located on a site blocks the addition of a new one until a sufficient amount of energy is given to the system.



Figure 20 – Plot of the occupation $\langle n \rangle$ in function of the chemical potential μ , for fixed U = 4 and $J_h = 0$, in units such that $k_b = 1$. When T = 0.1, the plateau arising in the interval $\Delta \mu = U$ centered in $\mu = U/2$ is the 'Mott gap'.

4.2.3 Particle-hole symmetry

The Hubbard Hamiltonian presents some useful symmetries. Of particular interest for this work is the particle-hole symmetry (PHS), which allows the mapping between the repulsive and attractive cases of the Hubbard model.

First, consider the following transformation, that exchanges the role of the creation and annihilation operators:

$$d^{\dagger}_{\mathbf{l}\sigma} = (-1)^{\mathbf{l}} c_{\mathbf{l}\sigma}$$

$$d_{\mathbf{l}\sigma} = (-1)^{\mathbf{l}} c^{\dagger}_{\mathbf{l}\sigma}$$
(4.22)

Notice that

$$d_{\mathbf{l}\sigma}^{\dagger}d_{\mathbf{l}\sigma} = (-1)^{2\mathbf{l}}c_{\mathbf{l}\sigma}c_{\mathbf{l}\sigma}^{\dagger} = c_{\mathbf{l}\sigma}c_{\mathbf{l}\sigma}^{\dagger}.$$
(4.23)

But as $\{c_{\mathbf{l}\sigma}, c_{\mathbf{l}\sigma}^{\dagger}\} = 1$, then

$$d_{\mathbf{l}\sigma}^{\dagger}d_{\mathbf{l}\sigma} = 1 - c_{\mathbf{l}\sigma}^{\dagger}c_{\mathbf{l}\sigma} = 1 - n_{\mathbf{l}\sigma}, \qquad (4.24)$$

that is, the roles of the occupations are interchanged:

$$d_{\mathbf{l}\sigma}^{\dagger} d_{\mathbf{l}\sigma} \left| 0 \right\rangle = 1 \left| 0 \right\rangle$$

$$d_{\mathbf{l}\sigma}^{\dagger} d_{\mathbf{l}\sigma} \left| 1 \right\rangle = 0 \left| 1 \right\rangle$$

$$(4.25)$$

Due to this property, this transformation is known as *particle-hole transformation* (PHT).

The PHT shows some interesting symmetries when one applies it to a model describing a bipartite lattice. This kind of lattice can be thought as being formed by two sublattices \mathcal{A} and \mathcal{B} , in a way that all the sites of \mathcal{A} have as orthogonal neighbours only sites belonging to \mathcal{B} and vice-versa. A lattice containing spins ordered in a antiferromagnetic configuration, as shown in Figure 21, is considered bipartite if each kind belongs to only one of the lattices \mathcal{A} and \mathcal{B} .



Figure 21 – Example of a two-dimensional bipartite lattice, with one sublattice represented by red circles and the other by blue triangles. If circles mean spin up and triangles mean spin down, it is a representation of a lattice ordered in an antiferromagnetic configuration.

For bipartite lattices, the factor $(-1)^{\mathbf{l}}$ of equation (4.22) is equal to 1 in one sublattice and -1 in the other. Therefore, $(-1)^{\mathbf{l}+\mathbf{j}} = -1$ for two neighbouring sites \mathbf{j} and \mathbf{l} . Noticing that $d_{\mathbf{l}\sigma}d^{\dagger}_{\mathbf{j}\sigma} = -d^{\dagger}_{\mathbf{l}\sigma}d_{\mathbf{j}\sigma}$, then

$$c_{\mathbf{l}\sigma}^{\dagger}c_{\mathbf{j}\sigma} = (-1)^{\mathbf{l}+\mathbf{j}} d_{\mathbf{l}\sigma} d_{\mathbf{j}\sigma}^{\dagger} = -d_{\mathbf{l}\sigma} d_{\mathbf{j}\sigma}^{\dagger} = d_{\mathbf{l}\sigma}^{\dagger} d_{\mathbf{j}\sigma}, \qquad (4.26)$$

and one can conclude that, for bipartite lattices, the kinetic energy term of the Hubbard Hamiltonian is unchanged under a PHT, that is, it presents a particle-hole symmetry (PHS).

To make the Hubbard Hamiltonian more symmetric under a PHT, it is useful to rewrite the Hubbard Hamiltonian in a way such that the PHS also appears in the interaction term. This can be achieved through the term

$$U\left(n_{\mathbf{j\uparrow}} - \frac{1}{2}\right)\left(n_{\mathbf{j\downarrow}} - \frac{1}{2}\right) = Un_{\mathbf{j\uparrow}}n_{\mathbf{j\downarrow}} - \frac{U}{2}(n_{\mathbf{j\uparrow}} + n_{\mathbf{j\downarrow}}) + \frac{U}{4},\tag{4.27}$$
that is equivalent to a shift of U/2 in the chemical potential and the introduction of an additive constant of U/4 to the total energy value. This way, the Hubbard Hamiltonian can be written as

$$\mathcal{H}_{H} = -J_{h} \sum_{\langle \mathbf{j}, \mathbf{l} \rangle} \sum_{\sigma=\uparrow,\downarrow} (c^{\dagger}_{\mathbf{j}\sigma} c_{\mathbf{l}\sigma} + c^{\dagger}_{\mathbf{l}\sigma} c_{\mathbf{j}\sigma}) + U \sum_{\mathbf{j}} \left(n_{\mathbf{j}\uparrow} - \frac{1}{2} \right) \left(n_{\mathbf{j}\downarrow} - \frac{1}{2} \right) - \mu \sum_{\mathbf{j}} (n_{\mathbf{j}\uparrow} + n_{\mathbf{j}\downarrow}). \quad (4.28)$$

Rewriting the Hubbard Hamiltonian in the form (4.28) will lead, in the single-site limit, to eigenenergies U/4, $-U/4 - \mu$, $-U/4 - \mu$, $U/4 - 2\mu$ for the eigenstates $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$ and $|\uparrow\downarrow\rangle$, respectively. This way, the occupation becomes

$$\langle (n_{\uparrow} + n_{\downarrow}) \rangle = \frac{2e^{-\beta(-U/4-\mu)} + 2e^{-\beta(U/4-2\mu)}}{e^{-\beta U/4} + 2e^{-\beta(-U/4-\mu)} + e^{-\beta(U/4-2\mu)}},$$
(4.29)

which is equal to 1 at $\mu = 0$. Therefore, the half-filling will always occur at $\mu = 0$ for any value of U and $\beta = 1/k_bT$. This is also true when $J_h \neq 0$. A plot of equation (4.29) is shown in Figure 22.



Figure 22 – Plot of the occupation $\langle n \rangle$ in function of the chemical potential μ , for fixed $J_h = 0$ and T = 0.1, in units such that $k_b = 1$. When the occupation is written according to equation (4.29), the Mott gap will be centered at $\mu = 0$ for any value of U, J_h and T.

4.2.4 Attractive case

The particle-hole transformation allows a connection between the two cases of the Hubbard Hamiltonian: the repulsive case, when the fermions repel each other (U > 0) and the attractive case, when the fermions attract each other (U < 0). Performing the PHT only on the spin down type, the number operator for the spin up stays unchanged:

$$\begin{array}{c} n_{\mathbf{j}\downarrow} \to 1 - n_{\mathbf{j}\downarrow} \\ n_{\mathbf{j}\uparrow} \to n_{\mathbf{j}\uparrow}, \end{array} \tag{4.30}$$

and the interaction term becomes

1

$$U\left(n_{\mathbf{j\uparrow}} - \frac{1}{2}\right)\left(n_{\mathbf{j\downarrow}} - \frac{1}{2}\right) \to -U\left(n_{\mathbf{j\uparrow}} - \frac{1}{2}\right)\left(n_{\mathbf{j\downarrow}} - \frac{1}{2}\right).$$
(4.31)

The chemical potential term becomes a Zeeman field term

$$\mu(n_{\mathbf{j\uparrow}} + n_{\mathbf{j\downarrow}}) \to -\mu(n_{\mathbf{j\uparrow}} - n_{\mathbf{j\downarrow}}), \qquad (4.32)$$

and conversely a field term in the repulsive case will become a chemical potential term in the attractive one. This shows that it is possible to obtain information from the attractive case studying the repulsive one, and vice-versa. This is specially useful when dealing with technical difficulties to reproduce one of these cases in experiments (9).

4.2.5 Two-site Hubbard and exact diagonalization

The study of the single-site limit shows the role of U in the Hubbard model, but considerations about the relations between the potential energy and the kinetic energy J_h must be done. This can be discussed through the example of the two-site Hubbard Hamiltonian. This model can be solved explicitly for $U \neq 0$ and $J_h \neq 0$ through the technique of *exact diagonalization*, which consists of constructing a basis for the entire Hilbert space, writing the matrix representation of the Hamiltonian and diagonalizing it.

The two site Hubbard Hamiltonian can be written as

$$\mathcal{H}_{H} = -J_{h} \sum_{\sigma=\uparrow,\downarrow} \left(c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma} \right) + U \sum_{j=1}^{2} \left(n_{j\uparrow} - \frac{1}{2} \right) \left(n_{j\downarrow} - \frac{1}{2} \right) - \mu \sum_{j=1}^{2} \left(n_{j\uparrow} + n_{j\downarrow} \right), \quad (4.33)$$

and is represented in the basis $\{|n_{1\uparrow}n_{1\downarrow}, n_{2\uparrow}n_{2\downarrow}\rangle\}$ of the number operators N_{σ} :

$$N_{\sigma} = n_{1\sigma} + n_{2\sigma},\tag{4.34}$$

with 16 possible states. The Hilbert space can be organized by noticing that the number operators for each site and spin commute with the Hubbard Hamiltonian ($[\mathcal{H}_H, N_\sigma] = 0$), so the number of fermions is conserved and the matrix of \mathcal{H}_H will be block-diagonal with 9 sectors ($N_{\uparrow}, N_{\downarrow}$) (14). The z-component of the total spin S_z , given by

$$S_z = \frac{1}{2} \sum_{j=1,2} (n_{\uparrow j} - n_{\downarrow j}), \qquad (4.35)$$

also commutes with HH, and therefore this is also a conserved quantity. It is more illustrative to represent the states $\{|n_{1\uparrow}n_{1\downarrow}, n_{2\uparrow}n_{2\downarrow}\rangle\}$ by arrows \uparrow, \downarrow (see Table 2).

Each block of the matrix of (4.33) can be diagonalized separately. The most interesting case is the subspace of dimension 4 related to $(N_{\uparrow}, N_{\downarrow}) = (1, 1)$, that is, half-filling $(\mu = 0)$, with $S_z = 0$. It has the matricial representation:

$$\begin{bmatrix} U/2 & -J_h & -J_h & 0\\ -J_h & -U/2 & 0 & -J_h\\ -J_h & 0 & -U/2 & -J_h\\ 0 & -J_h & -J_h & U/2 \end{bmatrix}$$
(4.36)

which can be diagonalized exactly as shown by Harris and Lange in (39). When written in the form (4.33), its eigenenergies are $\pm U/2$ and $\pm \sqrt{4J_h^2 + U^2/4}$. In particular, $-\sqrt{4J_h^2 + U^2/4}$ is the lowest possible energy value, therefore the ground state of the two-site Hubbard Hamiltonian lies in this subspace, denoting a preference for an antiferromagnetic configuration in the half-filling sector.

$(N_{\uparrow},N_{\downarrow})$	Possible states	Dimension	Total S_z
(0,0)	0,0 angle	1	0
(1,0)	$ \uparrow,0 angle, 0,\uparrow angle$	2	1/2
(0,1)	$ \downarrow,0 angle,\ 0,\downarrow angle$	2	-1/2
(1,1)	$ \uparrow\downarrow,0\rangle, \uparrow,\downarrow\rangle, \downarrow,\uparrow\rangle, 0,\uparrow\downarrow\rangle$	4	0
(2,0)	$ \uparrow,\uparrow angle$	1	1
(0,2)	$ \downarrow,\downarrow angle$	1	-1
(2,1)	$ \uparrow\downarrow,\uparrow angle, \uparrow,\uparrow\downarrow angle$	2	1/2
(1,2)	$ \uparrow\downarrow,\downarrow\rangle, \downarrow,\uparrow\downarrow\rangle$	2	-1/2
(2,2)	$ \uparrow\downarrow,\uparrow\downarrow angle$	1	0

Table 2 – All the possible states of the two-site Hubbard Hamiltonian, represented in the basis of the number operators N_{σ} ($\sigma = \{\uparrow, \downarrow\}$).

4.3 Mott-insulator transition

As shown in section 4.2.2, where the single-site limit was discussed, it costs an energy equal to U to add a second fermion to a site. This feature creates a region known as "Mott gap", which is as high as the value of U. This can be generalized to a lattice with more sites: if one supposes an empty lattice, it is easy to fill it with a new fermion as it is always possible to choose a site with no fermions to put the new one. However, when all sites are occupied with one fermion - that is, in the half-filling condition-, the addition of the next will have a cost of U. This sudden jump in the energetic cost is the Mott gap shown in section 4.2.2. It is possible to conclude that as U increases, it becomes energetically unfavorable to have double occupancy.

In a lattice with fermions moving between sites, a fermion always have to spend an energy equal to U to hop to a neighbour site occupied with another fermion. When the

potential energy is much larger than the kinetic energy $(U >> J_h)$, the fermions will prefer to stay in separated sites whenever it is possible, and thus the system becomes insulating as no charge is transported. This type of insulator which arises from the correlation between fermions is called a *Mott insulator* (8).

5 Quantum simulation of the Hubbard Hamiltonian

The use of computers to simulate the dynamics of physical systems is a widely applied technique. However, it turns out to be impossible to simulate quantum systems with a large number of particles. Feynman, in his 1982 paper (13), argues that a good simulator of a physical system must require a number of computer elements proportional to the spacetime volume of that physical system. However, to simulate a quantum system that grows polynomially, it requires exponentially large classical computers. This way, a quantum system can only be effectively simulated by another quantum system. This conclusion of Feynman motivated, in the following years, idealizations of quantum computers that could act as quantum simulators, such as proposed by Lloyd in 1996 (16) and Zalka in 1998 (17). But it was only in 1999 that Somaroo *et al.* (18) performed an experimental simulation of the dynamics of a truncated quantum harmonic oscillator using an NMR quantum computer as the simulator. This paper has shed light on the viability of real quantum simulations through quantum computers, and since then this research area has been growing.

In the present work, the experimental quantum simulation of the Hubbard Hamiltonian was performed in an NMR system. The experiment is going to be detailed in this chapter.

5.1 Quantum simulation

Quantum simulation is a process which consists of reproducing the dynamics of a quantum system using another quantum system. It is concerned with the solution of the Schrödinger equation. For a system in an initial state $|\psi(0)\rangle$ under the action of a time-independent Hamiltonian \mathcal{H}_S , the time evolution is given by the unitary operator (3.31), and therefore

$$\left|\psi(\Delta t)\right\rangle = e^{-i\mathcal{H}_S\Delta t/\hbar} \left|\psi(0)\right\rangle.$$
(5.1)

One must find a set of operations which reproduces the evolution given by equation (5.1) during the time interval Δt . A general scheme for quantum simulation is described by the diagram shown in Figure 23. The goal is to simulate the effect of the evolution $|s(0)\rangle \rightarrow |s(T)\rangle$ using the physical system P, which is done through an invertible map ϕ that correlates the states of P and of the simulated system S and their respective evolution operators \mathcal{U} and \mathcal{W} as

Simulated System
$$|s(0)\rangle \xrightarrow{\phi} |p(0)\rangle$$
 Physical System
 $\mathcal{U} \downarrow \qquad \qquad \downarrow \mathcal{W}$
 $|s(T)\rangle \xrightarrow{\phi^{-1}} |p(T)\rangle$

Figure 23 – Diagram that represents the implementation process of a quantum simulation.

In practice, the simulation is done through the implementation of a set of operations \mathcal{W}_i that can be performed in the system P such that

$$\mathcal{W} = \prod_{i} \mathcal{W}_{i}.$$
 (5.3)

After mapping the initial state $|s(0)\rangle$ into $|p(0)\rangle$, the evolution $|p(0)\rangle \rightarrow |p(T)\rangle$ is implemented via \mathcal{W} , with the inverse mapping ϕ^{-1} taking $|p(T)\rangle$ back into $|s(T)\rangle$, simulating the evolution $|s(0)\rangle \rightarrow |s(T)\rangle$ driven by \mathcal{U} .

In general, the exponentiation of the Hamiltonian \mathcal{H}_S to be simulated is not an easy task, which complicates the search for the mapping ϕ . However, the Hamiltonian of many physical systems can be written as a sum of local interactions, such that

$$\mathcal{H}_S = \sum_j \mathcal{H}_j,\tag{5.4}$$

where the terms \mathcal{H}_j are in general one-body Hamiltonian or two-particle interactions. If all the \mathcal{H}_j terms commute, then (14)

$$e^{\mathcal{H}_S} = e^{\sum_j \mathcal{H}_j} = e^{\mathcal{H}_1} e^{\mathcal{H}_2} \dots e^{\mathcal{H}_L}.$$
(5.5)

If not all \mathcal{H}_j terms commute, then equation (5.5) cannot be implemented, and the following theorem must be used:

Theorem 1 (Trotter formula) Let A and B be Hermitian operators. Then for any real t,

$$\lim_{n \to \infty} \left(e^{iAt/n} e^{iBt/n} \right)^n = e^{i(A+B)t}.$$
(5.6)

This theorem is valid even if $[A, B] \neq 0$. Modifications of equation (5.6) give approximations to implement quantum simulations, such as

$$e^{i(A+B)t} = e^{(iAt/2)}e^{(iBt)}e^{(iAt/2)} + O(t^3).$$
(5.7)

Higher order approximations can be constructed if more accuracy is required (15).

If the simulated Hamiltonian \mathcal{H}_s is time-dependent, equation (3.31) is not always valid, and it may not be possible to implement the time-evolution of equation (5.1) during

a period Δt . One approach to deal with these situations is to discretize \mathcal{H}_s into M + 1steps $\mathcal{H}_s(m)$, $m = 0 \to M$, such that \mathcal{H}_s can be considered time-independent in each step. Therefore the time evolution operator for each part can be obtained from equation (3.31):

$$\mathcal{U}_m = e^{-i\mathcal{H}_s(m)\Delta t/\hbar},\tag{5.8}$$

and the total evolution will be given by

$$\mathcal{U} = \prod_{m=0}^{M} \mathcal{U}_m.$$
(5.9)

When using the NMR system as a quantum simulator, the idea is to apply its tools to reproduce the dynamics of the evolution operator of \mathcal{H}_s , which include radiofrequency pulses and free evolutions under the action of the NMR natural Hamiltonian \mathcal{H}_{NMR} :

$$\mathcal{H}_{NMR} = \frac{\pi \hbar J_{12}}{2} \sigma_z \otimes \sigma_z. \tag{5.10}$$

As the Hamiltonian (5.10) is always active in an NMR system, these free evolutions are implemented experimentally by simply applying no RF pulses to the qubits. This consists of a delay in the pulse sequence denoted by $U(\Delta t)$, where Δt is the duration of the delay. Therefore, the evolution will be simulated by a consecutive implementation of these operations in the qubits, as shown in Figure 24.



Figure 24 – A quantum circuit that reproduces the dynamics of the evolution operator of the Hamiltonian \mathcal{H}_S to be simulated can be composed of unitary operations V and free evolutions $U(\Delta t)$ under the action of the NMR Hamiltonian during a time interval.

5.2 Experimental setting

In this work, the quantum simulation of the two-site Hubbard Hamiltonian was performed. Such case of the model was discussed in section 4.2.5. The problem was focused in the half-filling case with angular momentum $S_z = 0$, which implies that $\mu = 0$. To verify that the simulation is reproducing such system, some properties such as the Mott-insulator transition and the emergence of paired states for attractive cases were observed. This section will be dedicated to show all the experimental setting to perform such simulation, describing the mapping of the problem into the NMR system, the preparation of the initial states and the actual implementation of the simulation.

5.2.1 Hamiltonian mapping

In order to observe effects such as the Mott-insulator transition, it is necessary to change the value of one of the parameters J_h or U, resulting in a time dependent Hamiltonian. Assuming a constant J_h , and a time-dependent U, which varies linearly with time from a value U_0 to U_f during an evolution period T, the Hubbard Hamiltonian will be given by:

$$\mathcal{H}_{H} = -J_{h} \sum_{\sigma=\uparrow,\downarrow} (c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma}) + [(1 - s(t))U_{0} + s(t)U_{f}] \sum_{j=1}^{2} \left(n_{\uparrow j} - \frac{1}{2} \right) \left(n_{\downarrow j} - \frac{1}{2} \right), \quad (5.11)$$

where s(t) is a function such that

$$s(t) = \begin{cases} 0, & \text{if } t = 0\\ 1, & \text{if } t = T \end{cases}$$
(5.12)

The Hilbert space for this system has dimension 16, but the subspace for this particular case has dimension 4, and therefore can be mapped into a two-qubit problem.

The following codification was used to represent the states of the system in the computational basis:

$$|\uparrow\downarrow,0\rangle = |00\rangle, \ |\uparrow,\downarrow\rangle = |01\rangle, \ |\downarrow,\uparrow\rangle = |10\rangle, \ |0,\uparrow\downarrow\rangle = |11\rangle.$$
(5.13)

To write the Hamiltonian (5.11) in terms of quantum gates, it is necessary to determine how each of its terms act on the basis. The hopping term is given by

$$c_{1\uparrow}^{\dagger}c_{2\uparrow} + c_{2\uparrow}^{\dagger}c_{1\uparrow} + c_{1\downarrow}^{\dagger}c_{2\downarrow} + c_{2\downarrow}^{\dagger}c_{1\downarrow}$$

$$(5.14)$$

and acts on the basis elements as

$$\begin{aligned} |\uparrow\downarrow,0\rangle &\to |\downarrow,\uparrow\rangle + |\uparrow,\downarrow\rangle \\ |\downarrow,\uparrow\rangle &\to |0,\uparrow\downarrow\rangle + |\uparrow\downarrow,0\rangle \\ |\uparrow,\downarrow\rangle &\to |\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle \\ |0,\uparrow\downarrow\rangle &\to |\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle \,, \end{aligned}$$
(5.15)

which translates to the computational basis as

$$\begin{aligned} |00\rangle &\to |10\rangle + |01\rangle \\ |01\rangle &\to |11\rangle + |00\rangle \\ |10\rangle &\to |00\rangle + |11\rangle \\ |11\rangle &\to |01\rangle + |10\rangle \,. \end{aligned}$$
(5.16)

This effect can be reproduced by the following matrix

$$\begin{bmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{bmatrix} = \sigma_x \otimes \mathbb{1} + \mathbb{1} \otimes \sigma_x$$
(5.17)

The interaction term is

$$\left(n_{1\uparrow} - \frac{1}{2}\right)\left(n_{1\downarrow} - \frac{1}{2}\right) + \left(n_{2\uparrow} - \frac{1}{2}\right)\left(n_{2\downarrow} - \frac{1}{2}\right),$$
 (5.18)

whose action on both basis is given by

$$\begin{split} |\uparrow\downarrow,0\rangle &\to |\uparrow\downarrow,0\rangle \\ |\downarrow,\uparrow\rangle &\to -|\downarrow,\uparrow\rangle \\ |\uparrow,\downarrow\rangle &\to -|\uparrow,\downarrow\rangle \\ |0,\uparrow\downarrow\rangle &\to |0,\uparrow\downarrow\rangle \,, \end{split}$$
(5.19)

$$\begin{aligned} |00\rangle &\to |00\rangle \\ |01\rangle &\to - |01\rangle \\ |10\rangle &\to - |10\rangle \\ |11\rangle &\to |11\rangle \,. \end{aligned} \tag{5.20}$$

The quantum gate that reproduce this operation on the qubits is

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \sigma_z \otimes \sigma_z$$
(5.21)

Therefore, the Hubbard Hamiltonian written in terms of the quantum gates is given by

$$\mathcal{H}_H(t) = -J_h(\sigma_x \otimes \mathbb{1} + \mathbb{1} \otimes \sigma_x) + \frac{1}{2}[(1 - s(t))U_0 + s(t)U_f]\sigma_z \otimes \sigma_z.$$
(5.22)

5.2.2 Time evolution implementation

As stated before, to implement the time evolution under the action of $\mathcal{H}_H(t)$, it must be discretized into M + 1 steps as $\mathcal{H}_H(m)$, where m goes from $0 \to M$ in the time interval $0 \to T$. Therefore, the function s(t) must be

$$s(m) = \frac{m}{M},\tag{5.23}$$

which has the properties listed on condition (5.12). The evolution operator \mathcal{U}_m for each step, using units where $\hbar = 1$, can be written as

$$\mathcal{U}_m = \exp\left\{-i\left[-J_h(\sigma_x \otimes \mathbb{1} + \mathbb{1} \otimes \sigma_x) + \frac{1}{2}\left[\left(1 - \frac{m}{M}\right)U_0 + \frac{m}{M}U_f\right]\sigma_z \otimes \sigma_z\right]\tau\right\}, \quad (5.24)$$

where $\tau = T/(M+1)$ is the duration of each step. The total evolution will be given by

$$\mathcal{U} = \prod_{m=0}^{M} \mathcal{U}_m.$$
(5.25)

The hopping and the interaction terms do not commute with each other; therefore it is necessary to use the Trotter formula (5.7) with

$$A = \frac{1}{2} [(1 - s(t))U_0 + s(t)U_f] \sigma_z \otimes \sigma_z$$

$$B = -J_h(\sigma_x \otimes \mathbb{1} + \mathbb{1} \otimes \sigma_x).$$
(5.26)

Thus, equation (5.24) can be written as

$$\mathcal{U}_m = \exp\left\{-\frac{i}{4}\left[\left(1-\frac{m}{M}\right)U_0 + \frac{m}{M}U_f\right](\sigma_z \otimes \sigma_z)\tau\right\} \circ \exp\left\{iJ_h(\sigma_x \otimes \mathbb{1} + \mathbb{1} \otimes \sigma_x)\tau\right\}, (5.27)$$

where $V \circ W = VWV$. The first term has the same form of the evolution operator obtained from the Hamiltonian of an NMR of two spin 1/2:

$$\mathcal{U}_{NMR} = \exp\left\{-i\frac{\pi J_{12}}{2}\sigma_z \otimes \sigma_z \Delta t_m\right\},\tag{5.28}$$

provided that Δt_m obeys the condition

$$\Delta t_m = \frac{\left(1 - \frac{m}{M}\right)U_0 + \frac{m}{M}U_f}{2\pi J_{12}}\tau$$
(5.29)

In practice, as the static field B_0 is always on, equation (5.28) is implemented by a delay of duration Δt_m on the experiment. As $[\sigma_x \otimes \mathbb{1}, \mathbb{1} \otimes \sigma_x] = 0$, the second term can be written as

$$\exp\left\{iJ_h(\sigma_x\otimes\mathbb{1}+\mathbb{1}\otimes\sigma_x)\tau\right\}=\exp\left\{iJ_h(\sigma_x\otimes\mathbb{1})\tau\right\}\exp\left\{iJ_h(\mathbb{1}\otimes\sigma_x)\tau\right\}.$$
(5.30)

Notice that

$$\exp\left\{-i\frac{\theta}{2}(\sigma_x \otimes \mathbb{1})\right\} = \exp\left\{-i\frac{\theta}{2}\sigma_x\right\} \otimes \mathbb{1}$$
$$\exp\left\{-i\frac{\theta}{2}(\mathbb{1} \otimes \sigma_x)\right\} = \mathbb{1} \otimes \exp\left\{-i\frac{\theta}{2}\sigma_x\right\},$$
(5.31)

where $\exp\{-i\theta\sigma_x/2\} = R_x(\theta)$ is a rotation around the *x*-axis of an angle θ . Therefore, operation (5.31) represents a simultaneous rotation of an angle $\theta = -2J_h\tau$ on both qubits:

$$\exp\left\{iJ_h(\sigma_x\otimes\mathbb{1})\tau\right\}\exp\left\{iJ_h(\mathbb{1}\otimes\sigma_x)\tau\right\} = R_x(-2J_h\tau)\otimes R_x(-2J_h\tau).$$
(5.32)

Therefore, the evolution operator to be implemented in the experiment will be given by

$$\mathcal{U}_{m} = \exp\left\{-i\frac{\pi J_{12}}{2}\sigma_{z}\otimes\sigma_{z}\Delta t_{m}\right\}R_{x}(-2J_{h}\tau)\otimes R_{x}(-2J_{h}\tau)\times \exp\left\{-i\frac{\pi J_{12}}{2}\sigma_{z}\otimes\sigma_{z}\Delta t_{m}\right\},$$
(5.33)

whose quantum circuit is shown on Figure 25. This way, the values of the parameters J_h , U and T chosen to be simulated, as well as the number of steps M, determine the magnitude of the R_x rotations and delays.

$$\begin{array}{c|c}
\hline & R_x(-2J_h\tau) \\
\hline & U(\Delta t_m) \\
\hline & R_x(-2J_h\tau) \\
\hline \end{array} \\
\hline \\ & U(\Delta t_m) \\
\hline \\ \hline \end{array}$$

Figure 25 – Quantum circuit implemented in each step of the simulation. The $U(\Delta t_m)$ represents a delay of duration Δt_m .

To keep track of the system dynamics during the simulation, a measurement must be performed after each of the M + 1 steps of the experiment. However, as in the measurement process the quantum state at a given time t is lost (14), it is necessary to repeat the evolution from the beginning in order to measure the final state on the next step, as shown in Figure 26.

Figure 26 – The evolution is performed in M + 1 steps, in which the Hamiltonian is considered being time independent. After each step, a measurement is performed, and the experiment is repeated from the beginning until the next step, where a new measurement is made. This process goes on until the last step is reached.

It is important to notice that the time period T to be simulated is not equal to the duration of the experiment, which is given by the summation of all the delay periods Δt_m , plus the time necessary to apply the pulses. This information is important because of relaxation effects, which determine how long an experiment may last without losing coherence (see section 2.4).

The values chosen for the parameters U and J_h will determine the length of the delays and the rotation angles in the circuit shown in Figure 25. But as the duration of the experiment is limited to the relaxation times, U cannot have any value. Besides, the rotations in NMR have a precision of about 1.0° (40), which implies that the product $2J_h\tau$ must result in an angle above this limit. The number of steps is also important. A high value implies that more pulses will be applied to the qubits, which may lead to errors as each rotation has an uncertainty associated to it. A low value results in a higher size for the steps, which can be a problem as they need a small size to guarantee that the Hamiltonian can be considered time independent during each of them. In order to optimize the values of the parameters, a code was written to calculate the duration of the

experiment, the value of the rotation angles and how much of the magnetization would be lost due to relaxation, given the values of U, J_h , T and the number of steps.

The experiments were performed on a 500 MHz Varian spectrometer. The two qubits are the nuclear spins of ¹H and ¹³C from a molecule of chloroform (CHCl₃). These molecules were contained in a sample of chloroform diluted in a solution with 99% of deuterated acetone, so that they would not interact with each other. The relaxation times of each spins are shown in Table 3.

Nucleus	T_1 (s)	T_2 (s)
$^{1}\mathrm{H}$	7.0	0.62
$^{13}\mathrm{C}$	11.3	0.30

Table 3 – Relaxation times for the nuclear spins of ¹H and ¹³C of the chloroform molecule.

5.2.3 Preparation of initial states

The system begins in the pseudo-pure state $|00\rangle$ ($|\uparrow\downarrow,0\rangle$). Then, for a fixed value of the hopping term $J_h = 1$, it is prepared in one of the four eigenstates of the half-filling, $S_z = 0$ subspace of the two-site Hubbard Hamiltonian. In all experiments, the initial value of the interaction energy was set to $U_0 = -5$ or $U_0 = 0$. The eigenstates for both cases are presented in Tables 4 and 5.

State	U = -5
$ E_1\rangle$	$0.6672(\uparrow\downarrow,0\rangle + 0,\uparrow\downarrow\rangle) + 0.2341(\uparrow,\downarrow\rangle + \downarrow,\uparrow\rangle)$
$ E_2\rangle$	$rac{1}{\sqrt{2}}(\left \uparrow\downarrow,0 ight angle-\left 0,\uparrow\downarrow ight angle)$
$ E_3\rangle$	$rac{1}{\sqrt{2}}(\left \uparrow,\downarrow ight angle-\left \downarrow,\uparrow ight angle)$
$ E_4\rangle$	$0.2341(\uparrow\downarrow,0\rangle+ 0,\uparrow\downarrow\rangle)-0.6672(\uparrow,\downarrow\rangle+ \downarrow,\uparrow\rangle)$

Table 4 – Eigenstates of the two-site Hubbard Hamiltonian for U = -5, in increasing order of energy.

The quantum circuits that describe the preparation of the eigenstates $|E_1\rangle$ and $|E_4\rangle$ of the case $U_0 = 0$ are shown in Figure 27. Figure 28 shows the quantum circuits that describe the preparation of the states $|E_2\rangle$ and $|E_3\rangle$ of both $U_0 = 0$ and $U_0 = -5$ cases.

$$U = 0$$

$$|E_1\rangle \quad \frac{1}{2}(|\uparrow\downarrow, 0\rangle + |\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle + |0, \uparrow\downarrow\rangle)$$

$$|E_2\rangle \quad \frac{1}{\sqrt{2}}(|\uparrow\downarrow, 0\rangle - |0, \uparrow\downarrow\rangle)$$

$$|E_3\rangle \quad \frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)$$

$$|E_4\rangle \quad \frac{1}{2}(|\uparrow\downarrow, 0\rangle - |\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle + |0, \uparrow\downarrow\rangle)$$

Table 5 – Eigenstates of the two-site Hubbard Hamiltonian for U = 0, in increasing order of energy. The $|E_2\rangle$ and $|E_3\rangle$ states are degenerate.

$ 0\rangle$ — H —	$ 0\rangle - X - H$
$ 0\rangle$ — H —	$ 0\rangle - X - H$

Figure 27 – Quantum circuits that prepare the states $|E_1\rangle$ (left) and $|E_4\rangle$ (right), for $U_0 = 0$.



Figure 28 – Quantum circuits that prepare the states $|E_2\rangle$ (left) and $|E_3\rangle$ (right), for both $U_0 = 0$ and $U_0 = -5$.

To implement the states $|E_1\rangle$ and $|E_4\rangle$ of the $U_0 = -5$ case, the circuit shown in Figure 29 with controlled rotations around the *y*-direction was used. It is possible to implement such gates in the NMR experiment from the controlled- $R_z(\theta)$ gate, which is given by the following pulse sequence:

$$(\pi)_{1}^{x} - \left(\frac{\theta}{2\pi J_{12}}\right) - (\pi)_{1}^{x} - \left(\frac{\pi}{2}\right)_{a,b}^{y} - \left(\frac{\theta}{2}\right)_{a,b}^{x} - \left(-\frac{\pi}{2}\right)_{a,b}^{y}.$$
(5.34)

where $(\theta)_a^n$ represents a rotation on the qubit *a* of an angle θ around the *n*-axis; and (Δt) is a delay of duration Δt . In this notation, the pulses are applied from left to right. Using the fact that

$$R_x\left(-\frac{\pi}{2}\right)R_z(\theta)R_x\left(\frac{\pi}{2}\right) = R_y(\theta) \text{ and } R_x(-\pi/2)R_x(\pi/2) = \mathbb{1},$$
 (5.35)

the controlled $-R_y$ operation can be implemented through the application of the first circuit shown in Figure 30. That same operation with the conditional set to zero can

be achieved with two NOT operations applied on the control qubit before and after the controlled operation, as shown in the second circuit of Figure 30. The angles θ_1 , θ_2 and θ_3 of each rotation for each state are shown in Table 6.



Figure 29 – Circuit that prepares the states $|E_1\rangle$ and $|E_4\rangle$ for $U_0 = -5$.



Figure 30 – Circuits that implement the controlled- $R_y(\theta)$ operation.

State	$ heta_1$	θ_2	$ heta_3$
$ E_1\rangle$	90°	38.66°	141.3°
$ E_4\rangle$	90°	141.3°	38.66°

Table 6 – Rotation angles used to prepare the states $|E_1\rangle$ and $|E_4\rangle$ of the case $U_0 = -5$.

The fidelity is a quantity that measures the closeness of two quantum states ρ_1 and ρ_2 , and is given by (41):

$$F(\rho_1, \rho_2) = \left[\operatorname{Tr} \left\{ \sqrt{\sqrt{\rho_1} \rho_2 \sqrt{\rho_1}} \right\} \right]^2.$$
 (5.36)

It has the property $0 \le F(\rho_1, \rho_2) \le 1$, being equal to 0 for orthogonal states and 1 for two identical states. The initial states could be prepared with a fidelity higher than 0.95.

5.3 Results

With the data from each experiment, the density matrices were obtained and used to calculate some properties of the system. In all experiments, the parameter U was

increased from a set value of U_0 to a value of $U_f = 5$. As the initial state is always one of the eigenstates of \mathcal{H}_H , the simulated evolution time T was defined in such a way that the variation of U could be considered slow enough to guarantee that the system always stays in its instantaneous eigenstate (Table 7), which is asserted by the adiabatic theorem (42).

State	U = 5
$ E_1\rangle$	$0.2341(\uparrow\downarrow,0\rangle+ 0,\uparrow\downarrow\rangle)+0.6672(\uparrow,\downarrow\rangle+ \downarrow,\uparrow\rangle)$
$ E_3\rangle$	$rac{1}{\sqrt{2}}(\uparrow,\downarrow angle- \downarrow,\uparrow angle)$
$ E_2\rangle$	$rac{1}{\sqrt{2}}(\left \uparrow\downarrow,0 ight angle-\left 0,\uparrow\downarrow ight angle)$
$ E_4\rangle$	$0.6672(\uparrow\downarrow,0\rangle + 0,\uparrow\downarrow\rangle) - 0.2341(\uparrow,\downarrow\rangle + \downarrow,\uparrow\rangle)$

Table 7 – Eigenstates of the two-site Hubbard Hamiltonian for U = 5, in increasing order of energy.

The mean energy of the system was calculated for each step, and is given by

$$\langle \mathcal{H}_H \rangle = \text{Tr} \{ \mathcal{H}_H \rho \}.$$
 (5.37)

The results are shown in Figure 31. The colored circles are the experimental data, and the solid lines were calculated by obtaining the density matrix $\rho(t)$ as the solution of the Liouville von-Neumann equation (14)

$$\frac{\mathrm{d}[\rho(t)]}{\mathrm{d}t} = \frac{1}{i\hbar} [\mathcal{H}_H, \rho(t)], \qquad (5.38)$$

which was solved by the Gauss-Euler method (43). The uncertainty associated with each element of the density matrix after the quantum state tomography is of ± 0.02 (40).

To show that the quantum simulation carries the physics of the Hubbard Hamiltonian, the influence of the interaction U over the ordering of the two particles in the lattice was measured. From the density matrix of each time instant, the probabilities of having single and double occupancy, P_s and P_d , were calculated:

$$P_{s} = \operatorname{Tr}\{\rho \mid \uparrow, \downarrow \rangle \langle \uparrow, \downarrow |\} + \operatorname{Tr}\{\rho \mid \downarrow, \uparrow \rangle \langle \downarrow, \uparrow |\},$$

$$P_{d} = \operatorname{Tr}\{\rho \mid \uparrow \downarrow, 0 \rangle \langle \uparrow \downarrow, 0 |\} + \operatorname{Tr}\{\rho \mid 0, \uparrow \downarrow \rangle \langle 0, \uparrow \downarrow |\}.$$
(5.39)

In order to obtain the fidelity between experimental and theoretical results, a simulation in a classical computer was also performed, by dividing the evolution in the same M + 1number of steps and applying the evolution operator (5.24) in each step.

When the system is initially prepared in the ground state $|E_1\rangle$ for the interaction energy U = 0 (no interaction), none of the configurations is favored, which is denoted



Figure 31 – Energies of the four eigenstates of the half-filling, $S_z = 0$ subspace of the two site Hubbard Hamiltonian, as a function of the interaction energy U, normalized by J_h .

by the wave function of the system being given by a balanced distribution of the four possible states $|\uparrow\downarrow, 0\rangle$, $|\uparrow, \downarrow\rangle$, $|\downarrow, \uparrow\rangle$ and $|0, \uparrow\downarrow\rangle$ (see Table 5). When the strength of the repulsive interactions U increases and becomes much greater than the kinetic energy J_h $(|U| >> J_h)$, it is energetically costly for the particles to stay in the same site. Therefore, the ground-state of the system will prefer to adopt a single-occupancy configuration, in an analog of the crossover from a metallic to a Mott-insulator regime for the two-site, half-filling case (24). This result is shown in Figure 32.

When the system starts in the ground state $|E_1\rangle$ for $U_0 = -5$, the double occupancy is initially favored, even though $|U| >> J_h$. This can be explained by the fact that in this case the interaction energy U is attractive, favoring the formation of paired states, which can be interpreted as the two-particle analog of a charge-density wave state (9). As the magnitude of the attractive U is decreased, double occupancy becomes less favored until it reaches the balanced state in U = 0. The magnitude of U begins to increase again, but this time repulsively, and single occupancy becomes favored once again for $|U| >> J_h$. The whole process is shown in Figure 33.

The wave functions of the eigenstates $|E_2\rangle$ and $|E_3\rangle$ do not depend on U and J_h , and thus they have the same form for any value of those parameters (39). Therefore, $|E_2\rangle$ and $|E_3\rangle$ are stationary states of the Hubbard Hamiltonian, and if the system is prepared on one of them it will not evolve in time (14). The wave function for $|E_2\rangle$ contains non-zero



Figure 32 – Above: Probabilities of single and double occupancy as a function of the interaction energy U/J_h for the simulation with $U_0 = 0$, $U_f = 5$, T = 10, M = 30 and initial state $|E_1\rangle$ (ground state). The ground state of the system becomes an analog of a Mott-insulator for increasing repulsive interactions. The solid lines indicate the theoretical prediction of the Hubbard Hamiltonian, simulated on a classical computer by the Liouville von-Neumann equation (5.38). The fidelity between the classical and quantum simulations is shown in the green solid line. Below: Density matrices of the initial state $|E_1\rangle$ and the final state of the simulation.

components only for $|\uparrow\downarrow, 0\rangle$ and $|0,\uparrow\downarrow\rangle$, and thus the probability for double occupancy is $P_d = 1$, and $P_s = 0$ for single occupancy, for all values of U. For the state $|E_3\rangle$, these probabilities are reversed ($P_d = 0$ and $P_s = 1$), as the wave function contains non-zero components only for $|\uparrow,\downarrow\rangle$ and $|\downarrow,\uparrow\rangle$. These results are shown in Figures 34 and 35.

The highest-energy state $|E_4\rangle$ presents an opposite behavior from that observed



Figure 33 – Probabilities of single and double occupancy as a function of the interaction energy U/J_h and fidelity for the simulation with $U_0 = -5$, $U_f = 5$, T = 4, M = 30 and initial state $|E_1\rangle$ (ground state). In the attractive case, the double occupancy is favored as the magnitude of the interaction increases. Below: Density matrices of the initial state $|E_1\rangle$ and the final state of the simulation.

on the ground-state, as shown in Figure 36. The double occupancy is enhanced as the repulsive interaction is increased, which denotes a formation of a charge-density-wave state on a repulsive regime. This was expected from the Hubbard model theory, as in the repulsive case the configurations that present the highest energies are those in which the fermions occupy the same site. This way, as the repulsion U increases, the probability of finding double occupied sites should also increase, which was observed in the quantum simulation.



Figure 34 – Above: Probabilities of single and double occupancy as a function of the interaction energy U/J_h and fidelity for the simulation with $U_0 = -5$, $U_f = 5$, T = 4, M = 20 and initial state $|E_2\rangle$. As $|E_2\rangle$ is an eigenvalue of \mathcal{H}_H for all values of U and J_h , it will be an stationary state. Below: Density matrices of the initial state $|E_2\rangle$ and the final state of the simulation.



Figure 35 – Above: Probabilities of single and double occupancy as a function of the interaction energy U/J_h and fidelity for the simulation with $U_0 = -5$, $U_f = 5$, T = 4, M = 20 and initial state $|E_3\rangle$. As well as $|E_2\rangle$, $|E_3\rangle$ is also an eigenvalue of \mathcal{H}_H for all values of U and J_h , therefore it is also an stationary state. Below: Density matrices of the initial state $|E_3\rangle$ and the final state of the simulation.



Figure 36 – Above: Probabilities of single and double occupancy as a function of the interaction energy U/J_h and fidelity for the simulation with $U_0 = 0$, $U_f = 5$, T = 10, M = 30 and initial state $|E_4\rangle$. As U increases, the double occupancy is favored, which is the highest energy configuration that the system can reach.

6 Conclusion

The work that composes this dissertation performs the quantum simulation of the two site Hubbard model in an NMR quantum computer. Using the nuclear spins of the ¹H and ¹³C of a CHCl₃ molecule as the qubits, the physical system to be simulated was mapped on the simulator, using a procedure similar to that shown in the pioneer work of Somaroo *et al* (18). The mapping allowed to control, with good precision in the quantum computer, the kinetic energy J_h and the Coulomb interaction U of the Hubbard Hamiltonian. Varying these parameters in order to change the ratio U/J_h revealed that the ground state of the system undergoes a transition from a conductor to a Mott insulator under high repulsion regime ($U >> J_h$). In the attractive case, a regime of paired-states takes place when the same conditions are met. All the results agreed with the theoretic models. A simulation of the problem was also performed in a classical computer, using the Liouville equation to find the density matrix of the system. The data was compared with that of the quantum simulation, which showed a great fidelity with the theoretical expectation.

Excited energy states were also simulated, presenting the behavior expected from the Hubbard model, with the first two excited states being stationary and the higher energy level presenting the opposite configuration of the ground state. The results were also compared with the classical simulation, and presented great fidelity with the theoretical expectation.

The quantum simulation showed itself as a good approach to the problem of founding the dynamics of the one dimensional Hubbard Hamiltonian. We have several perspectives for future works. We would like to increase the number of sites on the one dimensional case, and study the two dimensional case of the model, which is a problem that has not been solved completely, and discover how the quantum simulations can bring new paradigms to the study of electron correlations and many body problems. Both goals will need more than two qubits to map the problem on a quantum computer. One of the ideas is to perform the simulations on commercial quantum computers such as those from *IBM* and *D-Wave*, which possess higher number of qubits and can be remotely controlled via Internet.

Bibliography

1 ASHCROFT, N. W.; MERMIN, N. D. *Solid state physics*. [S.l.]: New York: Holt, Rinehart and Winston, 1976. Quoted on page 21.

2 SOMMERFELD, A. Zur elektronentheorie der metalle auf grund der fermischen statistik. *Zeitschrift für Physik*, Springer, v. 47, n. 1-2, p. 1–32, 1928. Quoted on page 21.

3 SALINAS, S. Introdução à Física Estatística, 2a Edição. [S.l.]: Edusp, 2005. Quoted 4 times on pages 21, 31, 66, and 68.

4 KITTEL, C.; MCEUEN, P. Introduction to solid state physics. [S.l.]: Wiley New York, 1996. Quoted 3 times on pages 21, 44, and 67.

5 GUTZWILLER, M. C. Effect of correlation on the ferromagnetism of transition metals. *Physical Review Letters*, APS, v. 10, n. 5, p. 159, 1963. Quoted 2 times on pages 22 and 65.

6 KANAMORI, J. Electron correlation and ferromagnetism of transition metals. *Progress of Theoretical Physics*, Oxford University Press, v. 30, n. 3, p. 275–289, 1963. Quoted 2 times on pages 22 and 65.

7 HUBBARD, J. Electron correlations in narrow energy bands. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, The Royal Society London, v. 276, n. 1365, p. 238–257, 1963. Quoted 3 times on pages 22, 65, and 67.

8 GEBHARD, F. *The Mott Metal-Insulator Transition: Models and Methods*. [S.l.]: Springer-Verlag Berlin Heidelberg, 1997. Quoted 3 times on pages 22, 65, and 74.

9 HO, A.; CAZALILLA, M.; GIAMARCHI, T. Quantum simulation of the hubbard model: The attractive route. *Physical Review A*, APS, v. 79, n. 3, p. 033620, 2009. Quoted 3 times on pages 22, 72, and 86.

10 GREINER, M. et al. Quantum phase transition from a superfluid to a mott insulator in a gas of ultracold atoms. *Nature*, Nature Publishing Group, v. 415, n. 6867, p. 39–44, 2002. Quoted on page 22.

11 JÖRDENS, R. et al. A mott insulator of fermionic atoms in an optical lattice. *Nature*, Nature Publishing Group, v. 455, n. 7210, p. 204–207, 2008. Quoted on page 22.

12 LEBLANC, J. et al. Solutions of the two-dimensional hubbard model: benchmarks and results from a wide range of numerical algorithms. *Physical Review X*, APS, v. 5, n. 4, p. 041041, 2015. Quoted on page 22.

13 FEYNMAN, R. P. Simulating physics with computers. *International journal of theoretical physics*, Springer, v. 21, n. 6, p. 467–488, 1982. Quoted 3 times on pages 22, 51, and 75.

14 COHEN-TANNOUDJI, C.; DIU, B.; LALOE, F. *Quantum Mechanics, volume 1. Hermann and John Wiley & Sons.* [S.l.]: AAA, 1977. v. 1. Quoted 14 times on pages 23, 25, 31, 40, 52, 53, 59, 65, 68, 72, 76, 81, 85, and 86. 15 NIELSEN, M. A.; CHUANG, I. *Quantum computation and quantum information*. [S.l.]: AAPT, 2002. Quoted 7 times on pages 23, 51, 55, 58, 59, 61, and 76.

16 LLOYD, S. Universal quantum simulators. *Science*, JSTOR, p. 1073–1078, 1996. Quoted 2 times on pages 23 and 75.

17 ZALKA, C. Simulating quantum systems on a quantum computer. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, The Royal Society, v. 454, n. 1969, p. 313–322, 1998. Quoted 2 times on pages 23 and 75.

18 SOMAROO, S. et al. Quantum simulations on a quantum computer. *Physical review letters*, APS, v. 82, n. 26, p. 5381, 1999. Quoted 3 times on pages 23, 75, and 93.

19 GERSHENFELD, N. A.; CHUANG, I. L. Bulk spin-resonance quantum computation. *science*, American Association for the Advancement of Science, v. 275, n. 5298, p. 350–356, 1997. Quoted 3 times on pages 23, 58, and 60.

20 RABI, I. I. et al. A new method of measuring nuclear magnetic moment. *Phys. Rev.*, American Physical Society, v. 53, n. 4, p. 318–318, 1938. Quoted on page 23.

21 LEVITT, M. H. Spin dynamics: basics of nuclear magnetic resonance. [S.l.]: John Wiley & Sons, 2001. Quoted 8 times on pages 23, 36, 38, 39, 41, 42, 44, and 58.

22 HAHN, E. L. Spin echoes. *Physical review*, APS, v. 80, n. 4, p. 580, 1950. Quoted 2 times on pages 24 and 38.

23 OLIVEIRA, I. et al. *NMR quantum information processing*. [S.l.]: Elsevier, 2011. Quoted 9 times on pages 24, 26, 32, 39, 42, 51, 60, 61, and 63.

24 MURMANN, S. et al. Two fermions in a double well: Exploring a fundamental building block of the hubbard model. *Physical review letters*, APS, v. 114, n. 8, p. 080402, 2015. Quoted 2 times on pages 24 and 86.

25 KRANE, K. S.; HALLIDAY, D. et al. *Introductory nuclear physics*. [S.I.]: John Wiley & Sons Inc, 1987. Quoted on page 26.

26 SLICHTER, C. P. *Principles of magnetic resonance*. [S.l.]: Springer Science & Business Media, 2013. v. 1. Quoted 6 times on pages 26, 29, 35, 41, 59, and 60.

27 LEMOS, N. Mecânica analítica. [S.l.]: Livraria da Física, 2007. Quoted on page 27.

28 COHEN-TANNOUDJI, C. et al. *Quantum Mechanics*. [S.1.]: Wiley-Interscience, 2006. Quoted on page 30.

29 BLOCH, F. Nuclear induction. *Physical review*, APS, v. 70, n. 7-8, p. 460, 1946. Quoted on page 34.

30 RILEY, K. F.; HOBSON, M. P.; BENCE, S. J. Mathematical methods for physics and engineering: a comprehensive guide. [S.l.]: Cambridge University Press, 2006. Quoted on page 37.

31 CARR, H. Y.; PURCELL, E. M. Effects of diffusion on free precession in nuclear magnetic resonance experiments. *Phys. Rev.*, American Physical Society, v. 94, p. 630–638, 1954. Quoted on page 39.

32 NUSSENZVEIG, H. M. Curso de Física Básica: Eletromagnetismo (vol. 3). [S.1.]: Editora Blucher, 2015. Quoted on page 45.

33 DEUTSCH, D. Quantum theory, the church-turing principle and the universal quantum computer. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, The Royal Society London, v. 400, n. 1818, p. 97–117, 1985. Quoted on page 51.

34 BENENTI, G.; CASATI, G.; STRINI, G. *Principles of Quantum Computation and Information: Basic tools and special topics.* [S.l.]: World Scientific, 2004. v. 2. Quoted 2 times on pages 51 and 55.

35 BALIAN, R. From microphysics to macrophysics: methods and applications of statistical physics. [S.l.]: Springer Science & Business Media, 2007. v. 1. Quoted 2 times on pages 59 and 60.

36 D'ARIANO, G. M. Universal quantum estimation. *Physics Letters A*, Elsevier, v. 268, n. 3, p. 151–157, 2000. Quoted on page 61.

37 LEE, J.-S. The quantum state tomography on an nmr system. *Physics Letters A*, Elsevier, v. 305, n. 6, p. 349–353, 2002. Quoted 2 times on pages 62 and 63.

38 ESSLER, F. H. L. et al. *The One-Dimensional Hubbard Model.* [S.1.]: Cambridge University Press, 2005. Quoted on page 65.

39 HARRIS, A. B.; LANGE, R. V. Single-particle excitations in narrow energy bands. *Physical Review*, APS, v. 157, n. 2, p. 295, 1967. Quoted 2 times on pages 73 and 86.

40 PETERSON, J. P. et al. Reliability of digitized quantum annealing and the decay of entanglement. *Annalen der Physik*, Wiley Online Library, v. 530, n. 7, p. 1800007, 2018. Quoted 2 times on pages 81 and 85.

41 JOZSA, R. Fidelity for mixed quantum states. *Journal of modern optics*, Taylor & Francis, v. 41, n. 12, p. 2315–2323, 1994. Quoted on page 84.

42 GRIFFITHS, D. J.; SCHROETER, D. F. Introduction to quantum mechanics. [S.1.]: Cambridge University Press, 2018. Quoted on page 85.

43 SCHERER, C. *Métodos da Física Computacional*. [S.l.]: Livraria da Física, 2005. Quoted on page 85.