

**Numerical Treatment of the
Liouville-von Neumann Equation
for Quantum Spin Dynamics**

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Declaration

I declare that this thesis was composed by myself and that the work contained therein is my own, except where explicitly stated otherwise in the text.

(Giacomo Mazzi)

Abstract

This thesis is concerned with the design of numerical methods for quantum simulation and the development of improved models for quantum relaxation. Analysis is presented for the treatment of quantum systems using the density matrix formalism. This approach has been developed from the early days of quantum mechanics as a tool to describe from a statistical point of view a large number of identical quantum ensembles.

Traditional methods are well established and reliable, but they perform poorly for practical simulation as the system size is scaled up. Ad hoc schemes for nuclear spin dynamics appearing in the literature can be shown to fail in certain situations. The challenge is therefore to identify efficient reduction methods for the quantum system which are also based on a rigorous foundation. The method presented in the thesis, for the time-independent Hamiltonian case, combines a quantum density matrix formalism with a procedure based on Chebyshev polynomials; application of the method to Nuclear Magnetic Resonance (NMR) spectroscopy is considered, and it is shown that the new technique outperforms existing alternatives in term of computational costs.

The case of a time-dependent Hamiltonian in NMR simulation is studied as well and some splitting methods are presented. To the author's knowledge this is the first time such methods have been applied within the NMR framework, and the numerical results show a better error-to-cost rate than traditional methods.

In a separate strand of research, formulations for open quantum systems are studied and new dynamical systems approaches are considered for this problem.

Motivations

This thesis work is mainly focused on nuclear spin dynamics. Nuclear spin dynamics constitutes the basis for NMR, which is a very powerful spectroscopy technique that exploits the interaction between nuclear spins and magnetic fields. The same technique is used to reveal the presence of hydrogen atoms in the blood for Magnetic Resonance Imaging (MRI). Within this framework the role of simulations is extremely important, as it provides a benchmark for studies of new materials, and the development of new magnetic fields. The main computational issue is that with current software for NMR simulation it is extremely expensive to deal with systems made of more than few (7–10) spins. There is therefore a strong need to develop new algorithms capable of simulating larger systems.

In recent years NMR simulations have been found to be one of the most favorable candidates for quantum computing. There are two reasons for this: nuclear quantum states maintain extremely long coherences, and it is possible to attain a very strong control on the quantum state via the application of sequences of pulses. In order to develop a proper quantum computer it is fundamental to understand how the entangled states lose coherence and relax back to equilibrium by means of external interactions. This process is described as relaxation in an open quantum system. The theory for

such systems has been available for 50 years but there are still substantial limitations in the two main approaches. There are also relatively few numerical approaches for the simulation of such systems, for this reason it is important to develop numerical alternatives for the description of open quantum systems.

Thesis Outline

The thesis is organized as follow: the first two chapters provide background material to familiarize the reader with fundamental concepts of both quantum mechanics and nuclear spin dynamics; in this part of the thesis no new results are presented.

The first chapter introduces the concept of quantum systems and the mathematical environment with which we describe those systems. We also present the main equations we need to solve to determine the dynamics of a quantum system in a statistical framework.

In the second chapter we introduce the nuclear spin system, that is the physical system that has been the main reference frame in this work, for both tests and practical applications of the new algorithms. We describe how nuclear spin systems are at the basis of very important applications like NMR spectroscopy and MRI. We present in some detail the physical features of the NMR technique and the equations we need to solve to describe the dynamics of a spin system; we also focus on the relevance of numerical simulations for these systems, and consequently which must be the interest in developing new algorithms, and the major obstacles which must be overcome.

In the third chapter we investigate the numerical challenges that arise in simulation of quantum systems, we describe some of the methods that have been developed in the literature, focusing on the performances and the computational costs of them, setting the new developments of this thesis in the proper research frame. We discuss one of the major issues: the evaluation of the matrix exponential.

We also present the analysis we have done of a recent method called Zero Track Elimination (ZTE) that has been developed specifically for NMR simulations. This analysis shows the limitations of this method but also gives a mathematical explanation of why—and in which cases—it works.

In the fourth chapter we present the main result of the thesis, the development of a new method that directly evaluates the expectation values for a quantum simulation via a different application of the well known Chebyshev expansion. We have proved that this new method can provide an excellent boost in terms of performance, with computational costs that can be reduced by a factor ten in common cases. (The results of this chapter and the new method have been presented in international conferences and recently they have been submitted for publication).

We also present some attempts we have made in the application of splitting methods for the evolution of the system in a time dependent environment. To our knowledge this is the first time splitting methods have been used for NMR simulations. The results

of this approach are as follows: for a particular splitting technique combined with a Lanczos iteration method it is possible to speed up the calculation by a third if compared with a Lanczos type method whilst keeping the error below a critical threshold. This last approach is still a work in progress especially in terms of developing clever ways to split the Hamiltonian.

The last chapter of this thesis deals with simulation of quantum systems interacting with an external environment. After presenting the main theoretical approaches for the description of such systems we then survey several the techniques that are currently used for the numerical implementation of such theories. As a work in progress we present a considerably different new approach we have been developing aiming to overcome some of the issues that arise when treating this kind of system within usual frameworks. This is somewhat speculative work that gives rise to some new directions in the development of a numerical description for open quantum systems. We also present some numerical results. (The main core of this chapter has been presented in international conferences).

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Chapter 1

Background in Quantum Dynamics

1.1 Principles of Quantum Mechanics

In this section we introduce the main concepts of quantum mechanics, for a detailed and precise introduction on quantum mechanics we refer to classical texts like [74], [61].

Let us start by a simple analogy with the classical description: while a classical particle is completely defined by the position and the momentum, in quantum mechanics the state of the system is defined by a wave function $\Psi(q)$. The so called Born interpretation of the wave function, allows us to relate $\Psi(q)$ to the probability density $P(q) dq$ that is the probability to find the particle in the volume element $(q, q + dq)$ [13]

$$P(q) = \Psi^*(q)\Psi(q) = \|\Psi(q)\|^2. \quad (1.1)$$

Due to (1.1), the space where Ψ is defined is the Hilbert space of the square integrable functions of configuration space.

Within this space we may define a scalar product,

$$\langle \phi | \Psi \rangle = \int \phi(q)^* \Psi(q) dq. \quad (1.2)$$

To any dynamical quantity we associate a linear operator \hat{A} ; we define the mean value as

$$\langle \hat{A} \rangle = \langle \Psi | \hat{A} \Psi \rangle. \quad (1.3)$$

Due to the statistical nature of Ψ it is important to define also the variance, ΔA of \hat{A}

$$\Delta A^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle. \quad (1.4)$$

The condition for $\Delta A = 0$, that is to have a well defined value for \hat{A} , is

$$(\hat{A} - \langle \hat{A} \rangle \mathbb{I}) \Psi = 0 \rightarrow \hat{A} \Psi = \langle \hat{A} \rangle \Psi, \quad (1.5)$$

i.e. Ψ needs to be an eigenvalue of \hat{A} . At the same time, from (1.5), we see that the only precise values that $\langle \hat{A} \rangle$ can assume are elements of its spectrum.

1.1.1 The Dirac Formalism

So far we have been working in the so called space representation, i.e. treating Ψ as a function of the position. However this is not the only choice in terms of variable in Ψ : it is possible to change the representation for Ψ . We may reformulate all the previous section in a general form that does not depend on a particular representation.

Following Dirac we say that to each state of a quantum system is associated a vector in the complex space \mathbb{C} . This vector $|\Psi(t)\rangle$ is called *ket*. $|\Psi(t)\rangle$ may depend on the position q , on the momentum p , and on other variables of all the particles of the system. One of the postulates of quantum mechanics is that $|\Psi(t)\rangle$ contains all the information about the physical state. We may introduce also the *bra* vector, the bra vector is an

element of the bra space that is dual to the ket space. For any ket $|\Psi\rangle$ there exists a bra $\langle\Psi|$, and there is a one to one correspondence between the ket and the bra space, the bra dual of $c|\Psi\rangle$ where $c \in \mathbb{C}$ is a scalar quantity, is postulated to be $c^*\langle\Psi|$ and not $c\langle\Psi|$.

We may also define the inner product

$$\langle\Phi|\Psi\rangle = \langle\Psi|\Phi\rangle^*; \quad (1.6)$$

we say that two kets $|\Psi\rangle$ and $|\Phi\rangle$ are orthogonal if (1.6) is 0. We assume also that $|\Psi\rangle$ is normalized, that is $\langle\Psi|\Psi\rangle = 1$. The complex space spanned by the kets is a Hilbert space.

Experimentally it is not possible to observe directly $|\Psi(t)\rangle$: what can be measured in a quantum systems are the observables. If we look at the action of an operator $\hat{A} : D(A) \rightarrow L^2$ on bra and ket we have

$$\hat{A}|\Psi\rangle, \quad \langle\Psi|\hat{A} = \hat{A}^\dagger|\Psi\rangle, \quad (1.7)$$

where we have defined another operator \hat{A}^\dagger such that the right hand side of (1.7) holds. If $\hat{A} = \hat{A}^\dagger$ we say that \hat{A} is self-adjoint, or Hermitian. The observables are self-adjoint operators.

We define eigenkets of an Hermitian operator \hat{A} kets for which $\hat{A}|\psi_k\rangle = k|\psi_k\rangle$. Given an eigenpair k, ψ of \hat{A} and using the bilinearity of \hat{A} we may immediately see that

$$\langle\psi_k|\hat{A}|\psi_k\rangle = k^*\langle\psi_k|\psi_k\rangle = \langle\psi_k|\psi_k\rangle k_k, \quad (1.8)$$

so $k^* = k \in \mathbb{R}$. It is also possible to prove that $\langle\psi_k|\psi_{k'}\rangle = \delta_{k,k'}$. We may expand any given ket $|\Phi\rangle$ in terms of the eigenkets of A

$$|\Phi\rangle = \sum_k c_k |\psi_k\rangle, \quad c_k = \langle\psi_k|\Phi\rangle, \quad (1.9)$$

in other words

$$|\Phi\rangle = \sum_k |\psi_k\rangle \langle\psi_k|\Phi\rangle, \quad (1.10)$$

which may be seen as the action of a projection operator $|\psi_k\rangle\langle\psi_k|$ over $|\Phi\rangle$.

Because of the fact that (1.10) is true for any $|\Phi\rangle$ we have also the completeness relation

$$\sum_k |\psi_k\rangle\langle\psi_k| = 1. \quad (1.11)$$

The expectation value of an observable \hat{A} with respect to $|\Psi\rangle$ is

$$\langle A \rangle = \langle\Psi|\hat{A}|\Psi\rangle. \quad (1.12)$$

It is possible to represent an operator in a matrix formalism; if $|\psi_k\rangle$ is the N

dimensional base kets we may have, using twice (1.11)

$$\hat{B} = \sum_k \sum_{k'} |\psi_{k'}\rangle \langle \psi_{k'} | \hat{B} | \psi_k\rangle \langle \psi_k|. \quad (1.13)$$

We may write

$$\hat{B} = \begin{pmatrix} \langle \psi_1 | \hat{B} | \psi_1 \rangle & \dots & \langle \psi_1 | \hat{B} | \psi_N \rangle \\ \dots & \dots & \dots \\ \langle \psi_N | \hat{B} | \psi_1 \rangle & \dots & \langle \psi_N | \hat{B} | \psi_N \rangle \end{pmatrix}. \quad (1.14)$$

An important remark on observables is that if, for two observables, there holds

$$[\hat{A}, \hat{B}] = 0, \quad (1.15)$$

then we say that \hat{A} and \hat{B} are compatible, and that the representation of both of them in the same set of base kets is diagonal. This property is very useful when (as we will see in the spin dynamics case) one of the two eigenkets is degenerate, i.e. two or more $|\psi_k\rangle$ have the same eigenvalue. In this case we may use the eigenvalues of the other operator to label these degenerate kets. Using (1.15) it is possible to build a complete orthonormal basis set for \mathcal{H} , in fact we have to find a maximal set of operators for which these holds

$$[\hat{A}, \hat{B}] = [\hat{B}, \hat{C}] = [\hat{A}, \hat{C}] = \dots = 0. \quad (1.16)$$

The eigenvalues of individual operators may have degeneracies but the simultaneous eigenket of \hat{A}, \hat{B}, \dots , with eigenvalues a, b, c, \dots is uniquely specified.

To relate the Dirac formalism with the “usual” quantum mechanics formalism of wave functions Ψ we may apply it to a simple system. We may recast $\Psi(q)$ within this formalism. Let us introduce the position space for a single particle moving in one dimension, [74]. In this space the base kets used are the position kets

$$\hat{q}|q'\rangle = q'|q'\rangle, \quad (1.17)$$

where q' is a certain position while \hat{q} is the position operator, and

$$\langle q'' | q' \rangle = \delta(q'' - q'). \quad (1.18)$$

Any given ket $|\Psi\rangle$ may be expanded in this base

$$|\Psi\rangle = \int dq' |q'\rangle \langle q' | \Psi \rangle. \quad (1.19)$$

where $|\langle q' | \Psi \rangle|^2 dq'$ is the probability for the particle to be found in a neighborhood dq' around q' . As expected if $|\Psi\rangle$ is normalized the probability to find the particle somewhere between $-\infty$ and ∞ is

$$\langle \Psi | \Psi \rangle = \int_{-\infty}^{\infty} dq' \langle \Psi | q' \rangle \langle q' | \Psi \rangle = 1. \quad (1.20)$$

The well known $\Psi(q')$ for the state $|\Psi\rangle$ is

$$\Psi(q') = \langle q'|\Psi\rangle. \quad (1.21)$$

If we look at the inner product $\langle\Psi|\Phi\rangle$ and using the completeness of $|q'\rangle$ (1.11) we have

$$\langle\Psi|\Phi\rangle = \int dq' \langle\Psi|q'\rangle \langle q'|\Phi\rangle = \int dq' \Psi^*(q') \Phi(q'), \quad (1.22)$$

and (1.22) characterizes the overlap between the two wave function. An important remark is that $\langle\Psi|\Phi\rangle$ is a more general expression than the right hand side of (1.22) as it does not depend of the representation. Within the framework of this example we may also reformulate the ket expansion into the eigenkets by multiplying (1.10) with $\langle x'|$

$$\langle x'|\Phi\rangle = \sum_k \langle x'|\psi_k\rangle \langle\psi_k|\Phi\rangle, \quad (1.23)$$

that is

$$\Phi(x') = \sum_k c_k u_k(x'), \quad (1.24)$$

where we have introduced an eigenfunction of A with eigenvalue k

$$u_k(x') = \langle x'|\Phi\rangle. \quad (1.25)$$

1.2 The Schrödinger Equation

Now that we have introduced the features needed for a description of a quantum system we focus on the dynamics of such objects.

The equation of motion for $|\Psi(t)\rangle$ is the Schrödinger equation

$$\frac{\partial|\Psi(t)\rangle}{\partial t} = -\frac{i}{\hbar} H|\Psi(t)\rangle, \quad (1.26)$$

where $i = \sqrt{-1}$ and \hbar has the dimensions of energy divided by frequency; $\hbar = 1.054 \times 10^{-34}$ Joule per sec. For simplicity we suppose we are using physical quantities normalized so that $\hbar = 1$. We may define the time propagator $U(t, t_0)$ as

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle. \quad (1.27)$$

the propagator solves a similar differential equation to (1.26)

$$\frac{dU}{dt} = -iHU, \quad U(0) = \text{Id}. \quad (1.28)$$

When H is time independent it is possible to have an exact formulation of the solution. A theorem by Stone [80] guarantees the unitarity of the propagator.

Theorem 1.2.1 (Stone). *If H is Hermitian on a Hilbert space \mathcal{H} , there is a unique*

family of unitary operators e^{-iHt} with the following properties

- (group property): $e^{-iH(t+s)} = e^{-iHt}e^{iHs}$ for all $s, t \in \mathbb{R}$;
- (strong continuity): for every $|\Psi_0\rangle \in \mathcal{H}$,

$$e^{-iHt}|\Psi_0\rangle \rightarrow |\Psi_0\rangle \quad \text{as } t \rightarrow 0. \quad (1.29)$$

- (solution): the solution of the Schrödinger Equation is $|\Psi(t)\rangle = e^{-iHt}|\Psi_0\rangle$ for a initial value $|\Psi_0\rangle$

$$i\frac{d}{dt}e^{-iHt}|\Psi_0\rangle = He^{-iHt}|\Psi_0\rangle. \quad (1.30)$$

For the expectation value of operator \hat{A} over $|\Psi(t)\rangle$ we have that

$$\langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\Psi_0|U^\dagger(t) \cdot \hat{A} \cdot U(t)|\Psi_0\rangle. \quad (1.31)$$

For the last term of (1.31) we may think of U^\dagger, U as operators acting on the state $|\Psi_0\rangle$, and see (1.31) as the expectation value of \hat{A} over evolving states as the first term, or we could also think of the propagators acting on the operator \hat{A} that is then averaged over the static Ψ_0 . In the latter formulation, known as the Heisenberg picture, we have that

$$\langle\Psi_0|\hat{A}(t)|\Psi_0\rangle, \quad \hat{A}(t) = U^\dagger(t)\hat{A}U(t). \quad (1.32)$$

For time dependent \hat{A} we have

$$\frac{d\hat{A}}{dt} = -i[\hat{A}(t), \hat{H}] + \frac{\partial A}{\partial t}, \quad (1.33)$$

which is called Heisenberg equation.

From a mathematical point of view we may examine the treatment of the Schrödinger equation with a linear ordinary differential equation (ODE). To do that we assume that $|\Psi\rangle$ may be expanded into a basis set $|\Phi_k\rangle$, as in (1.23),

$$|\Psi(t)\rangle = \sum_{k=1}^K c_k(t)|\Phi_k\rangle. \quad (1.34)$$

The linear system of ODE for the time dependent coefficients $c_k(t)$ is

$$i\dot{c} = H_K c, \quad c = \begin{pmatrix} c_1 \\ \dots \\ c_K \end{pmatrix}, \quad (1.35)$$

as $\langle\Phi_k|\Phi_j\rangle = \delta_{kj}$, where the matrix H_K has elements

$$H_K^{k,j} = \langle\Phi_k|\hat{H}|\Phi_j\rangle. \quad (1.36)$$

With this specification we may rewrite (1.35) as

$$i\dot{\Psi} = H\Psi. \quad (1.37)$$

If \mathcal{H} is infinite dimensional we may define a variational version of (1.37), however in all the physical cases considered in this work we assume that it is possible to describe the system via (1.37).

1.2.1 Time Dependent Hamiltonian

When \hat{H} is time dependent we cannot write down an explicit expression for the propagator; however we may split the propagation over any time interval as a sequence of infinitesimal unitary operators: $U(t, t_0) = \prod_j U(t + (j-1)\delta t, t + j\delta t)$, where each $U(t + dt, t) = 1 - iHdt$, and the combined propagator is unitary as a product of unitary propagators is unitary, see e.g. Chap. 8 of [61]. In the physics literature the formal solution is written by introducing the Dyson time ordering operator [22, 25], in mathematics it is done via the Magnus expansion of the matrix exponential.

It is possible to express the Schrödinger equation in a ODE structure like (1.35) also when H is time dependent. In this case (1.37) becomes

$$i\dot{\Psi} = H_K(t)\Psi, \quad H_K^{k,j} = \langle \Phi_k | \hat{H}(t) | \Phi_j \rangle. \quad (1.38)$$

For the Dyson time ordering operator we have that $U(t, t_0)$ may be written as

$$U(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t dt_1 \dots \int_{t_0}^t dt_n T\{H(t_1) \dots H(t_n)\}, \quad (1.39)$$

or using the exponential

$$U(t, t_0) = T\{e^{-i \int_{t_0}^t dt' H(t')}\}, \quad (1.40)$$

where we have not consider the difficult problem of the convergence of the series. The time ordering operator T applied to a set of Hamiltonians H at different time, orders this set in such a way that the time arguments increases from right to left, i.e.

$$T\{H(t_1), H(t_2)\} = \begin{cases} H(t_1)H(t_2) & \text{if } t_1 > t_2, \\ H(t_2)H(t_1) & \text{if } t_2 > t_1, \end{cases} \quad (1.41)$$

In Appendix 1 we give a proof of (1.39).

From a mathematical perspective it is straightforward to write an approximate solution for (1.37) as a Magnus expansion [56]. The ansatz is that there exists a matrix $\Omega(t)$ such that it is possible to write a solution for the propagator equation as

$$U(t, t_0) = e^{-i\Omega(t)}, \quad (1.42)$$

We may prove that $\Omega(t)$ may be written as a series expansion

$$\Omega(t) = \sum_{n=1}^{\infty} \Omega_n(t), \quad (1.43)$$

where the firsts terms are

$$\Omega_1(t) = -i \int_{t_0}^t dt_1 H(t_1), \quad (1.44)$$

$$\Omega_2(t) = -i \frac{1}{2} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 [H(t_1), H(t_2)], \quad (1.45)$$

$$\begin{aligned} \Omega_3(t) = & -i \frac{1}{6} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 [H(t_1), [H(t_2), H(t_3)]] \\ & + [[H(t_1), H(t_2)], H(t_3)]. \end{aligned} \quad (1.46)$$

For a general review of the application of the Magnus expansion see [11]. Again we leave a more detailed description of the Magnus expansion to Appendix 1.

It is interesting to see the connection between the Dyson propagator (1.39) and the Magnus expansion (1.42) [11, 45]; if we compare (1.42) and (1.39) we have

$$\sum_{j=1}^{\infty} \Omega_j(t) = \log \left(I + \sum_{j=1}^{\infty} P_j(t) \right), \quad (1.47)$$

where $P_j(t) = \int_{t_0}^t dt_1 \dots \int_{t_0}^{t_{n-1}} dt_n H_1 \dots H_n$. In the last expression the time ordering has been performed and consequently $t_1 \leq t_2 \dots \leq t_n$. It is possible to prove that each term P_j (respectively Ω_j) may be written as a linear combination of Ω_j (respectively P_j) of the same order. If we look at the firsts terms of both the expansion we see that [16]

$$\begin{aligned} P_1 &= \Omega_1, \\ P_2 &= \Omega_2 + \frac{1}{2} \Omega_1^2, \\ P_3 &= \Omega_3 + \frac{1}{2} (\Omega_1 \Omega_2 + \Omega_2 \Omega_1) + \frac{1}{3} \Omega_1^3. \end{aligned}$$

A similar equation may be written for the Ω_j as functions of the P_j .

1.3 The Density Matrix

As seen in the previous section a single quantum system is described by a wave function $|\Psi\rangle$. Systems of this kind are called *pure* quantum systems.

If the initial state is unknown, or if the system is an ensemble of identical quantum systems but not identically prepared, it is possible and useful to introduce a statistical description of the quantum system.

As will become clear in Chapter 5, this formalism is the only one usable when

dealing with quantum systems interacting with an environment. For a general review of quantum statistical mechanics see [14] and the very recent [87].

As an example we may think of a quantum system that has a finite number of possible states, but such that the initial state is unknown; therefore we may think of weighting each state with a real (positive) number that indicates the fractional population of that state, or the probability to find the system in that precise state.

We consider a collection of M pure ensembles each described by a state vector $|\Psi_\alpha\rangle$, with weight w_α , this system is called a *mixed* quantum system. The fractional populations obey the normalization condition

$$\sum_{\alpha=1}^M w_\alpha = 1. \quad (1.48)$$

If we make a measure of some observable \hat{A} we have that

$$\langle \hat{A} \rangle = \sum_{\alpha=1}^M w_\alpha \langle \Psi_\alpha | \hat{A} | \Psi_\alpha \rangle, \quad (1.49)$$

introducing a new operator, called by von Neumann the density matrix operator ϱ [95], we have

$$\varrho = \sum_{\alpha=1}^M w_\alpha |\Psi_\alpha\rangle \langle \Psi_\alpha|, \quad (1.50)$$

we may then rewrite (1.49) as

$$\langle \hat{A} \rangle = \text{Tr}\{\hat{A}\varrho\}. \quad (1.51)$$

If we expand $|\Psi_\alpha\rangle$ in the basis set $|\phi_j\rangle$: $\Psi_\alpha = \sum_{j=1}^n c_j |\phi_j\rangle$ we may write down the matrix elements for ϱ in this basis set

$$\langle \phi_j | \varrho | \phi_{j'} \rangle = \sum_{\alpha=1}^M w_\alpha \langle \phi_j | \Psi_\alpha \rangle \langle \Psi_\alpha | \phi_{j'} \rangle. \quad (1.52)$$

From (1.50) and (1.52) we check that ϱ is Hermitian, positive definite and has unit trace

$$\varrho^\dagger = \varrho, \quad \varrho \geq 0, \quad \text{Tr}\{\varrho\} = 1. \quad (1.53)$$

If we take as basis set the eigenvalues of H $\{|\psi_j\rangle\}$ with energies $\{E_j\}$ we have that at the equilibrium the fractional population obeys the Boltzmann–Gibbs distribution i.e. $w_j \propto e^{-\beta E_j}$. Consequently

$$\varrho_{eq} = \frac{\sum_{j=1}^n e^{-\beta E_j} |\psi_j\rangle \langle \psi_j|}{Z}, \quad (1.54)$$

where β is $(k_B T)^{-1}$; with k_B being the Boltzmann constant and T the temperature of the system; Z is the partition function and may be written as $Z = \text{Tr}\varrho_{eq} = \sum_j e^{-\beta E_j}$, this is because the diagonal element $\varrho_{jj} = \langle \psi_j | \varrho | \psi_j \rangle$ indicates the fractional population

for the state j . In this basis set we may then write

$$\varrho_{eq} = \frac{e^{-\beta H}}{Z}. \quad (1.55)$$

1.4 The Liouville–von Neumann Equation

Having defined ϱ we may write down the equation for its dynamics. If we take the time derivative of (1.50) for the autonomous case we have

$$\frac{\partial \varrho}{\partial t} = \sum_{\alpha=1}^M w_{\alpha} \left[\left(\frac{\partial}{\partial t} |\Psi_{\alpha}\rangle \right) \langle \Psi_{\alpha}| + |\Psi_{\alpha}\rangle \left(\frac{\partial}{\partial t} \langle \Psi_{\alpha}| \right) \right], \quad (1.56)$$

and because $\partial \Psi_{\alpha} / \partial t = -iH\Psi_{\alpha}$ we may write

$$\frac{\partial \varrho}{\partial t} = \sum_{\alpha=1}^M w_{\alpha} (-iH|\Psi_{\alpha}\rangle \langle \Psi_{\alpha}| + |\Psi_{\alpha}\rangle \langle \Psi_{\alpha}| iH). \quad (1.57)$$

Finally we see that

$$\frac{d\varrho(t)}{dt} = -i[H(t), \varrho(t)], \quad (1.58)$$

which is the *Liouville–von Neumann equation*. If we write the equation for the propagators of Ψ_{α} we have

$$\varrho(t) = \sum_{\alpha} w_{\alpha} U(t, t_0) |\Psi_{\alpha}(t_0)\rangle \langle \Psi_{\alpha}(t_0)| U^{\dagger}(t, t_0), \quad (1.59)$$

and consequently we may also write a formal solution for (1.58) and get

$$\varrho(t) = U(t, t_0) \varrho(t_0) U^{\dagger}(t, t_0). \quad (1.60)$$

Within this description we may derive the dynamics for the expectations for the observables, from (1.31) we see that

$$\langle \hat{A} \rangle = \text{Tr}\{\hat{A}\varrho(t)\}. \quad (1.61)$$

The study of numerical algorithms for the solution of these equations (1.58) and (1.61) is the main aim of this work.

1.4.1 The Interaction picture

A very useful framework for the dynamics is called the interaction or intermediate picture. This picture is very useful when we have an Hamiltonian composed of two terms $H = H_0 + H_1(t)$, where we are supposed to know the solution of the problem

when $H = H_0$. From (1.61) and (1.60) we may write

$$\langle \hat{A} \rangle = \text{Tr}\{\text{AU}(t, t_0)\varrho(t_0)U^\dagger(t, t_0)\}. \quad (1.62)$$

We may define $U_0(t, t_0) = e^{-iH_0(t-t_0)}$ and $U_I = U_0^\dagger(t, t_0)U(t, t_0)$, then (1.62) becomes

$$\langle \hat{A}(t) \rangle = \text{Tr}\{U_0^\dagger(t, t_0)\hat{A}U_0(t, t_0)U_I(t)\varrho(t_0)U_I^\dagger(t, t_0)\} = \text{Tr}\{A_I(t)\varrho_I(t)\}. \quad (1.63)$$

where we have defined

$$\hat{A}_I(t) = U_0^\dagger(t, t_0)\hat{A}(t)U_0(t, t_0), \quad (1.64)$$

$$\varrho_I(t) = U_I(t, t_0)\varrho(t_0)U_I^\dagger(t, t_0). \quad (1.65)$$

For $U_I(t)$, we may show that it obeys

$$i\frac{d}{dt}U_I(t, t_0) = \tilde{H}_I(t)U_I(t, t_0), \quad U_I(t_0, t_0) = \text{Id}. \quad (1.66)$$

The interaction Hamiltonian $\tilde{H}_I(t)$ is

$$\tilde{H}_I(t) = U^\dagger(t, t_0)H_I(t)U(t, t_0). \quad (1.67)$$

This type of picture is useful as a starting point for a perturbation theory approach to the problem described by H but also to move from a time dependent description to a time independent one.

Chapter 2

Nuclear Magnetic Resonance

2.1 Introduction

The interaction of a material with a magnetic field is described via a magnetic moment μ , the energy of the magnetization may be written as

$$E = -\mu \cdot B, \quad (2.1)$$

where the minus indicates that a magnetic dipole is favorable to be aligned along the direction of B rather than in the opposite direction.

The reasons for a sample to have a magnetic momentum are: the circulation of the electrons about the nuclei, the electronic spin, and the nuclear spin.

The first experimental evidence for the existence of the spin came from the observation of the multiplet structure of the spectra of atoms. The Stern–Gerlach experiment performed in 1922, showed that particles with spin possess also a magnetic moment proportional to it. A beam of collimated atoms of silver was transmitted through a region where a spatial inhomogeneous magnetic field was active, the deflection of the particle showed that the electrons possess not only an angular spin due to their rotation about the nucleus but also an intrinsic spin.

For the electronic magnetic moment related with the spin we have

$$\mu_e = g_e \frac{e}{2m_e c} s, \quad (2.2)$$

where s is the spin, e the electric charge, m_e the mass of the electron and c the speed of the light. The constant $g_e \simeq 2$ can be derived via a relativistic theory for the electron and is in excellent agreement with the experimental data.

The theoretical formulation of this degree of freedom that each elementary particle possesses was introduced by Pauli: elementary particles were divided into those with integer spin called *bosons* and those with half-integer spin called *fermions*. Experimental measures showed the existence of a nuclear magnetic moment as well, both protons and neutrons have spin $\frac{1}{2}$, the magnetic moment of the proton is

$$\mu_p = g_p \frac{e}{2M_p c} I, \quad (2.3)$$

where M_p is the mass of the proton and $g_p \simeq 5.59$.

2.2 The Nuclear Magnetic Resonance technique

Nuclear Magnetic Resonance (NMR) is a powerful spectroscopy technique used both for analysis on materials and biological tissues (liquid and Solid–State NMR). This technique exploits the interaction between the nuclear magnetic moments and external magnetic fields. With this technique it is possible to get extremely accurate structure studies and also underline some dynamical properties of the samples.

It is important to compare experimental results with computer simulations, especially when dealing with structure studies. In this case it is fundamental the comparison of spectrum of unknown materials with numerical simulations of ad-hoc prepared samples.

For reasons that will become clear later, great efforts have been made to develop new sequences of pulses; a unique feature of NMR spectroscopy is that the electromagnetic pulses are not only used to detect the spectrum of the sample, as in any other spectroscopy technique, but they can also modify enhancing and suppressing parts of the spectrum itself.

For this reason again numerical simulations are very useful to test the effect of new sequences of pulses on test samples.

Under the influence of an external magnetic field the nuclear magnetic moment starts to precess about the direction of the field, the frequency of this precession is called Larmor frequency and it is given by

$$\omega_0 = -\gamma B, \tag{2.4}$$

where γ is the gyromagnetic ratio and B the magnetic field.

The precession of the nuclear spins about the direction of the magnetic field B induces a magnetization of the sample. This induced magnetization is a consequence of the fact that a magnetic dipole, as the nuclear spin, aligned with B has less energy than one aligned in the opposite direction; consequently when the magnetic field is active there will be more spin pointing up. An explicit formulation of this phenomenon will be given in the next section.

The energy difference can be detected by inducing transitions between energy levels; it is possible to manipulate the spectrum via the applications of pulses that can favour or stop part of these transitions.

However it is almost impossible to detect directly this longitudinal magnetization. Comparing (2.2) and (2.3) we see that, due to the fact that $m_e = 9.1 \cdot 10^{-31} \text{Kg}$ and $M_p = 1.67 \cdot 10^{-27} \text{Kg}$, it is clear that the nuclear magnetic moment, and consequently the induced magnetization is 4 orders of magnitude smaller than the electronic one.

It is possible to overcome this issue via a rotation of the nuclear magnetization creating a perpendicular magnetization, as it will be shown in the next section, this rotation is performed applying one or more radio-frequency pulses to the sample, 2.3.1.

After the sequence of pulses has been applied the system is allowed to relax back to the equilibrium. During this relaxation time the signal called Free Induction Decay (FID) is measured, the Fourier transform of this signal gives the spectrum of the sample, where each spike is a energy gap between energy levels.

2.3 Microscopic Description

In a microscopic quantum description each atom is described by a spin wave function $|\Psi\rangle$, which depends only on spin variables, while the spin angular momentum is an operator \hat{I} , with three components $\hat{I}_x, \hat{I}_y, \hat{I}_z$. As any other angular momentum operators the components obey the commutation relations

$$[\hat{I}_x, \hat{I}_y] = i\hat{I}_z, \quad [\hat{I}_y, \hat{I}_z] = i\hat{I}_x, \quad [\hat{I}_z, \hat{I}_x] = i\hat{I}_y, \quad (2.5)$$

indeed in quantum mechanics an angular momentum is defined just as a vector operator that obeys (2.5) [61]. It is possible to prove that any components x, y, z of \hat{I} commute with \hat{I}^2 . Since they commute it is possible to form a complete set of common eigenfunctions of let us say \hat{I}_z and \hat{I}^2 .

From (2.5) we can prove that if a state has eigenvalue $I(I+1)$ with respect to \hat{I}^2 , then for that state there are $I+1$ possible eigenstates of \hat{I}_z with eigenvalues m that run from $-I, -I+1, \dots, I$. This set of eigenstates defined by the pair I, m are called the Zeeman set: $|I, m\rangle$. In the absence of an external magnetic field all these levels will be degenerate with respect to m .

For many elements, the nuclear spin has value $I = \frac{1}{2}$ and so \hat{I}^2 has got just one eigenvalue. Consequently the possible values for m are $\pm\frac{1}{2}$. For a single spin the two Zeeman eigenstates are

$$\begin{aligned} |\alpha\rangle &= \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \\ |\beta\rangle &= \left| \frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned} \quad (2.6)$$

In a matrix formalism we can set

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2.7)$$

$$|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (2.8)$$

If we use this basis set we may write down a matrix representation of the operators $\hat{I}_x, \hat{I}_y, \hat{I}_z, \hat{I}^2$, these matrices are called the *Pauli matrices*:

$$\sigma_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.9)$$

It is useful also to define the shift up and shift down operator \hat{I}_+, \hat{I}_- :

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y, \quad (2.10)$$

$$\hat{I}_- = \hat{I}_x - i\hat{I}_y. \quad (2.11)$$

These operators shift states from m to $m + 1$ and from m to $m - 1$. For instance $\hat{I}_+|\beta\rangle = |\alpha\rangle$, while $\hat{I}_-|\beta\rangle = 0$. Their matrix representation reads:

$$\sigma_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \sigma_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (2.12)$$

If a magnetic field B is applied along z the Hamiltonian will be $H = -\gamma BI_z$; there will be a split of the energy level, in fact,

$$H|\alpha\rangle = -\frac{\gamma B}{2}|\alpha\rangle, \quad (2.13)$$

$$H|\beta\rangle = +\frac{\gamma B}{2}|\beta\rangle, \quad (2.14)$$

and $\Delta E = \gamma B$ is the energy gap between $|\alpha\rangle$ and $|\beta\rangle$. Due to the fact that ϱ obeys the Boltzmann–Gibbs distribution we have that

$$\varrho = \frac{e^{-\beta H}}{\text{Tr } e^H}. \quad (2.15)$$

The energy difference makes more favorable the state $|\alpha\rangle$ rather than $|\beta\rangle$. The probability density for the population obeys the Boltzmann–Gibbs distribution, so for a state with energy E_k we have that the population, i.e. $\varrho_{[k,k]} = |\Psi_k\rangle\langle\Psi_k|$, satisfies

$$\varrho_{[k,k]} = \frac{e^{-E_k\beta}}{Z}, \quad (2.16)$$

where $\beta = 1/k_B T$ and k_B is the Boltzmann constant and T is the temperature of the system; Z is the distribution function. For Z we have

$$Z = \sum_s e^{-E_s\beta}. \quad (2.17)$$

However if we look at the order of magnitudes of the quantities we see that at room temperature $k_B T \simeq 4 \times 10^{-21} J$, while for the energy we have that $\hbar\omega_0 = -\hbar\gamma B^0 \simeq 3.3 \times 10^{-25} J$ for a proton when the magnetic field is $B^0 \simeq 10$ Tesla.

The four orders of magnitude of difference allows a simplification of (2.16); we may define the Boltzmann factor \mathcal{B}

$$\mathcal{B} = \frac{\hbar\gamma B^0}{k_B T} \simeq 10^{-4}. \quad (2.18)$$

We may then expand the exponential in terms of \mathcal{B} and have $e^{\pm\mathcal{B}} \simeq 1 \pm \mathcal{B}$, so $Z \simeq 2$,

for the populations we have

$$\varrho_{[|\alpha\rangle,|\alpha\rangle]} \simeq \frac{1}{2} + \frac{1}{4}\mathcal{B}, \quad (2.19)$$

$$\varrho_{[|\beta\rangle,|\beta\rangle]} \simeq \frac{1}{2} - \frac{1}{4}\mathcal{B}. \quad (2.20)$$

$$(2.21)$$

In a matrix form we have

$$\varrho^{\text{eq}} = \begin{pmatrix} \frac{1}{2} + \frac{1}{4}\mathcal{B} & 0 \\ 0 & \frac{1}{2} - \frac{1}{4}\mathcal{B} \end{pmatrix}, \quad (2.22)$$

that is, $\varrho^{\text{eq}} = \frac{1}{2}\text{Id} + \frac{1}{2}\mathcal{B}\hat{I}_z$. From now we consider as equilibrium, and as initial state, the situation when the static magnetic field is active, and has been active for enough time to have an equilibrium in the population of spin-up and spin-down particles.

For a system with n particles with spin I there is only a finite number of combinations up/down that the spins can take, and this number is $(2I + 1)^n$, so the Hilbert space where the simulation is performed has a finite dimension. Given the eigenstates of \hat{I}_z and \hat{I}^2 for a one spin system (2.6), it is possible to get those for n spin via a Kronecker product of the single spin states.

A system of n spins $\frac{1}{2}$ may also be expanded into the Zeeman basis set (2.6). For the general state we have

$$|m_1, m_2 \dots, m_n\rangle = |m_1\rangle \otimes |m_2\rangle \otimes \dots \otimes |m_n\rangle \quad (2.23)$$

where each m_j is either $+\frac{1}{2}$ or $-\frac{1}{2}$ and \otimes is the Kronecker product. It is elementary to show that the Kronecker product is not commutative, but is associative. Having defined the basis set for a general n spins system it is possible to write the matrix elements for the spin operators $\hat{I}_x, \hat{I}_y, \hat{I}_z$. It is important to see that because of the fact that I_ζ^j , where ζ can be either $\{x, y, z, +, -\}$ acts only on the spin j , we have that elements of the basis set are simultaneously an eigenstate of \hat{I}_z^j with eigenvalue m_j and of $\hat{I}_z = \sum_j \hat{I}_z^j$ with eigenvalue $m = \sum_j m_j$. Once we have constructed the basis set it is straightforward to get the matrix elements for the operators. Again we use the Kronecker product and define

$$I_\zeta^j = \text{Id} \otimes \dots \otimes I_\zeta \otimes \text{Id} \dots \otimes \text{Id}. \quad (2.24)$$

As we have seen in Chapter 1, the equation we need to solve to get the dynamics is the Liouville-von Neumann equation. The formal solution of $\varrho(t)$ is

$$\varrho(t) = U(t, t_0)\varrho_0 U(t, t_0)^\dagger. \quad (2.25)$$

Experimentally we can only measure the energy gap between energy level; the operator related to this quantity is the shift operator (up or down); so the quantity we

are interested in is the the expectation value of \hat{I}_+ :

$$f(t) = \langle \hat{I}_+ \rangle = \text{Tr}\{\varrho(t)\hat{I}_+\}. \quad (2.26)$$

Because of the unitarity nature of the propagator U in (2.25), there is no dissipation effect in the dynamics of $\varrho(t)$ and consequently of $f(t)$. For this reason if we evaluate the Fourier transform of $f(t)$ we will have a set of delta functions peaked at the energy differences between the states. On the the other hand when dealing with real experiments there will always be an interaction between the external environment and the spin system; this interaction will slowly destroy the coherence between states. The effect will be a relaxation of the signal and a return of $\varrho(t)$ to ϱ_{eq} . To take into account this relaxation effect, that will be analyzed in more detail in Chapter 5, it is common practice to smooth $f(t)$ by applying an exponential damping term, so that the Fourier Transform is not evaluated for $f(t)$ but for $\tilde{f}(t)$ where

$$\tilde{f}(t) = f(t)e^{-\Gamma t}. \quad (2.27)$$

The choice of Γ usually results from other experiments with similar composition are used but the procedure is still under discussion.

2.3.1 The Hamiltonian

In the general case the spins, as magnetic moments, do not simply interact with the external magnetic fields but also with each other. For a system consisting of n spins $\frac{1}{2}$, the Hamiltonian takes the form

$$H(t) = H_0 + H_{\text{rf}}(t) + H_{\text{CS}}(t) + H_{\text{D}}(t) + H_{\text{J}}(t). \quad (2.28)$$

In this section we will indicate with a Θ -dependency those elements of the Hamiltonian which depends on the orientation of the atoms (or of the respective orientation of a pair of atoms). The nature of the systems whether liquid, solid or an anisotropic material sample will change drastically the effect of this dependency. For instance in a fast moving isotropic liquid all the orientation-dependent terms will result in an averaged value over all possible orientations. On the other hand for solids the motion is very restricted, but at the same time we may think of a sample as a (large) collection of small samples each with its own orientation with respect to the sample; this condition is called “powder averaging” as the spectrum will be the combination of all the different elements of the powder. Let us now analyze the different terms of (2.28) one by one. H_0 takes into account the static magnetic field B that splits the energy levels, and it is proportional to \hat{I}_z . This, by orders of magnitude, is the largest contribution of the Hamiltonian.

H_{rf} describes the action of the sequence of radio-frequency pulses. The general

interaction with a magnetic field (time dependent or time independent) is

$$H_{\text{rf}}^j = -\gamma_j \hat{I}_j \cdot B(t). \quad (2.29)$$

Due to the key role of this term in NMR simulation, we will analyze it in the next section.

H_{CS} takes into account the “local” effects of the static magnetic field; these effects are due to the magnetic interaction of the environment that surrounds each atom. For instance the influence of B on the electrons will induce a current, this induced current will generate a magnetic field B^{ind} . B^{ind} varies from atom to atom for local conditions, so the effective magnetic field acting on the nucleus j is

$$B_j^{\text{eff}} = B + B_j^{\text{ind}}. \quad (2.30)$$

B_j^{ind} is proportional to B and we may write

$$B_j^{\text{ind}} = \delta_j \cdot B. \quad (2.31)$$

δ_j is called the chemical shift tensor. Because of the fact that B has only z component and using (2.29) we have

$$H_{\text{CS}} = -\gamma_j \delta_{xz}(\Theta)^j B \hat{I}_x^j - \gamma_j \delta_{yz}(\Theta)^j B \hat{I}_y^j - \gamma_j \delta_{zz}(\Theta)^j B \hat{I}_z^j. \quad (2.32)$$

For liquids usually only the isotropic component of δ^j remains due to the integration over all the possible orientations, for solids or anisotropic liquids the different orientation will generate a “dirt spectrum” where a broad peak is generated by the sum of all the different peaks coming from different molecules.

H_{D} is the term that describes the dipole-dipole interaction between nuclear spins. It depends on the mutual position of the spins with respect to the magnetic field B .

The general expression is the usual expression for an interaction between magnetic dipoles

$$H_{\text{D}} = \sum_{k,j} -\frac{\mu_0 \gamma_k \gamma_j \hbar}{4\pi r_{kj}^3} [3(\hat{I}^k \cdot e_{kj})(\hat{I}^j \cdot e_{kj}) - \hat{I}^k \cdot \hat{I}^j], \quad (2.33)$$

where r_{kj} and e_{kj} are, respectively, the distance between the nucleus and the dipolar unit vector. We may define the coupling constant

$$b_{kj} = -\frac{\mu_0 \gamma_k \gamma_j \hbar}{4\pi r_{kj}^3}. \quad (2.34)$$

The magnitude of this constant varies for different elements ranging from -4.5 kHz for two protons at 3 \AA to -15 Hz for two ^{13}C at 8 \AA . Clearly this term is strongly dependent on the nuclei orientation via the dot product in (2.33).

H_{J} is a peculiar term that is due to an indirect interaction between two spins mediated by the electrons. It basically takes into account the difference in energy

between respective orientations up–down of the electrons and the spins. This term may be written as

$$H_J = \sum_{kj} 2\pi \hat{I}^k \cdot J_{kj}(\Theta) \hat{I}^j, \quad (2.35)$$

where $J_{kj}(\Theta)$ is the J–coupling tensor. In most cases the anisotropic component of (2.35) is discarded [53], so (2.35) is replaced by the isotropic form

$$H_J = 2\pi J_{kj} \hat{I}^k \cdot \hat{I}^j. \quad (2.36)$$

Due to the fact that, typically, the Zeeman interaction $\omega_0^j \hat{I}_z^j$ is orders of magnitude larger than any other term of the Hamiltonian, it is possible to expand the other interactions into the Zeeman basis set retaining only the interactions with near–degenerate eigenstates [53]. This approximation is called the secular approximation and leads to a simpler expression for the Hamiltonian, which is the usual form used when dealing with simulations

$$\begin{aligned} H_{\text{CS}} &= \sum_j -\gamma_j B \delta_{zz}^j(\Theta) \hat{I}_z^j, \\ H_{\text{D}} &= \sum_{k,j} b_{k,j} \frac{1}{2} (3 \cos^2(\Theta_{kj}) - 1) (3 \hat{I}_z^k \hat{I}_z^j - \hat{I}^k \cdot \hat{I}^j), \\ H_J &= \sum_{k,j} 2\pi J_{kj} \hat{I}_z^k \hat{I}_z^j \quad (\text{for heteronuclear spins}), \\ H_J &= \sum_{k,j} 2\pi J_{kj} \hat{I}^k \cdot \hat{I}^j \quad (\text{for homonuclear spins}), \end{aligned}$$

where Θ refers to an angular dependency of that term, we will see in Sec. 2.3.3 that from this angular dependency comes the internal time dependency of the Hamiltonian. We refer to the Appendix for a brief review of the secular approximation.

2.3.2 The Pulse

In order to observe an NMR spectrum we need to irradiate the sample with electromagnetic radiation with frequency close to the Larmor frequency (ω_0). It is straightforward to see the effect of a pulse on a single spin system.

The magnetic field B_{rf} generated by the pulses, usually chosen with direction x may be written as a

$$B_{\text{rf}}(t) = B_{\text{rf}} \cos(\omega_{\text{rf}} t + \phi_p) e_x. \quad (2.37)$$

Because of the fact that the x and y component of I are rotating in the x, y plane, the field in (2.37) may be decomposed into two rotating components with the same frequency but rotating in opposite directions; as long as $|B| \gg |B_{\text{rf}}|$ only the component that is rotating in the same direction as the spin enters into the Hamiltonian [53, 74]. In the Appendix we prove this statement for a single spin via approximation theory.

We may then write

$$B_{\text{rf}}(t) = \frac{1}{2}b_{\text{rf}}\{\cos(\omega_{\text{rf}}t + \phi_p)e_x + \sin(\omega_{\text{rf}}t + \phi_p)\}e_y. \quad (2.38)$$

Obviously when the pulse is off $B_{\text{rf}}(t) = 0$. The effect of the pulse is to rotate the magnetization. Because of the rotation of $B_{\text{rf}}(t)$ in (2.38) it is convenient to introduce a time dependent frame, rotating with frequency ω_{rf} about the z axis and express all the quantities in such a frame. The relationship between the wave function in the laboratory frame (fixed) and the rotating frame is

$$|\tilde{\Psi}\rangle = R_z(-\Phi(t))|\Psi\rangle, \quad (2.39)$$

where $\Phi(t) = \omega_{\text{rf}}t$.

It is possible to prove that in the rotating frame the Schrodinger equation is expressed as

$$|\dot{\tilde{\Psi}}\rangle = -i\tilde{H}|\tilde{\Psi}\rangle, \quad (2.40)$$

with $\tilde{H} = R_z(-\Phi(t))HR_z(\Phi(t)) - \omega_{\text{rf}}I_z$, the last term may be easily included in H_0 as it is proportional to I_z . The rotating frame H_{RF} becomes time independent and we have for the whole Hamiltonian,

$$\tilde{H} = \frac{1}{2}\gamma b_{\text{rf}}\hat{I}_x + (\omega_0 - \omega_{\text{rf}})\hat{I}_z. \quad (2.41)$$

If $\omega_0 = \omega_{\text{rf}}$, i.e. if the rotation frequency is equal to the Larmor frequency, we have that the effect of the Hamiltonian on the wave function is a rotation about the x axis. In fact if we plug (2.41) into (2.40) we find that

$$|\tilde{\Psi}\rangle = e^{-i\beta_{\text{rf}}\hat{I}_x}|\tilde{\Psi}\rangle = R_x(\beta_{\text{rf}})|\tilde{\Psi}\rangle, \quad (2.42)$$

and the rotation angle is $\beta_{\text{rf}} = \frac{1}{2}\gamma b_{\text{rf}}\tau_{\text{rf}}$, where τ_{rf} is the duration of the pulse. In the literature usually $\frac{1}{2}\gamma b_{\text{rf}}$ is called the nutation frequency and has a range of 1–200 kHz, that is orders of magnitude smaller than the Larmor frequency. With this simple example we see that it is possible by a sequence of pulses to rotate the magnetization by any angle about any axis.

Because of the fact that we need a resonance condition $\omega_0 = \omega_{\text{rf}}$, from this simple example it is clear that pulses with frequency close to the ones of particular interactions may enhance or repress these interactions, whilst being almost negligible for all the others.

2.3.3 The Time Dependency

The time dependent terms of the Hamiltonians come from two different factor: the first one being the pulse itself, the second one being, for solid state-NMR the rotation of the sample. If we look at the dipole-dipole interaction we see that if $\cos^2(\Theta_{kj}) - 1 = 0$,

that is when $\Theta_{k,j} \simeq 54.7^\circ$, this component vanishes.

It may be proven that if the sample is rotating at high speed about an axis making an angle of 54.7° with respect to the z direction, the dipole–dipole interaction practically vanishes. This condition is called magic angle spinning (MAS) and it is widely used for solid–state NMR experiment, [60].

Due to this rotation the only terms of the Hamiltonian that will be affected are those which depend on the orientation Θ ; consequently we have that the time dependency enters as a pre-factor $\omega(t)$ before each term

$$\begin{aligned}
H_{\text{RF}} &= \sum_k \omega_{\text{RF}}^k(t) (I_x^k \cos \phi_k + I_y^k \sin \phi_k), \\
H_{\text{CS}} &= \sum_k \omega_{\text{CS}}^k(t) I_z^k, \\
H_{\text{J}} &= \sum_{k,j} \omega_{\text{Jiso}}^{kj}(t) \frac{1}{\sqrt{3}} I_k \cdot I_j + \omega_{\text{Janiso}}^{kj}(t) \\
&\quad \times \frac{1}{\sqrt{6}} (3I_z^k I_z^j - I_k \cdot I_j), \\
H_{\text{D}} &= \sum_{k,j} \omega_{\text{D}}^{kj} \frac{1}{\sqrt{6}} (3I_z^k I_z^j - I_k \cdot I_j).
\end{aligned}$$

In fact all the $\omega_\Lambda(t)$, with $\Lambda = \text{CS, J, D}$ are scalar time dependent functions that multiply fixed matrices.

Because of the fact that what matters is the reciprocal orientation of the sample, and of the different I_x^j, I_y^j, I_z^j with respect to the magnetic field, all these interactions may be written in terms of irreducible spherical tensors.

The rank–zero tensors describe the isotropic component of the interaction while the rank–two take into account the anisotropic part. The isotropic part is time independent while the anisotropy will change with the rotation of the sample,

$$H_\Lambda = A_{00}^\Lambda T_{00}^\Lambda + [A_{20}^\Lambda]^L, \quad (2.43)$$

where the apex L indicates in the Laboratory frame. Obviously if the system is rotating we need to get the spherical tensor $[A_{20}^\Lambda]^L$ as a sequence of transformations from $[A_{20}^\Lambda]^P$ where P indicates the principal axis frame, that is the reference frame for which the matrix $[A_{20}^\Lambda]$ is diagonal.

At this point it is useful to remember that to transform a spherical tensor between frames of reference we may use the Wigner rotation operators; so for the transformation of a general rank two spherical tensor $[A_{2m}]$ from the system P to system L we have that

$$[A_{2m}]^L = \sum_{m'=-2}^2 [A_{2m'}]^P D_{mm'}^2(\Omega_{PL}), \quad (2.44)$$

where $D_{mm'}$ is the matrix element m, m' of the Wigner rotation operator. These

operators are the tools used in quantum mechanics to move an angular momentum from a frame of reference to another. In fact they are defined as

$$\hat{D}(\alpha_{PL}, \beta_{PL}, \gamma_{PL}) = e^{-i\alpha_{PL}\hat{I}_z} e^{-i\beta_{PL}\hat{I}_y} e^{-i\gamma_{PL}\hat{I}_z}, \quad (2.45)$$

the $\{\alpha_{PL}, \beta_{PL}, \gamma_{PL}\} = \Omega_{PL}$ are the Euler angles which identify the rotation from P to L . The matrix elements that appear in (2.44) are

$$D_{mm'}^l = \langle lm' | \hat{D}(\Omega_{PL}) | lm \rangle. \quad (2.46)$$

We rewrite the time dependent frequency terms (2.43) as

$$\omega_{\Lambda, m'} = \sum_{m=-2}^2 \omega_{\Lambda, m}^{(m)} e^{im\omega_r t}, \quad (2.47)$$

where ω_r is the spinning frequency of the sample.

2.3.4 The Averaged Hamiltonian

It is possible to derive extra information about the system exploiting the fact that (2.47) is periodic [57]. We may rewrite the Magnus expansion for the solution of the propagator as

$$U(t) = e^{\Omega(t)}, \quad (2.48)$$

where $\Omega(t) = \Omega^1(t) + \Omega^2(t) + \dots$ and for example

$$\Omega^1(t) = -i \int_0^t H(t_1) dt_1, \quad (2.49)$$

$$\Omega^2(t) = -\frac{i}{2} \int_0^t \int_0^{t_1} [H(t_2), H(t_1)] dt_2 dt_1. \quad (2.50)$$

NMR theory is recognized as one of the field where the Magnus expansion has been systematically used, [11].

Some simplifications are possible if $H(t) = H(t + T)$. In fact if $U(t)$ has been evaluated for $t \in [0, T]$, we may extend it for all the other periods

$$U(NT) = [e^{-iH(T)}]^N. \quad (2.51)$$

To provide a time independent effective Hamiltonian we may set

$$\bar{H}_0 = \frac{1}{T} \int_0^T H(t_1) dt_1, \quad (2.52)$$

$$\bar{H}_1 = \frac{-i}{2T} \int_0^T \int_0^{t_1} [H(t_2), H(t_1)] dt_1 dt_2, \quad (2.53)$$

where (2.52) is called the averaged Hamiltonian, and for most NMR systems, if one is interested in the evaluation of $\varrho(t)$ only at given time nT , then

$$\varrho(nT) = e^{-i\bar{H}_0 nT} \varrho_0 e^{i\bar{H}_0 nT}, \quad (2.54)$$

provides a good approximation.

2.4 The role of simulations

Before going forward to analyze numerical methods for the description of spin system let us underline where the importance of simulations for such systems lies. Usually NMR experiments refer to samples which contains many molecules, possibly hundreds of atoms like in the case of proteins. At the same time none of the software packages available can actually deal with more than a few (less than 10) spins [93, 6, 79]; to overcome this gap most of the time researchers simulate each single part of the system and put them together afterwards. One of the main purposes of simulation is to recover, via this sequence of partial pictures, the signals coming from experiments. Obviously this approach is just an approximation and in many cases, when many spins are interacting with each other, it is far from accurate.

The main need within the NMR community is the development of new algorithms focused on performance, capable of dealing with the largest system possible; for a review of the computational steps required for a simulation of nuclear spin systems, especially for solid-state NMR, see [23, 24].

Chapter 3

Algorithms for Spin Dynamics

3.1 Introduction

In this chapter we present some of the best known methods used for the solution of the Schrödinger equation. Due to the fact that the Liouville–von Neumann equation for the density matrix (1.58) is the result of a double application of the Schrodinger equation on the bra and ket vectors we may expect the numerical issues arising in both systems of equations to be similar. For a review of numerical approaches for the solution of the Schrödinger equation see [49, 55].

In this section we will not focus on techniques which approximate the Schrödinger equation, that is a partial differential equation, by a system of ordinary differential equations. We assume that there exists a suitable basis set $\{\psi_k\}$ of \mathcal{H} such that it is possible to write, as we did in Chapter 1,

$$i\dot{c} = H_K c, \quad c = \begin{pmatrix} c_1 \\ \dots \\ c_K \end{pmatrix}, \quad (3.1)$$

with a matrix H_K that may be time dependent and has entries

$$H_K^{lj} = \langle \psi_l | \hat{H} | \psi_j \rangle. \quad (3.2)$$

From now on we will refer to H as the matrix expression via the basis set $\{\psi_k\}$ of the operator \hat{H} , and to Ψ as the vector of coefficients c_k .

It is also possible to express the density matrix in a similar form as

$$\rho_{kj} = \Psi^{*T} \Psi = c^{*T} c = \begin{pmatrix} c_1^* c_1 & \dots & c_1^* c_K \\ \dots & & \dots \\ c_K^* c_1 & \dots & c_K^* c_K \end{pmatrix}. \quad (3.3)$$

Given the Liouville–Von Neumann equation for the density matrix

$$\dot{\rho} = -i[H, \rho], \quad (3.4)$$

it is possible and sometimes preferable to rewrite it by introduction of the Liouvillian $L = \text{Id} \otimes \hat{H} - \hat{H} \otimes \text{Id}$, where Id is the identity matrix, allowing us to recast ρ as a vector

$$\dot{\rho}(t) = -iL\rho. \quad (3.5)$$

3.2 Time Independent Case

Let us now consider the case where the Hamiltonian H , and consequently the Liouvillian L , is time independent.

We may rewrite also the general solution for (1.26) when H is time independent

$$\Psi(t) = e^{-iHt}\Psi_0, \quad (3.6)$$

while for (3.5) we have

$$\varrho(t) = e^{-iLt}\varrho_0. \quad (3.7)$$

3.2.1 Splitting Methods

When the wave function Ψ depends on the particle positions q and momenta p it is very common to adopt a splitting method for the Hamiltonian, $H = T + V$. In this case, with a system of n particles of equal mass m we may write the Schrödinger equation as

$$i\frac{d\Psi(q)}{dt} = -\frac{\nabla^2}{2m}\Psi(q) - V(q)\Psi(q), \quad q \in \mathbb{R}^{3n}, \quad (3.8)$$

where ∇^2 is the Laplacian. $V(q)$ is a diagonal operator in the position space while for the kinetic operator $T = -\frac{\nabla^2}{2m}$ we may solve it by transforming Ψ to Fourier space. For a given Ψ in the Schwartz space of rapidly decaying smooth functions we have that the Fourier transform $\tilde{\Psi} = \mathcal{F}\Psi$ is

$$\tilde{\Psi}(k) = \frac{1}{(2\pi)^{3n/2}} \int_{\mathbb{R}^{3n}} e^{-ik \cdot q} \Psi(q) dq, \quad k \in \mathbb{R}^{3n}. \quad (3.9)$$

The Fourier transform of the Laplacian $\nabla^2\Psi$ is $|k^2|\tilde{\Psi}(k)$, where $k^2 = k_1^2 + \dots + k_{3n}^2$. So T is diagonal in Fourier space.

Due to the fact that T and V do not commute we cannot solve for $\Psi(t)$ as

$$\Psi(t) = e^{-iHt}\Psi_0 \neq e^{-iTt}e^{-iVt}\Psi_0. \quad (3.10)$$

However a theorem by Trotter [86] gives an expression of e^{-iHt} in terms of e^{-iTt} and e^{-iVt} . Given T, K and $H = T + V$ Hermitians on \mathcal{H} then for any Ψ and any time t it is possible to prove that

$$e^{-iHt}\Psi = \lim_{m \rightarrow \infty} \left(e^{-i\frac{T}{m}t} e^{-i\frac{V}{m}t} \right)^m \Psi. \quad (3.11)$$

This theorem is at the basis of many splitting methods that have been developed for the solution of various splitting methods, one of the most used is a symmetric second order splitting called Trotter–Strang factorization [81]

$$e^{-iHdt} \simeq e^{-iV\frac{dt}{2}} e^{-iTdt} e^{-iV\frac{dt}{2}}, \quad (3.12)$$

With this approach the main cost is the evaluation of a Fast Fourier Transform (FFT) to switch between the x -grid and the p -grid; the cost of this transform is $O(N \log N)$, [37]. However when the wave function depends on other variables, like the spin of the particles, it is not straightforward to apply a splitting method. In

the next chapter we will present some attempts at the development of new splitting methods in the spin dynamics case.

The size of H grows with the dimension of basis elements we use, and even for very simple systems this number can be prohibitively large. In the case of nuclear spin dynamics, as we have seen in the previous chapter, the general wave function Ψ depends only on the spin and not on the position and momentum of the particles. In this case we use the Zeeman functions as a basis set and the size of Ψ scales as $(2I + 1)^n$ where I is the spin of the particle and n the number of spins. If we deal only with spin $\frac{1}{2}$ we have that the basis set scales exponentially with the number of particles as 2^n .

3.2.2 The Matrix Exponential

From (3.6) it is clear that from a numerical point of view the main issue is the evaluation of the matrix exponential.

The exponential of a matrix may be formally defined via a Taylor expansion

$$e^A = \text{Id} + A + \frac{A^2}{2!} + \dots, \quad (3.13)$$

but this is not a suitable method for its evaluation in finite precision machines, as higher terms of the series would be large and of opposite signs resulting in numerical instability [62]. This problem goes back to the early days of numerical linear algebra; as an historical remark one of the first 80 functions that were included in the first *MATLAB* release was a function for the evaluation of a matrix exponential [62].

Over the years many different numerical methods have been developed for the evaluation of the matrix exponential, for a general review of these methods see the famous paper “Nineteen Dubious ways to evaluate the exponential of a Matrix” by Moler and Van Loan [63].

One of the simplest approaches to evaluate (3.13) is simply to diagonalize A . Obviously it might not be possible to diagonalize a general matrix A , however due to the fact that the Liouvillian L is Hermitian, we may always apply this to (3.6). We may then write the exponential in terms of the eigenvalues and eigenvectors:

$$e^A = Qe^DQ^T, \quad (3.14)$$

where D is diagonal and Q is orthogonal and, obviously,

$$e^{tA} = Qe^{tD}Q^T. \quad (3.15)$$

The main issue of such approach is the computational cost of the evaluation of the eigenvalue–eigenvector pairs. This cost with a QR factorization scales as $\sim O(N^3)$ [31].

From a computational efficiency point of view the choice of a full diagonalization is extremely poor, but it is surprising to find that this is the method that is applied in some of the most used software packages for nuclear spin dynamics [6].

This method can be inserted in the most general frame of the evaluation of the matrix exponential via a matrix decomposition, in fact if it is possible to transform $A = SBS^{-1}$ then we also have that

$$e^{tA} = Se^{tB}S^{-1}, \quad (3.16)$$

where the idea is to find an S for which e^B is easy to compute, other alternatives to a diagonalization are Bloch diagonalization and Jordan canonical form, but these are also not well suited to quantum systems.

3.2.3 Padé Expansion

There are other methods for the evaluation of a matrix exponential that are more efficient than a full diagonalization when dealing with large and sparse matrices. Sparse linear algebra deals with computations of matrix operations when most of the entries of the matrices are zero, generally it is possible to gain orders of magnitude in speed using this technique [73].

One of these methods is based on polynomial expansion. The idea is to approximate the exponential with an ad-hoc combination of power of A

$$e^A \simeq \sum_m P_m(A), \quad (3.17)$$

an example of such choice for P_m are the Padé polynomials, the so-called (p, q) Padé approximation to e^A is [63]

$$e^A \simeq [D_{pq}(A)]^{-1}N_{pq}(A), \quad (3.18)$$

where

$$N_{pq}(A) = \sum_{j=0}^p \frac{(p+q-j)!p!}{(p+q)!j!(p-j)!} A^j, \quad (3.19)$$

while

$$D_{pq}(A) = \sum_{j=0}^q \frac{p+q-j)!p!}{(p+q)!j!(q-j)!} (-A)^j. \quad (3.20)$$

There are two immediate drawbacks for such an approximation:

- for large p $N_{pp} \rightarrow e^A$, while $D_{pp} \rightarrow e^{-A}$, cancellation errors may easily prevent the accurate determination of the ratio between the two;
- the matrix $D_{pq}(A)$ may be poorly conditioned with respect to the inversion.

If $\|A\|$ is not too large then it is still possible to use Padé approximants, when instead $\|A\|$ is large it is common choice to join a Padé approximation with a scaling and squaring technique [63]. For any exponential we have that

$$e^A = (e^{\frac{A}{m}})^m, \quad (3.21)$$

we may then choose a value of m such that m is the smallest power of two for which $\|A\|/m \leq 1$, apply (3.18) to the scaled matrix $e^{A/m}$, and then get e^A by repeated squaring. This method is very robust and can be applied to any matrix A ; for this reason the MATLAB function *expm* relies on a version of it. However it performs quite poorly when dealing with large matrices.

3.2.4 The Chebyshev expansion

Another set of polynomials that has been widely applied specifically for the solution of (3.6) is the expansion of the exponential into Chebyshev polynomials. This method has been first applied for the solution of the Schrödinger equation in [84], more recently in [66, 18, 94], and also for NMR calculations [97]. The k -th Chebyshev polynomial is defined as

$$T_k(x) = \cos(k\theta), \quad \text{with } \theta = \arccos(x) \quad x \in [-1, 1], \quad (3.22)$$

We may prove that on $x \in [-1, 1]$ the Chebyshev polynomials are orthogonal with respect to the weight function $(\sqrt{1-x^2})^{-1}$:

$$\int_{-1}^1 \frac{1}{\sqrt{1-x^2}} T_k(x) T_l(x) dx = \delta_{kl}. \quad (3.23)$$

It is also possible to define a recurrence relation for $T_k(x)$

$$T_{k+1}(x) = 2xT_k(x) - T_{k-1}(x), \quad T_0(x) = 1, \quad T_1(x) = x, \quad (3.24)$$

obtained by the trigonometric identity

$$\cos((n+1)\theta) + \cos((n-1)\theta) = 2\cos(\theta)\cos(n\theta). \quad (3.25)$$

It is also useful to write another relation for T_k

$$2T_k(x) = (x + \sqrt{x^2-1})^k + (x - \sqrt{x^2-1})^k. \quad (3.26)$$

A given holomorphic function can be expanded into a Chebyshev polynomial; we follow here the derivation from [58]. Given a smooth complex function $f(x)$ with $x \in [-1, 1]$, we expand $f(\cos(\theta))$ in a Fourier series. Due to the fact that $f(\cos(\theta)) = f(\cos(-\theta))$ we find:

$$f(\theta) = c_0 + 2 \sum_{k=0}^{+\infty} c_k \cos(k\theta), \quad c_k = \frac{1}{\pi} \int_0^\pi \cos(k\theta) f(\cos(\theta)) d\theta. \quad (3.27)$$

If we substitute $x = \cos(\theta)$ into (3.27) and use $d\theta = dx/\sqrt{1-x^2}$ we arrive at the

Chebyshev expansion of $f(x)$:

$$f(x) = c_0 + 2 \sum_{k=1}^{\infty} c_k T_k(x), \quad c_k(x) = \frac{1}{\pi} \int_{-1}^1 T(x) f(x) \frac{dx}{\sqrt{1-x^2}}. \quad (3.28)$$

It is possible to derive an estimate of the error made when truncating the series in (3.28) at the m -th term. To do so we may derive a version of the Bernstein theorem, as in [58, 55]. First we define the conformal map $\Phi(z)$ from the complement of $[-1, 1]$ to the exterior of the unit disk, and its inverse $\Psi(w)$, specifically

$$\Phi(z) = z + \sqrt{z^2 - 1}, \quad (3.29)$$

$$\Psi(w) = \frac{1}{2} \left(w + \frac{1}{w} \right). \quad (3.30)$$

We may then state:

Theorem 3.2.1. *Let $r > 1$, let $f(z)$ be an holomorphic function in the interior of the ellipse $\|\Phi(z)\| < r$ and continuous on the closure. Then the error for the truncated Chebyshev series is*

$$\|f(x) - S_m f(x)\| \leq 2\mu(f, r) \frac{r^{-m}}{1 - r^{-1}}, \quad (3.31)$$

where $-1 \leq x \leq 1$, $S_m f(x) = c_0 + 2 \sum_{k=1}^{m-1} c_k T_k(x)$ and μ is the mean value defined as

$$\mu = \frac{1}{2\pi r} \int_{\|w\|=r} \|f(\Psi(w))\| \cdot \|dw\|. \quad (3.32)$$

Proof. The first step is to evaluate the Cauchy integral over the ellipse $\Gamma = \{z := \|\Phi(z)\| = r\} = \{\Psi(w) : \|w\| = r\}$:

$$f(x) = \frac{1}{2\pi i} \int_{\Gamma} \frac{f(z)}{z-x} dz = \frac{1}{2\pi i} \int_{\|w\|=r} f(\Psi(w)) \frac{\Psi'(w)}{\Psi(w)-x} dw. \quad (3.33)$$

We then expand at ∞ the fraction into the integral in power series of w we have

$$\frac{\Psi'(w)}{\Psi(w)-x} = \sum_{k=0}^{\infty} a_k(x) w^{-k-1} \text{ for } \|w\| > 1, \quad (3.34)$$

where

$$a_k(x) = \frac{1}{2\pi i} \int_{\|w\|=r} w^k \frac{\Psi'(w)}{\Psi(w)-x} dw = \frac{1}{2\pi i} \int_{\Gamma} \frac{\Phi(z)^k}{z-x} dz. \quad (3.35)$$

At this point we may use (3.26) to relate Φ^k and T_k . In fact since the Laurent expansion at ∞ of $(z - \sqrt{z^2 - 1})^k$ contains only powers z^{-j} with $j \geq k$ we have that the integral over the closed contour Γ vanishes by Cauchy's theorem and:

$$2T_k(x) = \frac{1}{2\pi i} \int_{\Gamma} \frac{\Phi(z)^k}{z-x} dz = a_k(x). \quad (3.36)$$

In this way we may write

$$f(x) - S_m f(x) = \frac{1}{2\pi i} \int_{\|w\|=r} f(\Psi(w)) \cdot 2 \sum_{k=m}^{\infty} T_k(x) w^{-k-1} dw, \quad (3.37)$$

since $\|T_k(x)\| \leq 1$ for $x \in [-1, 1]$ and that $\|w\| = r > 1$, we may set an upper bound for the inner sum

$$\left| \sum_{k=m}^{\infty} T_k(x) w^{-k-1} \right| \leq \sum_{k=m}^{\infty} r^{-k-1} = \frac{r^{-m-1}}{1 - r^{-1}}, \quad (3.38)$$

and the result follows. \square

Let us now focus on the evaluation of the exponential in (3.7). The preliminary step of this method is to rescale the matrix within the interval $[-1, 1]$, as outside this interval the Chebyshev polynomials grow rapidly, and the expansion becomes unstable; to do so we need to evaluate the two extremes of the spectrum of L . In order to obtain extreme values we propose, as already mentioned in the literature [8], to perform a few steps of Lanczos iteration, as this provides a good approximation for the extreme eigenvalues, for small computational cost. If we define these two values as α and β , i.e. $\beta \leq \sigma(L) \leq \alpha$, we may rewrite L as $L = (S \text{Id} - L_s D)$, where $D = (\alpha - \beta)/2$, $S = (\alpha + \beta)/2$, and $-1 \leq \sigma(L_s) \leq 1$. We may then expand the exponential of L_s in the Chebyshev polynomials and we arrive at the following equation for ϱ

$$\varrho(t) = e^{-iLt} \varrho_0 \approx e^{-itS} \left(\sum_{k=0}^{n_{\max}} c_k(t_D) T_k(L_s) \varrho_0 \right), \quad (3.39)$$

with $t_D = Dt$. Both $c_k(t_D)$ and $T_k(L_s)$ may be calculated iteratively

$$c_k(t) = (2 - \delta_{k,0}) (-i)^k J_k(t), \quad (3.40)$$

$$T_{k+1}(x) = 2T_k(x)x - T_{k-1}(x), \quad (3.41)$$

with initial values $T_0(x) = \text{Id}$, $T_1(x) = x$. $J_k(t)$ is the k -th Bessel function of the first kind.

J_k may be evaluated directly by using a three-term recurrence relation

$$J_{n+1}(t) = \frac{2n}{t} J_n(t) - J_{n-1}(t). \quad (3.42)$$

It is well known that (3.42) becomes numerically unstable for $n > t$, see [68]. To improve the method, we may exploit the linear nature of the iterative algorithm. It is possible to use Miller's algorithm, and to solve an inverted form of (3.42), i.e. to solve for J_{n-1} given J_n , J_{n+1} [68]. When using Miller's Algorithm it is suggested to expand the number of terms (providing a sort of buffer), i.e. to start the backward iteration process from $m_{\text{start}} = n + r$, where n is the actual order of the function we are

interested on and r is some small expansion. In this case we need to know already from an a priori error analysis how many iterations need to be performed to get below the threshold ε .

From Theorem 3.2.1 on the approximation of a holomorphic function via Chebyshev expansion we may get an estimate for the error on the exponential function [55].

Theorem 3.2.2. *Given the complex exponential $e^{i\omega x}$, with $\omega \in \mathbb{R}$, the error of the Chebyshev approximation $S_m(e^{i\omega x})$ is bounded by*

$$\max_{x \in [-1, 1]} \|S_m(e^{i\omega x} - e^{i\omega x})\| \leq 4 \left(e^{1-(t/2m)^2} \frac{t}{2m} \right)^m \text{ for } m \geq \|\omega\|. \quad (3.43)$$

Proof. The proof comes from the estimate of the mean value μ for the exponential function; $\mu(e^{i\omega x}, r) \leq \max_{z \in \Gamma} \|e^{i\omega z}\| = e^{|\omega|(r-r^{-1})/2}$. From Theorem 3.2.1 we then have

$$\max_{x \in [-1, 1]} \|S_m(e^{i\omega x} - e^{i\omega x})\| \leq \frac{2r^{-m}}{1-r^{-1}} e^{|\omega|(r-r^{-1})/2}. \quad (3.44)$$

We may then choose r depending on m to balance the growth of $\mu(e^{i\omega z}, r)$ with r against the decay of r^{-m} . If we set $r = 2m/\|\omega\| \leq 2$ we get (3.43). \square

This theorem holds also for any diagonal matrix, and consequently it can be applied also for any diagonalizable matrix, e.s. L , since the transformation is unitary, we just need to take into account the extremes of the spectrum.

For the rescaled Hermitian matrix L_s , when applied to a vector of unit Euclidian norm, we have

$$\|P_{m-1}(tL_s)\varrho_0 - e^{-itL_s}\varrho_0\| \leq 4 \left(e^{1-(t/2m)^2} \frac{t}{2m} \right)^m, \text{ for } m > t, \quad (3.45)$$

where $P_m(t)$ is the order m expansion in Chebyshev polynomials.

This equation indicates that there is a superlinear decay of the error when $m > t$. We may then use the relation $4(\exp\{1 - (t/2m)^2\} \frac{t}{2m})^m \leq \varepsilon$ to approximate m .

From practical point of view the usual way of applying Chebyshev is to evaluate [93, 84]

$$\varrho_{n+1} = e^{-iLdt}\varrho_n \simeq P_{n_{\max}}(dtL)\varrho_n, \quad (3.46)$$

where

$$P_{n_{\max}} = e^{-iSdt} \sum_{k=0}^{n_{\max}} c_k(dtD)T_k(L_s). \quad (3.47)$$

n_{\max} may be evaluated from (3.45). Obviously n_{\max} depends on the choice of the time interval dt , so depending on how often we need to evaluate $\varrho(t)$ the computational costs of this method may change considerably. To avoid numerical instabilities coming from the iterative formula for the Bessel functions it is also possible to get P_m for a given m

via the Clenshaw Algorithm [19, 55]

$$d_k = c_k \varrho_n + 2L_s d_{k+1} - d_{k+2} k = m - 1, m - 2, \dots, 0, \quad (3.48)$$

with initial values $d_{m+1} = d_m = 0$, and $P_m(dtL)\varrho_0 = d_0 - d_2$. In Chapter 4 we will present a different algorithm we have developed for the evaluation of the Chebyshev expansion for the matrix exponential.

3.2.5 Krylov Expansion

For large sparse matrices, methods like the methods usually applied are those based on expansion in Krylov subspace [72, 38, 75].

This kind of methods has become so popular in recent years that has been added as the “twentieth” way in the famous paper “Nineteen Dubious ways to evaluate the exponential of a Matrix” by Moler and Van Loan in the “25 years later” edition. Even before an accurate error analysis had been developed some physics papers developed the idea of projecting the exponential of a large sparse matrix onto a small Krylov subspace [4, 70], even for NMR calculations [65].

The main idea is to project (3.5) onto the subspace

$$K_m(L, \varrho_0) = \text{span}\{\varrho_0, L\varrho_0, L^2\varrho_0, \dots, L^m\varrho_0\}. \quad (3.49)$$

For a general matrix A and given a vector v with $\|v\| = 1$, we may get an approximate basis set for the Krylov subspace $K_m(A, v)$ via the well-known Arnoldi algorithm:

Inputs: A square matrix, v vector;

Outputs: $e^A v$;

1. $v_1 := v$
2. **for** $j = 1 : m$
3. $w := Av_j$
4. **for** $l = 1 : j$
5. $h_{l,j} := w \cdot v_l$
6. $w := w - h_{l,j}v_l$
7. **end**
8. $h_{j+1,j} := \|w\|$
9. $v_{j+1} := \frac{w}{h_{j+1,j}}$
10. **end**

The inner cycle is nothing but a modified Gram-Schmidt process. From the algorithm we get two matrices: an orthonormal matrix V_m whose columns form an orthonormal basis $[v_1, \dots, v_m]$ and an upper Hessenberg matrix H_m with the coefficients $h_{l,j}$; in fact

$$AV_m = V_m H_m + h_{m+1,m} v_{m+1} e_m^T, \quad (3.50)$$

where e_m is the m -th canonical base. From (3.50) we get $A = V_m H_m V_m^T$ and

$$e^A v \simeq V_m e^{H_m} e_1. \quad (3.51)$$

Due to the fact that $tA = V_m tH_m V_m^T$ we may, in the same way, approximate e^{tA} :

$$e^{tA} v \simeq V_m e^{tH_m} e_1. \quad (3.52)$$

If, as in the case of the Liouvillian, the matrix is Hermitian then H_m needs to be Hermitian as well, and because it is also an upper Hessenberg matrix it becomes tridiagonal. In this way we may recast the Arnoldi algorithm with the same inputs and outputs as a three term recursion, termed Lanczos iteration [46]:

1. $v_1 := v, v_0 := 0, \beta_1 = 0$
2. **for** $j = 1 : m$
3. $w_j := Av_j - \beta_j v_{j-1}$
4. $\alpha_j = w_j \cdot v_j$
5. $w_j = w_j - \alpha_j v_j$
6. $\beta_{j+1} = \|w_j\|$
7. $v_{j+1} = \frac{w_j}{\beta_{j+1}}$
8. **end**

Here V_m is still the collection of the orthonormal vectors v_m , while T_m is tridiagonal symmetric

$$T_m = \begin{bmatrix} \alpha_1 & \beta_1 & \dots & \dots & \dots \\ \beta_1 & \alpha_2 & \beta_2 & \dots & \\ \beta_{n-1} & & & & \\ \dots & \dots & \dots & \beta_{n-1} & \alpha_n \end{bmatrix}, \quad (3.53)$$

We remark that historically the Lanczos method had been developed first, as a generalization of the power method for the evaluation of the eigenvalues of a symmetric matrix [46, 20], the Arnoldi method is a generalization of the Lanczos method for a general matrix [51].

If we apply this for the evaluation of $\varrho(t)$, we obtain:

$$\varrho(t) = e^{-iLt} \varrho_0 \approx \|\varrho_0\| V_m e^{-iT_m t} e_1, \quad (3.54)$$

where T_m and V_m come from the Lanczos algorithm and e_1 is the first vector of the canonical basis of size n .

A lemma of Saad [72] gives us the first insight into an error analysis:

Lemma 3.2.3. *Let A be any matrix and V_m, H_m the results of the m -th steps of the Arnoldi or Lanczos method applied to A . Then for any polynomial p_j of degree $j \leq m-1$ the following equality holds*

$$p_j(A)v = V_m p_j(H_m) e_1. \quad (3.55)$$

Proof. Let $\pi_m = V_m V_m^T$ the orthogonal projection on K_m . We can prove by induction that $A^j v = V_m H_m^j e_1$ for $j = 0, 1, \dots, m-1$.

(3.55) it is clearly true for $j = 0$. Assuming it is true for $j \leq m-2$ we have

$$A^{j+1}v = \pi_m A^{j+1}v = \pi_m A A^j v = \pi_m A \pi_m A^j v, \quad (3.56)$$

because of the fact that both $A^{j+1}v$ and $A^j v$ belong to K_m . We have that $\pi_m A \pi_m = V_m H_m V_m$, by the induction hypothesis we get

$$A^{j+1}v = V_m H_m V_m^T V_m H_m^j e_1 = V_m H_m^{j+1} e_1. \quad (3.57)$$

□

From this lemma it is already possible to sketch an error analysis based on the remainder of a polynomial expansion of the exponential [27]. If p is a polynomial of degree less than m approximating e^{-z} with remainder $r_m(z) = e^{-z} - p(z)$ then

$$\|e^A v - V_m e^{H_m} e_1\| \leq \|r_m(A)\| + \|r_m(H_m)\|. \quad (3.58)$$

From (3.58) it is possible to have an estimate on the error for the Lanczos method [72]

$$\|e^A - V_m e^{H_m} e_1\| \leq 2 \frac{R^m e^R}{m!}, \quad (3.59)$$

where $R = \|A\|$. From the last equation we see that for e^{At} we have that the error for a given t is proportional to $\frac{\|tA\|^m}{m!}$, hence for $m \gg \|tA\|$ we have superlinear convergence. However (3.59) holds for a general matrix A ; for special matrices such as Hermitian matrices, with uniformly distributed eigenvalues Hochbruck and Lubich [38] proved that the superlinear decay begins for m close to $\|tA\|$.

Due to the fact that we are interested on Lanczos algorithm for the solution of the Schrödinger equation we propose here a demonstration of a better error estimate than (3.59) developed by Park and Light [70] and presented in [55]. This different error analysis is based on the interpretation of the Krylov approximation (3.54) as a Galerkin approximation of the solution of the Schrödinger equation projected onto the Krylov subspace.

Since the early days of quantum mechanics Dirac and Frenkel [26] derived a variational principle for the solution of the Schrodinger equation on a manifold. Given

$$\frac{d\Psi}{dt} = -iH\Psi, \quad (3.60)$$

let us define a smooth manifold \mathcal{M} of the Hilbert space \mathcal{H} and for $u \in \mathcal{M}$ denote $T_u\mathcal{M}$ the tangent space at u . \mathcal{M} may be seen as an approximation manifold on which an approximate solution $u(t)$ of (3.60) lies, with initial data $u(0) = \Psi(0) \in \mathcal{M}$. $u(t)$ is determined from the condition on its derivative $du/dt \in T_u\mathcal{M}$, such that

$$\langle v | \frac{du}{dt} + iHu \rangle = 0 \quad \forall v \in T_u\mathcal{M}. \quad (3.61)$$

The last condition may be seen as a Galerkin condition on the state-dependent approximation space $T_u\mathcal{M}$. We approximate (3.61) as du/dt is chosen so that $w \in T_u\mathcal{M}$ and satisfies

$$w = \operatorname{argmin}_{w \in T_u\mathcal{M}} \|w + iHu\|. \quad (3.62)$$

In this last formulation, (3.61) states that du/dt is the orthogonal projection of $-iHu$ onto $T_u\mathcal{M}$

$$\frac{du}{dt} = P(u)(-iHu), \quad (3.63)$$

where $P(u)$ is the orthogonal projection operator on $T_u\mathcal{M}$. It is possible to evaluate the error of the variational approximation [55]:

Theorem 3.2.4. *If $u(0) = \Psi(0) \in \mathcal{M}$, then the error of the variational approximation is bounded by*

$$\|u(t) - \Psi(t)\| \leq \int_0^t \operatorname{dist}(-iHu(s), T_{u(s)}\mathcal{M}) ds. \quad (3.64)$$

Proof. If we subtract the orthogonal projection (3.62) from (3.61) we get

$$\frac{d}{dt}(u - \Psi) = -i(H(u - \Psi) - P^\perp(u)Hu), \quad (3.65)$$

with $P^\perp(u) = \operatorname{Id} - P(u)$. Multiplying by $u - \Psi$ and taking the real part we get

$$\begin{aligned} \|u - \Psi\| \frac{d}{dt} \|u - \Psi\| &= \frac{1}{2} \frac{d}{dt} \|u - \Psi\|^2 = \operatorname{Re} \langle u - \Psi | \frac{d}{dt} (u - \Psi) \rangle \\ &= \operatorname{Re} \langle u - \Psi | -P^\perp(u)H \rangle \leq \|u - \Psi\| \|iP^\perp(u)Hu\|. \end{aligned} \quad (3.66)$$

If we divide by $\|u - \Psi\|$ and we note that

$$\operatorname{dist}(-iHu, T_u\mathcal{M}) = \|P^\perp(u)iHu\| = \left\| \frac{du}{dt} + iHu \right\|, \quad (3.67)$$

we get the assumption (3.64). \square

If we apply Theorem (3.2.4) to the Lanczos approximation we see that

$$\|u_m(t) - v(t)\| \leq \int_0^t \text{dist}(Au_m(s), K_m(A, v(0))) ds. \quad (3.68)$$

Due to (3.50) we know that

$$Au_m(s) = AV_m e^{-isT_m} e_1 = V_m T_m e^{-isT_m} e_1 + T_{[m+1,m]} v_{m+1} e_m^T e^{-isT_m} e_1, \quad (3.69)$$

and therefore

$$\text{dist}(Au_m(s), K_m(A, v(0))) = T_{[m+1,m]} | [e^{-isT_m}]_{m,1} |. \quad (3.70)$$

From the latter it is possible to choose a stopping criterion for Lanczos iteration [38].

For a given t we can find m such that

$$t [T_m]_{m+1,m} \|e^{-itT_m}\|_{m,1} \leq \varepsilon. \quad (3.71)$$

One of the well known drawbacks of the Lanczos method arises due to the fact we are usually restricted to finite precision machines. It can be numerically proven that while in exact calculations the vectors v_m form an orthonormal set in finite precision the fact that the orthogonality is checked only to a certain accuracy on the nearest neighborhood vectors is weak; in fact orthogonality is lost for large m . This phenomenon does not occur in the Arnoldi algorithm as each v_j is made orthogonal to all the previous vectors of the basis set via the inner Gram–Schmidt procedure. A possible correction for the loss of orthogonality has been proposed in [8], consisting of a partial re-orthogonalization of the basis set. In our numerical tests however we did not iterate the Lanczos algorithm long enough to suffer from this effect.

The Lanczos method is very powerful for short time simulations, because with few iterations m it is possible to have remarkably good approximations, but for longer times larger Krylov subspaces would be needed to stay close to the real solution. On the other hand if we do not consider enough terms in the Lanczos algorithm for longer times, (3.54) is no longer a reliable approximation.

In our experiments the best way to implement a Krylov expansion was to evaluate at each step

$$\varrho_{n+1} = e^{-iLdt} \varrho_n \approx \|\varrho_n\| V_m^n e^{-iT_m^n t} e_1. \quad (3.72)$$

In this way with less than 10 Lanczos iterations per step it was possible to have a fast and accurate benchmark. The obvious drawback is that no information passes from step n to step $n + 1$. However in our numerical tests the use of a longer timestep that would allow a common Krylov subset $K_m(L, \varrho)$ for more than one step ϱ_n was not preferable as it required more iterations of the algorithm. Because of the fact that the equation (3.71) involves the evaluation of the exponential of a tridiagonal matrix, when m becomes large this operation may become a serious bottleneck for the whole

simulation.

3.2.6 The Zero–Track–Elimination method

Recently a new method for the simulation of large spin system has been presented, [44].

This technique is based on the idea of pruning out the elements of $\varrho(t)$ which do not belong to $K(L, \varrho_0)$, exploiting the fact that most of the time the initial density matrix ϱ_0 is a sparse vector.

In order to reduce the steps needed to evolve the full system, we monitor the elements of $\varrho(t)$ that stay below a chosen threshold ξ during this first evolution steps and introduce structural zeros based on these observations. The evolution is then performed in this reduced state space (ϱ_Z, L_Z) . The idea is extremely appealing, as once the propagator for L_Z is evaluated all the subsequent steps have the cost of a reduced matrix–vector multiplication, and it is possible to use standard techniques for the propagator for the reduced system.

The initial time length is set as the inverse of largest the Larmor frequency. The Larmor frequency is a given quantity for each element that depends on the physical property of the nucleus and is the frequency of resonance for a non–interacting spin: $\omega_0^j = -\gamma_j B$, where $-\gamma_j$ is the gyromagnetic ration of the nucleus and B the applied magnetic field.

The time–length of the initial check is then

$$t_{\text{in}} = \frac{1}{t_{\text{lar}}} = \frac{2\pi}{\min_j \{\omega_0^j\}}, \quad (3.73)$$

where ω_0^j is the Larmor frequency of the j -th spin. A theorem given in [44] assures that it is possible to prune out from the evolution those states that remain exactly 0 during the firsts time steps. It is possible to prove that for a state $|l\rangle$ there holds

$$\text{if } \langle l|e^{-iLt}|\varrho_0\rangle = 0, \quad t \in [0, t_{\text{in}}] \Rightarrow \langle l|e^{-iLt}|\varrho_0\rangle = 0, \quad t \in [0, \infty). \quad (3.74)$$

To prove (3.74) it is sufficient to expand e^{-iLt} into a Taylor expansion:

$$\langle l|e^{-iLt}|\varrho_0\rangle = \langle l|\sum_{k=0}^{\infty} L^k \frac{(-it)^k}{k!}|\varrho_0\rangle = \sum_{k=0}^{\infty} \frac{(-it)^k}{k!} \langle l|L^k|\varrho_0\rangle t \in [0, t_{\text{in}}], \quad (3.75)$$

the last is true for any $t \in [0, t_{\text{in}}]$ only if $\langle l|L^k|\varrho_0\rangle = 0$ for all the k , but this means that $\langle l|e^{-iLt}|\varrho_0\rangle = 0$ for $t \in [0, \infty)$.

However from a practical point of view few states $|l\rangle$ obey (3.74), a much higher number of states will stay *close* to 0 during the first j time steps, where $j = t_{\text{in}}/dt$. So the states $|l\rangle$ that are pruned out are those for which

$$\langle l|e^{-iLt}|\varrho_0\rangle < \epsilon, \quad t \in [0, t_{\text{in}}] \quad (3.76)$$

It is claimed [44] that the error of such an approximation is similar to what would be obtained by considering in the Krylov expansion the contributions coming from high values of n in $L^n \varrho_0$.

The main problem of this approach is the choice of t_{in} , i.e. the duration of the initial propagation. In fact if we look at a full diagonalization of L we see that

$$\varrho(t) = X e^{-iDt} X^{-1} \varrho_0, \quad (3.77)$$

so each element of $\varrho(t)$ can be written as a sum of oscillators vibrating at the different frequencies $\lambda_j \in \sigma(L)$.

$$\varrho_k(t) = \sum_{j=1}^n X_{[k,j]} \mu_j e^{-i\lambda_j t}, \quad \mu_j = \sum_{l=1}^N X_{[j,l]}^{-1} \varrho_0^l. \quad (3.78)$$

From (3.78) it is clear that to ensure that we are not pruning out the low frequencies modes we would need at least $t_{\text{in}} \propto 1/\min_j\{|\lambda_j|\}$, and this could be different from the lowest Larmor frequency $\min_j\{|\omega_0^j|\}$ as the latter is a quantity related to the non-interacting spins. It is possible to have an estimate of the lowest eigenvalue of L using a technique like the one we used for the Chebyshev expansion (3.2.4), but this is not enough to ensure the validity of (3.76).

In fact, within this framework we may restate (3.76) in a simpler form for a one dimension function and show that:

Theorem 3.2.5. *Given a function $f(t) = \sum_{j=1}^n e^{-\lambda_j t} \mu_j$ s.t. $|f(t)| < \epsilon$ for $t \in [0, 2\pi/\min_j\{\lambda_j\}]$, this is not sufficient to ensure that $|f(t)| < \epsilon$ for $t \in [0, \infty)$.*

Proof. To prove (3.2.5) we may check that if the λ_j are not well separated then it is possible to have a combination of similar frequencies that build up on a total frequency that is the lowest common multiplier of the initial frequencies. In the general form if for one or more ϱ_k we have the resonance condition

$$\varrho_k(t) = \alpha e^{-i2\pi\lambda t} - \sum_j \beta_j e^{-i2\pi(\lambda+\delta^j)t}, \quad (3.79)$$

and $\beta_j, \alpha > 0$ rationals such that $\alpha = \sum_j \beta_j$. $\exists \delta_j$ sufficient small such that we have $|\varrho_k(t)| < \epsilon$, $t \in [0, t_{\text{in}}]$, but at the periodic maximum $t > t_{\text{in}}$ such that $|f(t)| = \alpha + \sum_j \beta_j \gg \epsilon$. \square

Having stated 3.2.5 it is straightforward to write down a specific counter-example for the Zero Track Elimination. In Fig.3.1 we plot the absolute value of the function

$$f(t) = e^{-i2\pi t} - \frac{1}{2} e^{-i2\pi(1.001)t} - \frac{1}{2} e^{-i2\pi(0.999)t}. \quad (3.80)$$

If we look at the t_{in} evaluated looking at the lowest isolated frequency we have that $t_{\text{in}} \simeq 1$. Within this time, we have that $\max |f(t)| \simeq 2 \times 10^{-5}$ but clearly the maximum

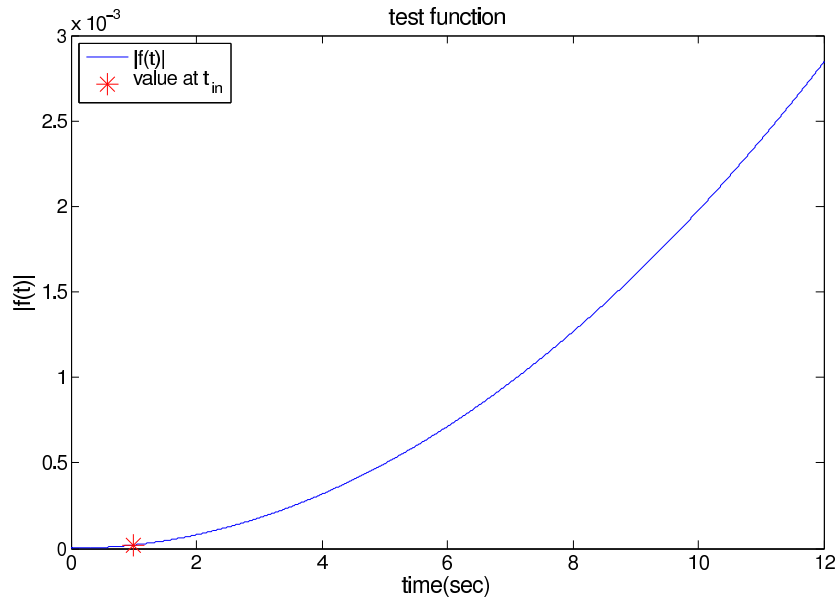


Figure 3.1: t against $|f(t)|$ plot, the asterisk is the value at time t_{in} .

amplitude of this periodic function will be 2.

In order to ensure the validity of (3.76) even with t_{in} that depends on $\sigma(L)$ rather than the Larmor frequencies, we need to check the separation of the eigenvalues, and obviously an analysis of that kind would be as expensive as a whole simulation.

In practice, it might be argued that we are unlikely to have a dynamics like (3.79), but especially in systems of many spins, a wide variety of behaviors are certainly possible in the general situation.

Focusing on NMR simulations however the reason why ZTE performs well [44] lies on the fact that the numerical comparison with other methods is not performed on $\rho(t)$ but on the observables. In particular for experimental reasons the only quantity that can be compared with experiments is the FID

$$f(t) = \text{Trace} \{ \rho(t) I_p \}. \quad (3.81)$$

where I_p is the shift up operator: $I_p = I_x + iI_y$. The Fourier transform of $f(t)$ gives then the spectrum of the sample, where each resonance frequency is revealed by a peak. Due to relaxation effects in the experiments the shape of the resonance peaks is not a delta function, as it would come out from (3.78), but it is smoother. As stated in Chapter 2, to recover this smoothness also for the simulated data it is common practice to evaluate the Fourier transform not of (3.81) but of an exponentially decaying function $\tilde{f}(t)$

$$\tilde{f}(t) = e^{-\xi t} f(t), \quad (3.82)$$

where the parameter ξ comes from other fitted data [53]. The main effect of (3.82) is exactly to smooth out all the long time frequency modes that will differentiate $\rho(t)$ from $\rho_Z(t)$.

Even for the NMR case there are however some drawbacks:

- for this method there is no available convergence theory;
- the performance depends strongly from the initial condition ϱ_0 , and on H . As expected, in our tests the size of the reduced system could change by a factor 2 depending on the number of interacting spins. The reason for this effect comes from the fact that the less sparse is L the more non-zero states will appear within the first steps and this will make a less effective reduction L_z .
- Another reason of the strong dependence of ZTE with respect to the initial conditions comes from (3.73); depending on the Larmor frequencies, and on the timestep size the number of evolution steps at the beginning may become large, and being this the most expensive part of the simulation the influence of it on the total computation costs can become important.

3.3 Time Dependent Case

As seen in Chapter 1 the general form of the solution for the propagator when H is time dependent is through the Magnus expansion

$$U(t) = e^{\Omega(t)} = \sum_{k=1}^{\infty} e^{\Omega_k(t)}. \quad (3.83)$$

Many numerical methods have been developed starting from (3.83) [41, 39], in the form of

$$\varrho_{n+1} = e^{\Omega_n} \varrho_n e^{-\Omega_n} \quad (3.84)$$

where Ω_n is a suitable approximation of $\Omega(t)$. The approximations come by the truncation of the series in(3.83) and by the numerical approximation of the integrals involved in Ω_k . For instance with a midpoint rule we get

$$\Omega_n = -i\Delta t H(t_n + \frac{\Delta t}{2}), \quad (3.85)$$

while for a Gauss quadrature we have a fourth order scheme

$$\Omega_n = \frac{\Delta t}{2}(H_1 + H_2) + \frac{\sqrt{3}\Delta t^2}{12}[H_2, H_1], \quad (3.86)$$

with $H_j = H(t_n + c_j\Delta t)$, and $c_{1,2}$ are the nodes of the quadrature, $c_{1,2} = 1/2 \pm \sqrt{3}/6$.

The main issue on the development of numerical methods involving higher order terms of the Magnus expansion is the evaluation of the commutators of the Hamiltonian. However some commutator free Magnus expansions have been developed [12], these methods are based on finding combinations of integrals of H with which to approximate Ω_n . For nuclear spin simulations most of the time it is enough to stop at the first term of

the Magnus expansion, [92], and to approximate the integral of $\Omega_1(t)$ with a mid-point rule

$$\Omega_1^m = e^{-i\Delta t H(t_m)}, \quad t_m = \Delta t(m + \frac{1}{2}), \quad (3.87)$$

so that we may approximate the total propagator $U(t, 0)$ as the product of piecewise constant propagators

$$U(t, 0) = \prod_{m=1}^N U_m, \quad U_m = e^{-iH(t_m)\Delta t}, \quad N\Delta t = t, \quad (3.88)$$

The solution for the Liouville-von Neumann equation is then

$$\varrho(t_{n+1}) = e^{-iL_n \Delta t} \varrho(t_n), \quad (3.89)$$

where $L_n = L(dt(n + \frac{1}{2}))$ is evaluated at the mid-point of each time step.

For (3.89) we have to evaluate a different matrix exponential each step; for the single step all the methods we have analyzed in the time independent case still apply. Both the Lanczos method and the Chebyshev expansion have been applied successfully to the time dependent case. In the next chapter we analyze the numerical results of these methods in a both time dependent and time independent environment.

Chapter 4

New Methods and Numerical Results

4.1 Direct Computation of expectations via Chebyshev polynomials

The common point of all the methods presented in the previous section is that they all involve the propagation of the matrix ϱ , and for this reason they suffer from requiring that matrix operations (or matrix-vector operations) be performed at each step of calculation of

$$\varrho(t) = e^{-iLt} \varrho_0. \quad (4.1)$$

It is important to remark again that no matter how large the density matrix is, experimentally it is not possible to measure directly the density matrix, what is possible to measure in experiments are the expectation values of the observables.

Let us recall that for an operator \hat{Q} we have that the expectation value is

$$\langle \hat{Q}(t) \rangle = \text{Tr}\{\varrho(t)\hat{Q}\}. \quad (4.2)$$

As is clear from (4.2) while $\varrho \in \mathbb{C}^{2N}$ for a N dimension system, $\langle \hat{Q} \rangle \in \mathbb{R}$. We remark that (4.2) is an exact formula that does not involve any approximation on the system. The information we get from (4.1) is exactly the same that we get from (4.2). The starting point of the method we developed is to exploit this “natural reduction” from \mathbb{C}^{2N} to \mathbb{R} , trying to solve directly (4.2) instead than (4.1). The method we have developed relies on a particular application of the Chebyshev expansion technique presented in the previous chapter, that allows a “almost” direct solution of (4.2). For this reason the method is called *Direct Expectations via Chebyshev expansion (DEC)*.

The first step of DEC is to perform the usual Chebyshev expansion of $\varrho(t)$ (3.39), to get

$$\varrho(t) = e^{-iLt} \varrho_0 \approx e^{-itS} \left(\sum_{k=0}^{n_{\max}} c_k(t_D) T_k(L_s) \varrho_0 \right). \quad (4.3)$$

If we insert (4.3) into (4.2) we find

$$\langle \hat{Q}(t) \rangle = \text{Tr} \left\{ \left(e^{-itS} \sum_{k=0}^{n_{\max}} c_k(t_D) T_k(L_s) \varrho_0 \right) \hat{Q} \right\}. \quad (4.4)$$

By exploiting the linearity of the trace operation we switch the (finite) sum and the trace, and pull out of the trace all time dependent parts. In fact we may rewrite (4.4) as

$$\langle \hat{Q}(t) \rangle = e^{-itS} \sum_{k=0}^{n_{\max}} c_k(t_D) \text{Trace} \left\{ T_k(L_s) \hat{Q} \right\}. \quad (4.5)$$

This is the key equation of the DEC method. It is possible to store an array of scalar values $\tilde{T}_k = \text{Tr}\{T_k \varrho_0 \hat{Q}\}$. All the time dependent terms are just scalar values that

have to be multiplied by \tilde{T}_k to get the evolution of \hat{Q} at any time

$$\langle \hat{Q}(t) \rangle = e^{-itS} \sum_{k=0}^{n_{\max}} c_k(t_D) \tilde{T}_k. \quad (4.6)$$

If more than one observable is required it is still possible to use DEC. The only difference with the single expectation case is that we need to store different sets of \tilde{T}_k^j , one for each operator \hat{Q}^j .

4.1.1 Stopping Criterion

The main remaining issue now is the choice of a stopping criterion for the series expansion. The number of terms for the polynomial expansion in (3.39) depends on a prescribed tolerance ε , and on the time t_D .

Clearly for DEC the most computational expensive routine is the evaluation of the array \tilde{T}_k . The size of it depends on n_{\max} and each T_k evaluation costs $O(n^2)$ as we need to evaluate a matrix vector multiplication.

For the stopping criterion we could have used the estimate (3.45) combined with the Clenshaw algorithm (3.48), but (3.45) gives an upper estimate for n_{\max} , this is the price to pay to have a stable algorithm for the evaluation of c_k .

In our numerical tests however the forward formula for the Bessel functions (3.42) proved to be stable up to an error threshold of $\varepsilon \simeq 10^{-7}$; for this reason, to avoid the computation of even few extra terms, we chose to check directly the convergence of the series below the given threshold. If an higher accuracy is needed, then to avoid the well known instabilities of the iterative formula for the Bessel functions, it is better to apply the Clenshaw algorithm.

This way of directly checking the convergence has been applied already in the literature [93, 84], and the following has been suggested as a stopping criterion

$$n_{\max} \quad \text{s.t.} \quad \|c_{n_{\max}}(t_D)\| < \varepsilon. \quad (4.7)$$

Due to the zeros of the Bessel function J , at fixed time t_D , (4.7) may hold for some n , even though the expansion has not yet reached the convergence regime; it may happen that for $n_1 > n$ we have that $c_{n_1}(t_D) > c_n(t_D)$. To avoid this effect it is enough to use as a stopping criterion a combination of two Bessel functions; the cost of such a stopping criterion is that at most we need to perform an extra iteration step (3.40). In our numerical tests we have used the following

$$n_{\max} \quad \text{s.t.} \quad \sqrt{\|c_{n_{\max}-1}(t_D)\|^2 + \|c_{n_{\max}}(t_D)\|^2} < \varepsilon. \quad (4.8)$$

We remark also that all the c_k are scalar so the cost of either (4.8), (4.7) is negligible.

The total time τ plays a role here, since the larger τ the more terms (T_k, c_k) will be needed to get $|c_k|$ below the threshold ε .

4.1.2 Computation of the Expansion

In order to optimise the number of terms we evaluate, but without having to check at each step whether we have already evaluated enough terms T_k , we propose to evaluate first $\langle \hat{Q}(t) \rangle$, at the final time τ , and to store the N_{\max} values of \tilde{T}_k . We may prove that:

Theorem 4.1.1. *Given a Chebyshev expansion for an exponential $e^{-iLt}\varrho_0$, if (4.8) holds for a given time τ and small enough ε , then (4.8) holds for any time $t \leq \tau$.*

Proof. From equation (3.40) it is clear that c_k depends on the Bessel functions. If we look at the asymptotic behaviour of the Bessel function of first kind, for any $k \in \mathbb{N}$, we have that, for fixed k [2] there holds

$$J_k(t) \sim \frac{1}{\Gamma(k+1)} \left(\frac{t}{2}\right)^k, \quad \lim_{t \rightarrow 0}, \quad (4.9)$$

where $\Gamma(t)$ is the Euler- Γ and for $n \in \mathbb{Z}$ we have that $\Gamma(n) = (n-1)!$. Equation (4.9) shows that for any $k \neq 0$, in a neighbourhood of $t = 0$, $J_k(t)$ is increasing monotonically with respect to t . This behaviour is maintained for the whole interval $[0, j'_k]$ where j'_k is the first zero of the derivative of J_k . It is possible to show (see [2], Eq.9.5.2), that $k \leq j'_k$; consequently we may say that if (4.8) holds for a given n_{\max} at τ and $\tau \leq n_{\max}$, then we are in the monotonically increasing region for $J_{n_{\max}}$ and $J_{n_{\max}+1}$. In this case, equation (4.8) holds also for any $t \leq \tau$. \square

By applying 4.1.1 we are sure that we have stored enough \tilde{T}_k for the whole simulation, but that at the same time we are not evaluating any extra unnecessary iteration of the Chebyshev formula.

4.1.3 Numerical Results

As in many other physical systems, nuclear spin dynamics provides a perfect setting to test DEC, because the final outcome of the simulations is an observable, the free induction decay (FID) signal, and this result is the sole important quantity, as it is the only data available from experiments.

As Hamiltonian we assumed a sum of isotropic chemical shift and the isotropic term of the Homonuclear J-couplings, that depends on the inner product $I_j \cdot I_k$ [53]

$$H = - \sum_{j=1}^n \omega_j^0 I_j^z + \sum_{j,l=1}^n J_{jl} I_j \cdot I_l. \quad (4.10)$$

For the initial density matrix we set $\varrho_0 = -I_y$, that is the result of the application of a so called x -pulse to a sample already under the effect of a strong constant magnetic field along the z direction [53]. This is the usual initial condition when the acquisition of the signal starts.

An illustration of the structure of the Liouvillian matrix is presented in Fig.4.1. The sparsity depends on the number of interactions among the spins. In most cases

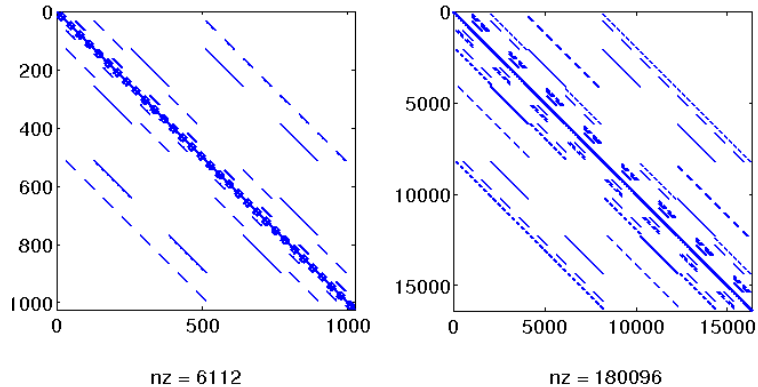


Figure 4.1: Left: Sparse structure of the Liouvillian ($n = 1024$, $nz = 6112$) for a system of 5 spins. Right: Structure of the Liouvillian ($n = 16384$, $nz = 180096$) for a system of 7 spins. Both the systems are in a weak coupling condition, each spin interacts with approximately half the other spins.

the J-coupling interaction matrix J is relatively sparse. In our numerical test a strong coupling system, where J is dense and each spin interacts with every other spins, was simulated.

Due to the fact that our implementation involves only matrix-vector multiplication, techniques developed both for structured and unstructured sparse matrices may be exploited.

For comparison of computational costs we tested this method with an increasing number of spin particles using different methods to evaluate the exponential, as presented in the previous chapter.

In particular, to examine the error, we compared DEC with the *expm* function of *MATLAB*, that uses a scaling and squaring algorithm with Pade' approximation. In this way we evaluate once for all $U = e^{-iL\Delta t}$ where Δt is the stepsize of the simulation, and then at each timestep we propagate ρ

$$\rho_{n+1} = U \rho_n. \quad (4.11)$$

It is well known that in terms of computational costs this simplistic approach performs poorly, as this method do not exploit the matrix sparsity and in general is of order $\sim O(N^3)$, so we compared DEC also with a Krylov expansion via Lanczos [78], the Chebyshev expansion, and ZTE [44].

For the Lanczos method we have used the function *expv* of the package EXPOKIT [78] written in *MATLAB*. This package is widely used within the numerical linear algebra community [63]. All the numerical tests have been performed on a Dell PowerEdge 1950 with 4GB RAM and a DualCore Intel processors running in 32bit mode. The language used is *MATLAB*.

The error-to-cost (measured in CPU time) diagrams are shown in Figure 4.2 for all

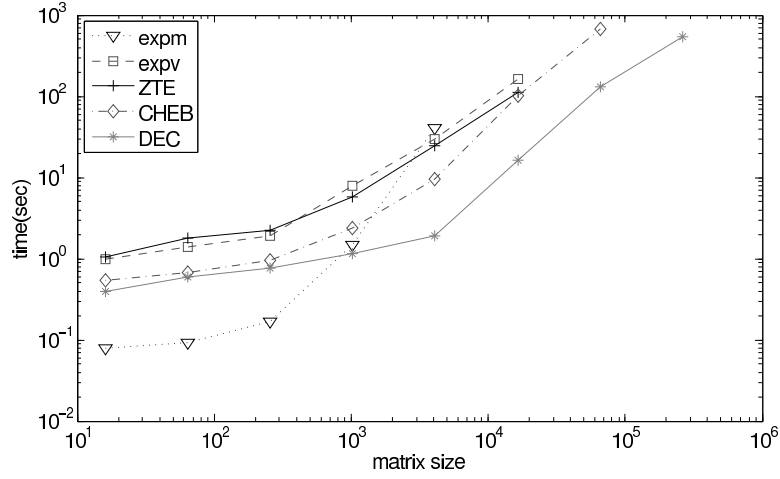


Figure 4.2: Logarithmic comparison of computational costs for Chebyshev (CHEB), Lanczos (expv), Zero Track Pruning (ZTE) and Direct Expectations via Chebyshev (DEC), with $\Delta t = 0.1$ $N = 1000$.

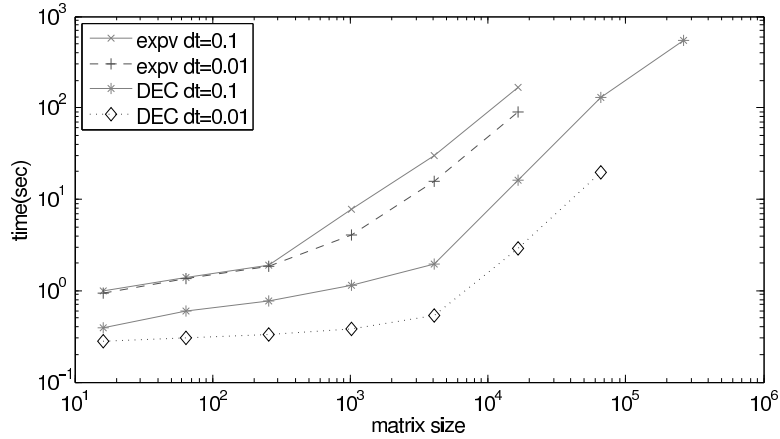


Figure 4.3: Logarithmic comparison of computational costs for Lanczos and DEC when simulating for the same number of total steps N but with different stepsize Δt . $N = 1000$ in both the cases.

the methods described.

It is clear that DEC is almost an order of magnitude more efficient than the alternatives. To avoid instabilities coming from the evaluation of the Bessel functions in these numerical tests we set the tolerance to be $\varepsilon = 10^{-7}$.

DEC performs at its best for short time simulations (i.e. when total time τ is small), so that we do not need to evaluate a large number of T_k , and when at the same time the use of small time step Δt is required, as the cost for any step after the first is negligible. For instance, while for all the other methods the cost of a 1000 step simulation with $\Delta t = 0.1$, is at most half the cost of a simulation of 1000 steps with $\Delta t = 0.01$, for DEC there is a gain of almost an order of magnitude, see Fig.4.3.

Matrix size	expm	expv	Chebyshev	ZTE	Reduced ¹	DEC
16	0.08	0.99	0.54	1.06	8	0.39
64	0.1	1.41	0.68	1.79	30	0.60
256	0.17	1.88	0.95	2.26	112	0.76
1024	1.5	7.87	2.40	5.80	420	1.14
4096	40.84	29.78	9.60	24.51	1584	1.93
16384		165.06	102.92	112.85	6006	16.11
65536			677.22			129.93
262144						542.98

Table 4.1: Comparison of computational costs, CPU time in seconds, for $\Delta t = 0.1$, $N = 1000$.

4.1.4 Extension of DEC

It is interesting to explore possible extensions of DEC, in this section we focus on two main directions. The natural question is whether it is possible to apply DEC directly to the Schrödinger wave function. The extension to the Schrödinger case is straightforward as a wave function Ψ may always be written as a “pure state” in a density matrix, in that case the density matrix is diagonal. In the Schrödinger wave function the observables are still evaluated as

$$\langle \hat{Q} \rangle = \langle \Psi | \hat{Q} | \Psi \rangle, \quad (4.12)$$

and for $\Psi = \sum_{k=1}^N c_k \psi_k$ defined in a finite dimension Hilbert space we have that (4.12) becomes

$$\langle \hat{Q} \rangle = [c_1 \dots c_N]^\dagger \cdot Q \cdot \begin{bmatrix} c_1 \\ \dots \\ c_N \end{bmatrix}, \quad (4.13)$$

where Q is the matrix representation of \hat{Q} with entries $Q_{ij} = \langle \psi_i | \hat{Q} | \psi_j \rangle$. The time dependent values $\langle \hat{Q}(t) \rangle$ can be evaluated via the propagation of the $c_j(t)$.

The other main extension would be the application of DEC in the case of a time dependent Hamiltonian. The main issue is that as we have seen in Chapter 3 for a time dependent Hamiltonian it is not possible to write an explicit solution for the propagator, and more over it does not exist a Chebyshev expansion for a time dependent matrix function. Consequently if $H = H(t)$ we may apply DEC only on the trivial case where $H = H(t) = f(t)H_0$ where $f(t)$ is a scalar. In this case for the propagator we have

$$U(t, t_0) = e^{-iH \int_{t_0}^t f(t') \Delta t'}, \quad (4.14)$$

and by setting $\tau' = \int_{t_0}^t f(t') dt'$ we reduce (4.14) to the evaluation at a sequence of times $\tau'_j = \int_{t_0}^{t_j} f(t') dt'$, where $t_j = j\Delta t$ of the evolution of a time independent Hamiltonian H_0 . To properly apply DEC we need just to reorder in increasing order the τ'_j and get the largest for the evaluation of all the needed coefficients \tilde{T}_k .

4.2 Time Dependent Case

It is important to remark that while DEC is a general tool for the evaluation of expectations, in NMR simulation the time dependency of the Hamiltonian is rather peculiar. Due to the fact that it is possible to express H as a sum of spherical tensors, the time dependency enters only as scalar coefficients multiplied by fixed matrices [88]. In fact we may write

$$H(t) = \sum_{m=-2}^2 e^{im\omega_r t} F_m, \quad (4.15)$$

where ω_r is the rotation frequency and F_m are fixed matrices that depend on the spin-spin interactions. Our aim in this section, is to develop a splitting method that takes into account this particular time dependency.

4.2.1 Spherical Tensors Splitting

As a straightforward attempt it is possible to write down a splitting method [83, 98, 59, 10] and evaluate separately the exponential of each F_m . For a first order method we have

$$e^{-iL(t_k)\Delta t} \simeq \prod_{m=-2}^2 e^{-iLF_m\omega_m(t_k)\Delta t}, \quad (4.16)$$

with $LF_m = F_m \otimes \text{Id} - \text{Id} \otimes F_m$. We may also apply twice a Trotter-Strang type of method to get a second order splitting

$$e^{-iL(t_k)\Delta t} \simeq e^{-iLF_{-2}\omega_{-2}(t_k)\Delta t/2} \dots q e^{-iLF_1\omega_1(t_k)\Delta t/2} e^{-iLF_2\omega_2(t_k)\Delta t} e^{-iLF_1\omega_1(t_k)\Delta t/2} \times e^{-iLF_{-2}\omega_{-2}(t_k)\Delta t/2}. \quad (4.17)$$

The main idea is now to develop a method that solves $e^{-iLF_j\omega_j(t)}$ as a function of e^{-iLF_j} to be evaluated once for all for the whole simulation. An option is to perform a complete diagonalization of each $LF_m = X_m D_m X_m^T$. For the first order split we have

$$\varrho_k = X_{-2} e^{-iD_{-2}\omega_{-2}(t_k)\Delta t} X_{-2}^T X_{-1} e^{-iD_{-1}\omega_{-1}(t_k)\Delta t} X_{-1}^T \dots X_2 e^{-iD_2\omega_2(t_k)\Delta t} X_2^T \varrho_{k-1}. \quad (4.18)$$

In this way after having evaluated the five matrix pairs X_j, D_j , we may get any value ϱ_k as a short sequence of matrix-vector multiplications. For the numerical tests we chose the same type of system we used in the previous chapter; the Hamiltonian is

$$H = \sum_k \omega_0^k(t) \hat{I}_z^k + \sum_{k,j} J_{kj}(t) \hat{I}^k \cdot \hat{I}^j, \quad (4.19)$$

where both $\omega_0(t)$ and $J_{kj}(t)$ now are time dependent. If we compare the computational costs of this splitting method with a Lanczos method we see that for small matrices the splitting approach is very convenient, but on the other hand when the matrix size increases the cost of the diagonalization becomes extremely relevant, and the splitting

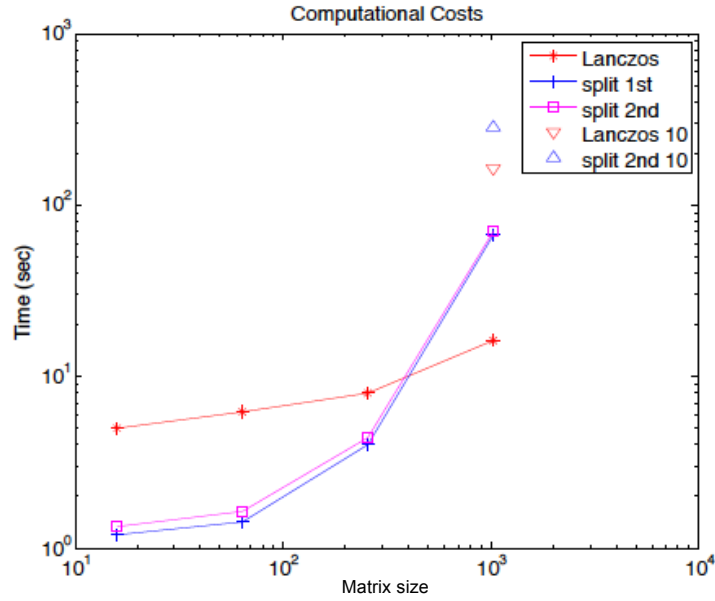


Figure 4.4: Logarithmic comparison of computational costs with $\Delta t = 0.01$ $N = 1000$, *Lanczos10* and *split 2nd 10* are the results with $N = 10000$.

method becomes more expensive, see Fig. 4.2.1.

For the same reason it is not possible to use higher order splitting techniques [12], as such techniques involve many matrix multiplications, making it less competitive than Krylov–Lanczos from a computational point of view.

If we look at a single step, the cost of Lanczos is $\sim m \times N^2$ where N is the size of ρ and m is the number of iterations, as for each of these iteration we need to perform a matrix vector multiplication, in our numerical tests $m \leq 10$. For the splitting method, on the other hand, we have that each diagonalization is of order $O(N^3)$, while each subsequent step costs $\sim 5 \times N^2$ for the first order and consequently the cost of a single step for the splitting theoretically would be roughly half the cost of a Krylov one. By exploiting this fact it could be possible to have that for very long simulations eventually the computational cost of Krylov overcomes the one for the splittings. In Fig. 4.2.1 we show that for longer simulations the gap between the two costs is reducing with the number of timesteps. However, as we show in the next section, the number of iterations for Krylov depends strongly from the step size, as we will see in the next section it is possible to propagate the system with as much as 5–7 iterations for very short time steps, rendering effectively inconvenient the choice of the splitting method in this last case.

In figure Fig.4.2.1 we show the expected behavior of the numerical errors for the first and the second (symmetric) splitting methods.

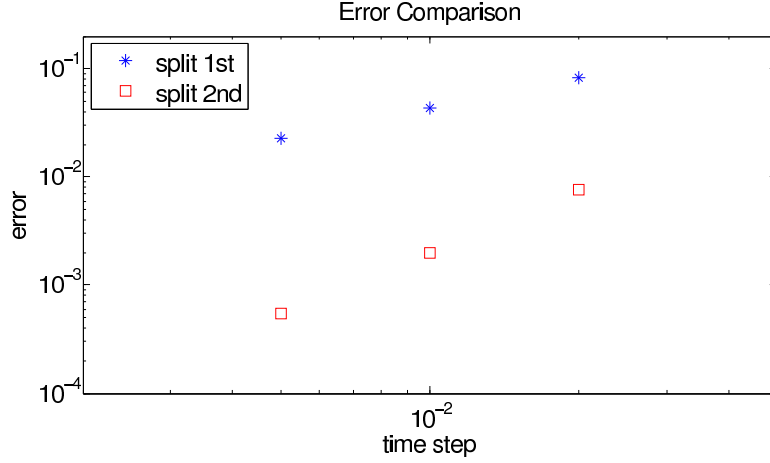


Figure 4.5: Logarithmic comparison of the numerical error, for a system with 4 spins, $T_{tot} = 100$, $\Delta t = 0.02, 0.01, 0.005$.

4.2.2 Diagonal Splittings

The splitting among the spherical tensors is the only “time independent” splitting but it is not the only option. It is important to remark that in many NMR systems the major interactions and consequently the largest elements in the Hamiltonian matrix come from the external magnetic field. It is not unreasonable to assume an order of magnitude between the ω_0^j and the J_{kj} in (4.19), see e.g. Chap. 7 of [53]. If we call LD and LN respectively the diagonal and the off-diagonal matrices built from L :

$$L(t) = LD(t) + LN(t), \quad \forall t. \quad (4.20)$$

We may split each each $L(t)$ in a similar way as (4.17) and get :

$$e^{-iL(t_k)\Delta t} \simeq e^{-iLD(t_k)\frac{\Delta t}{2}} e^{-iLN(t_k)\Delta t} e^{-iLD(t_k)\frac{\Delta t}{2}}. \quad (4.21)$$

Both LD and LN are time dependent, we evaluate directly the exponential of LD at any time because it is a diagonal matrix.

For LN we may use a Krylov–Lanczos with starting vector $e^{-iLN(t_k)\Delta t/2} \rho_{k-1}$. Due to the fact that LN is more sparse than L we know that the iterations needed for the evaluation of (4.21) are less than those needed for the evaluation of complete exponential $e^{-iL(t_k)\Delta t}$, resulting in better performance.

The natural comparison of such method is the Krylov–Lanczos with different convergence tolerances. As seen in the previous chapter, the number of iterations m are related with the the chosen tolerance via

$$t[T_m]_{m+1,m} \|e^{-itT_m}\|_{m,1} \leq \varepsilon. \quad (4.22)$$

where T_m is the tridiagonal matrix resulting from the m -th Lanczos iteration.

In Tab. 4.2.2 we compare the different methods: the diagonal splitting (DS), and the

Method Type	iterations ¹	error ²
L13	7	-
L7	4.5	10^{-5}
L4	3	10^{-2}
DS	2	10^{-4} - 10^{-5}

Table 4.2: Relevant data for Diagonal Splitting and Krylov–Lanczos, $\Delta t = 0.01$, $N = 1000$.

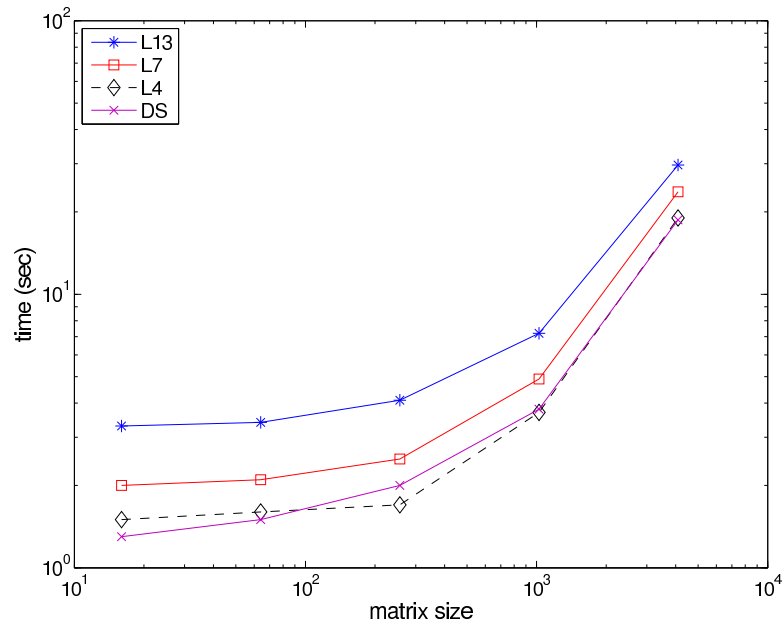


Figure 4.6: Logarithmic comparison of the computational costs, for Krylov–Lanczos with different tolerances and Diagonal Splitting, $\Delta t = 0.01$, $N = 1000$.

Krylov–Lanczos iteration with 3 different tolerances 10^{-13} (L13), 10^{-7} (L7), 10^{-4} (L4). For the error evaluation we choose L13 as the benchmark. All of these methods present the same behavior (in terms of averaged number of iterations and of errors) when the size of the system increases. In Fig. 4.2.2 we compare the different performances as the system scales, we see that DS performs up to 30% better than L7, and, as shown in Tab. 4.2.2, the errors are comparable. The computational costs of DS and L4 are very similar but as outlined in Tab. 4.2.2 the error of L4 is orders of magnitude larger than the one of DS.

For large matrices there is not much difference among the methods in terms of the total time. This is due to the fact that for large matrices the cost for the update of the time dependent coefficients in the Hamiltonian becomes important, and can take the higher percentage of the total simulation time. As an example we see that for a 7 spins system we have a total time of 130 sec for L7, and 115 for DS, but if we compare only the time spent on the propagation routine we see that it takes 52 sec for L7 and only 31 for DS to evaluate it.

Overall we see that, if we consider only the cost of the propagation, DS provides a better cost–to–performance behavior than Krylov–Lanczos, roughly 30% better. At the same time the error for this approximation remains comparable with high tolerance Krylov–Lanczos methods.

4.3 Discussion

In this chapter we have presented results for both autonomous and non autonomous Liouville–von Neumann equation. For the autonomous case DEC method has been discussed. At this point an extension of this method to the time dependent case looks very difficult mainly to the fact that it has not yet been developed an analog for the Chebyshev expansion for non autonomous systems. There are however other possible directions of research:

- It would be interesting to perform some numerical tests using DEC to solve the Schrödinger equation rather than the Liouville–von Neumann equation.
- As we will show in the next chapter the Chebyshev expansion has been used to solve for short time length the Liouville–von Neumann equation in the case of open quantum systems [97, 35]. We could apply DEC in this case and compare the performances with other existing methods. The main difference is that the Liouvillian is not Hermitian, so it is not possible to use a Krylov–Lanczos method but the more expensive Krylov–Arnoldi algorithm should be applied. Potentially DEC would perform even better than in the closed dynamics case.

For the time dependent Hamiltonian case the main direction of research would be the development of better splitting techniques. By exploiting the characteristic of the time dependency it may be possible to find other ways of splitting the Hamiltonian rather

than the simple diagonal and non-diagonal. For instance we might apply some splittings methods that have been developed for classical Hamiltonian like $H = H_0(t) + \epsilon H_1(t)$, with $\epsilon \ll 1$, [47].

We have also checked that, due to the fact that for very short timesteps the convergence of the Lanczos iterations is reached within the first 2 – 3 steps in these cases the best approach in terms of error-to cost is definitely Krylov-Lanczos.

Chapter 5

Open Questions for Open Quantum Systems

In this chapter we present a work in progress that has been carried out in the last part of my PhD.

5.1 Open Quantum Systems

As we saw in the previous section, spin relaxation plays a fundamental role in Nuclear Magnetic Resonance (NMR).

Nuclear spin dynamics has become a hot spot of research also as a single spin is one of the most plausible candidates to be a qbit, the fundamental brick for the construction of quantum computers [21, 91]. The main reason of this choice is that it is possible to build up coherences between states, like spin up and spin down that last up to seconds, for some particular states with a zero total spin even a length of minutes have been measured [17]! Another important reason for the choice of a nuclear spin as qbit is that it is very easy to rotate the spin, i.e. to modify the information, via selected pulses [90]. One of the main task that needs to be accomplished on the road to quantum computing is exactly being able to have long time coherences. In a general quantum system coherences between states are destroyed after a short while because of the fact that a quantum system is never fully isolated. In a fully isolated (closed) quantum system once a coherence has been built up it will last, however if the system is interacting with an external environment then the coherence will be destroyed.

For this extremely important task a great deal of effort has recently been put towards a better description of open quantum systems, i.e. of quantum systems exchanging energy with an external environment. So far however there are still few numerical methods explicitly developed for the simulations of such systems.

In order to describe the dynamics of such a system we need to introduce the concept of open quantum system. If we look at the propagator for the Schrödinger equation for the time independent Hamiltonian case, we see that

$$|\Psi(t)\rangle = U(t, t_0)|\Psi_0\rangle, \quad U(t, t_0) = e^{-iH(t-t_0)}, \quad (5.1)$$

is a unitary propagator. The dynamics of this system is *conservative*, as an example it is straightforward to see that if the initial $|\Psi_0\rangle$ is an eigenvector of the Hamiltonian then the system will remain in that state for the whole duration of the evolution but for a phase factor

$$|\Psi(t)\rangle = e^{-iH(t-t_0)}|\Psi_0\rangle = e^{-i\lambda t}|\Psi_0\rangle, \quad (5.2)$$

where λ is the eigenvalue associated with the eigenvector Ψ_0 . (5.1) holds only for an isolated system that does not exchange energy with the environment. In most of physical cases, the size of an “isolated system” would be extremely large, with possibly tens, or even hundreds of molecules. It is very difficult or even impossible to simulate such a system without making some approximations. At the same time if we are interested on relaxation to equilibrium we need to take into account some kind of

interaction with an external bath at a given temperature.

5.2 Spin Relaxation

In this section we describe from a phenomenological point of view the relaxation process for a nuclear spin system. After a pulse, or a sequence of pulses, the system is put out of equilibrium, then via external and internal interactions, relaxation processes take place and the system recovers the equilibrium state. During this period of time the FID signal is measured. The main effect of the relaxation is to smooth the peaks in the FID spectrum, which otherwise would be a set of delta functions. From a numerical point of view the inclusion of relaxation is not straightforward and the main issues are related to the description of the environment that is responsible for the relaxation.

The FID is then the expected value of the I_p operator where $I_p = I_x + I_y$. It measures the “coherence” between different states

$$f(t) = \text{Tr}\{\rho(t)I_p\}. \quad (5.3)$$

To make an example, if the system is composed only by one spin, and the Hamiltonian is $H = -\omega_0/2I_z$, the FID is

$$f(t) = e^{-i\omega_0 t}, \quad (5.4)$$

i.e. an oscillating solution and the spectrum is a delta function peaked at the energy gap ω_0 between the two states. Again this is due to the unitary nature of the propagator.

But this is clearly not the outcome of the experiment, rather than being a unitary propagation the density matrix will be degraded by relaxation processes to the equilibrium density matrix ρ_{eq} , and this would gradually destroy the coherence. In fact the “coherence” between two different quantum states $\{|i\rangle, |j\rangle\}$ is measured by the off-diagonal element ρ_{ij} . As we have seen in Chapter 1 the equilibrium density obeys the Boltzmann–Gibbs distribution and is diagonal in the Hamiltonian eigenbasis

$$\rho_{\text{eq}} = \frac{e^{-\beta H}}{\text{Tr}\{e^{-\beta H}\}}. \quad (5.5)$$

An extremely crude approximation, that is mostly used in the NMR simulation community is to damp the signal $f(t)$ by multiplying it with an exponentially decaying function so that the (5.4) becomes

$$f(t) = e^{-i\omega_0 t - \gamma t}. \quad (5.6)$$

Usually γ is evaluated via careful fittings of experimental data of various systems. Even if the results of this process are then comparable with most of the experiments, this approximation might be too in some cases crude, for two main reasons:

- it assumes an exponential decay, and this is not always the case, especially if

relevant quantum effects affect the motion of the particles [15, 40];

- it assumes the exponential coefficient γ to be the same for the all contributions to the signal, contributions that may be due to very different phenomena, with very different relaxation parameters.

5.3 Theory of Open Quantum Systems

The theory of spin relaxation has been studied for more than forty years now [1, 30]. The spin relaxation process may be viewed as a part of open quantum system theory. Currently there are two main ways to introduce dissipation–relaxation phenomena into quantum systems. In this section both of these methods will be presented, underlining the strengths and the weaknesses of them. For a general literature review on these two methods see [14, 67].

5.3.1 The Bloch–Redfield Method

The first method had been initially developed in the field of nuclear spin dynamics. We sketch here the steps for this method:

- The starting point is to couple the quantum system S with a thermal bath B .
- Next we write down the Hamiltonian for the full system $H = H_S + H_B + H_I(t)$, where H_S and H_B are the Hamiltonian respectively for the isolated system and the isolated bath, and $H_I(t)$ the term describing the interaction. The dynamics of the whole system is unitary, we will call $S + B$ universe while S will be the system and B the bath.
- Finally we may write down an equation of motion for the reduced density matrix $\varrho_S = \text{Tr}_B\{\varrho\}$ where ϱ is the density matrix of the whole ($S + B$) system. It is possible to prove that the reduced dynamics is described by a dynamical map that is dissipative and that will bring the system to its equilibrium.

Clearly depending on the interaction term $H_I(t)$ and on the bath characteristics we may have different solution for ϱ_S . This approach is usually called the perturbative treatment, in the sense that some approximations regarding the nature of the interaction Hamiltonian are needed. The interaction Hamiltonian H_I acts as a perturbation to the states of the system that are the eigenvectors of H_S . It is also possible, but we will not go in details here, to develop a similar set of equations assuming a second order perturbative expansion of the exact solution for ϱ_S [30, 28].

Following [14], we will focus only on the weak–coupling case where the interaction $H_I(t)$ is much smaller than both H_S and H_B . The Hilbert space for the universe is a direct product of system and bath parts

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B, \tag{5.7}$$

this happens because any state of the universe can be written as a direct product between a bath and a system state; the density matrix consequently is

$$\varrho_{ij,i'j'} = \langle \psi_i^S | \langle \psi_j^B | \hat{\varrho} | \psi_{j'}^B \rangle | \psi_{i'}^S \rangle. \quad (5.8)$$

The reduced density matrix may be evaluated by performing a partial trace of $\varrho_{ij,i'j'}$ over the bath degrees of freedom

$$\varrho_{ii'}^S = \sum_j \varrho_{ij,i'j} = \text{Tr}_B \{ \varrho \}. \quad (5.9)$$

If we rewrite the Liouville–von Neumann equation for the universe in the interaction picture we have that

$$\frac{d\tilde{\varrho}(t)}{dt} = -i[\tilde{H}(t), \tilde{\varrho}(t)], \quad (5.10)$$

where $\tilde{f} = e^{iH_0 t} f e^{-iH_0 t}$ is the expression for the quantity f in the interaction picture. We suppress now the \sim as every expression will be written in this picture. A formal solution for ϱ gives

$$\varrho(t) = \varrho(0) - i \int_0^t [H_I(t'), \varrho(t')] dt', \quad (5.11)$$

if we insert this expression into the (5.10) we get

$$\frac{d\varrho}{dt} = -i[H_I(t), \varrho(0)] - \int_0^t [H_I(t), [H_I(t'), \varrho(t')]] dt', \quad (5.12)$$

performing a partial trace over the bath degrees of freedom in both the sides of the equation

$$\frac{d\varrho_S(t)}{dt} = -i\text{Tr}_B[H_I(t), \varrho(0)] - \int_0^t \text{Tr}_B[H_I(t), [H_I(s), \varrho(s)]] dt'. \quad (5.13)$$

We may assume it is always possible to combine H_S, H_B, H_I such that the first term $\text{Tr}_B[H_I(t), \varrho(0)] = 0$. At this point we make the first approximation, known as the Born approximation in the literature. We suppose that, because of the weak coupling between the system and the bath, the influence of the system on the bath is small, consequently the density matrix of the bath ϱ_B is only negligibly affected by the interaction with the system and we may approximate the density matrix of the universe as

$$\varrho(t) \simeq \varrho_S(t) \otimes \varrho_B, \quad (5.14)$$

it is important to underline that this does not mean that there are not excitations on the bath caused by the system, but simply that these excitations decay over shorter times than those involved in the dynamics of the system. With this first approximation we may rewrite (5.13) as an integro–differential equation

$$\frac{d\varrho_S(t)}{dt} = - \int_0^t \text{Tr}_B[H_I(t), [H_I(s), \varrho_S(s) \otimes \varrho_B]] dt'. \quad (5.15)$$

In order to achieve a Markovian limit for the memory kernel we first suppose that the timescales that matter in the integral are short enough that we may replace $\varrho_S(s)$ with $\varrho_S(t)$, assuming that the state of the system at time t is time local, we get

$$\frac{d\varrho_S(t)}{dt} = - \int_0^t \text{Tr}_B[\mathbf{H}_I(t), [\mathbf{H}_I(s), \varrho_S(t) \otimes \varrho_B]] dt', \quad (5.16)$$

the last is called *Redfield equation*. (5.16) is not yet a Markovian master equation as it still contains an explicit dependence on the initial state of the system at time 0. The last step is the substitution into the integral of t with $(t - s)$ and the extension of the upper limit of it to infinity. This is permissible if we assume that the integrand function decays to zero sufficiently fast for $t' \gg \tau_B$, where τ_B is the time scale over which the bath correlation functions decay, and this τ_B needs to be large than τ_R that is the time scale over which the system varies appreciably. The final version of (5.13) is

$$\frac{d\varrho_S(t)}{dt} = - \int_0^\infty \text{Tr}_B[\mathbf{H}_I(t), [\mathbf{H}_I(t - t'), \varrho_S(t) \otimes \varrho_B]] dt', \quad (5.17)$$

This whole approximation procedure is called the Born–Markov approximation in the literature [14].

Let us now focus on the interaction Hamiltonian, we may decompose it into a direct product of system operators and bath operator

$$H_I(t) = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha}, \quad (5.18)$$

where A_{α} is a set of system operators and B_{α} is a set of environment operators. We define the bath correlation functions

$$C_{\alpha\beta}(s) = \langle B_{\alpha}^{\dagger}(t) B_{\beta}(t - s) \rangle = \text{Tr}_B\{B_{\alpha}^{\dagger}(s) B_{\beta}(0)\}, \quad (5.19)$$

where in the last term we have supposed that ϱ_B is stationary, i.e. $[H_B, \varrho_B] = 0$. We may rewrite (5.17) as

$$\begin{aligned} \frac{d\varrho_S(t)}{dt} &= \int_0^\infty \text{Tr}_B \{ \mathbf{H}_I(t - t') \varrho_S(t) \otimes \varrho_B \mathbf{H}_I(t) - \mathbf{H}_I(t) \mathbf{H}_I(t - t') \varrho_S(t) \otimes \varrho_B \} dt' + h.c. \\ &= \int_0^\infty \sum_{\alpha, \beta} C_{\alpha\beta}(t') \left[A_{\beta}(t - t') \varrho_S(t) A_{\alpha}^{\dagger} - A_{\alpha}^{\dagger}(t) A_{\beta}(t - t') \varrho_S(t) \right] dt' + h.c., \end{aligned} \quad (5.20)$$

From (5.20) it is clear that via different choices of correlation functions for $C_{\alpha\beta}$ we may completely define the features of the bath (like the temperature, or the spectrum. The main drawback of this method is that there is plenty of evidence that in some cases this equation does not satisfy some of the basic requirements of the reduced density matrix [28].

Any density matrix by definition contains information about the probability of finding the system in a certain configuration. So we need $\rho(t)$ to satisfy some requirements

throughout the whole evolution, [96]. We need $\rho(t)$ to be:

- *Hermitian*, so that all the probabilities are real;
- *Trace-preserving*, because the sum of the probabilities over any complete set must be one;
- *Positive*, otherwise some probabilities might be negative.

Because of the perturbative approach some of these requirements might not be fulfilled. Given the fact that the eigenvalues of ϱ_S describe the probability to find the system S in a given state, this should also imply that

$$\det \varrho_S = \prod_{k=1}^N w_k > 0, \quad (5.21)$$

It has been known for many years now that if the initial conditions $\varrho_S(t_0)$ are put close to the boundary of (5.21) then (5.20) does not preserve the positivity [3, 82]. It has been claimed that this non conservation is due to the fact of not having taken into account the memory effects in the early time evolution, at those times $< \tau_B$ the bath correlation functions are rapidly varying and they cannot be considered time independent, this affects the dynamics of ϱ_S that cannot be accurately described by (5.20).

5.3.2 The Lindblad Form

There is another approach, where the model is built up starting by the previous requirements, these may be summed up by asking the propagator for ϱ to be a generator of a dynamical semigroup.

Starting from the propagator for the universe $U(t, 0)$, we may define a dynamical map $\Lambda(t)$ s.t.

$$\varrho_S(t) = \Lambda(t)\varrho_S(0) = \text{tr}_B\{U(t, 0)[\varrho_S(0) \otimes \varrho_B]U^\dagger(t, 0)\}. \quad (5.22)$$

$\Lambda(t)$ is a one-parameter family of dynamical maps satisfying the semigroup property $\Lambda(t_1)\Lambda(t_2) = \Lambda(t_1 + t_2)$.

We may look at the most general form for the generators of the map $\Lambda(t)$ such that ϱ_S conserves its properties.

The main papers on this area are [54, 32] and we follow [14] for a brief description of the mathematical basis of the theory.

If the evolution is Markovian, Lindblad, [54] proved that the most general generator of a dynamical semigroup has the form:

$$\frac{d}{dt}\varrho_S(t) = -i[H_S, \varrho_S(t)] - \sum_{n=1}^{N^2-1} \gamma_n(\Gamma_n \varrho_S(t) \Gamma_n^\dagger - \frac{1}{2}\Gamma_n^\dagger \Gamma_n \varrho_S(t) - \frac{1}{2}\varrho_S(t) \Gamma_n^\dagger \Gamma_n), \quad (5.23)$$

where N is the dimension of the Hilbert space. and the Γ_n are called the Lindblad operators and are appropriate linear combinations of a complete set of orthonormal operators for the system S .

The γ_n are coefficients related to the orthonormal set Γ_n and have to be greater than 0; they are set by hand to get some fundamental conditions like the detailed balance to be fulfilled. Albeit the Lindblad theory provides to be formally correct and avoids any pitch-fall like the negative probability, suffers from not being able to describe any features of the bath.

As an example of the form the Γ take we use the Lindblad form to describe the dissipation for a two state system, i.e. a single spin for which we set $H_0 = -\frac{1}{2}\omega_0 I_z$, for simplicity of notation in these two examples we will drop the S from ρ_S .

The first example is for a population preserving decay, we take a single $\Gamma = \sqrt{\gamma}\sigma_p$ that is the Pauli matrix $\sigma_p = \sigma_x + i\sigma_y$, with only a non zero entry at the position $\Gamma_{12} = 1$. In this case the dissipation is

$$\mathcal{D}(\rho) = \begin{pmatrix} \gamma\rho_{22} & -\frac{1}{2}\gamma\rho_{12} \\ -\frac{1}{2}\gamma\rho_{12} & -\gamma\rho_{22} \end{pmatrix} \quad (5.24)$$

For this system the solution for $\rho(t)$ reads

$$\begin{aligned} \rho_{11}(t) &= \rho_{11}(0) + \rho_{22}(0)[1 - e^{-\gamma t}], \\ \rho_{11}(t) &= \rho_{22}e^{-\gamma t}, \\ \rho_{12}(t) &= \rho_{21}(0)e^{(i\omega_0 - \frac{\gamma}{2})t}, \\ \rho_{21}(t) &= \rho_{12}(0)e^{(-i\omega_0 - \frac{\gamma}{2})t}. \end{aligned} \quad (5.25)$$

Another more interesting dissipation phenomena occurs when we consider for the same system and the same H_0 three different Lindblad operators:

$$\Gamma_1 = \sqrt{\gamma_1}\sigma_p, \quad (5.26)$$

$$\Gamma_2 = \sqrt{\gamma_2}\sigma_m,$$

$$\Gamma_3 = \sqrt{\gamma_3}\sigma_z,$$

$$(5.27)$$

Γ_1 describes the relaxation from $|\alpha\rangle$ to $|\beta\rangle$ with the emission of energy, Γ_2 describes the reverse relaxation from $|\beta\rangle$ to $|\alpha\rangle$, and Γ_3 describes a pure dephasing process. The equation of motion for ρ becomes

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} &= i\omega_0 \begin{pmatrix} 0 & \rho_{12} \\ -\rho_{21} & 0 \end{pmatrix} + \gamma_1 \begin{pmatrix} \rho_{22} & -\frac{1}{2}\rho_{12} \\ -\frac{1}{2}\rho_{21} & -\rho_{22} \end{pmatrix} \\ &+ \gamma_2 \begin{pmatrix} -\rho_{11} & -\frac{1}{2}\rho_{12} \\ -\frac{1}{2}\rho_{21} & \rho_{11} \end{pmatrix} + \gamma_3 \begin{pmatrix} 0 & -2\rho_{12} \\ -2\rho_{21} & 0 \end{pmatrix}, \end{aligned} \quad (5.28)$$

We have two different relaxation times T_1 and T_2 for the diagonal and off-diagonal terms given respectively as

$$\frac{1}{T_1} = \gamma_1 + \gamma_2; \quad \frac{1}{T_2} = 2\gamma_3 + \frac{1}{2}(\gamma_1 + \gamma_2), \quad (5.29)$$

and at the equilibrium we have that for the populations there holds $\varrho_{11}^{\text{eq}}\gamma_1 = \varrho_{22}^{\text{eq}}\gamma_2$. In order to have the detailed balance condition satisfied we need to choose γ_1, γ_2 such that

$$\frac{\gamma_1}{\gamma_2} = e^{-\beta\omega_0}. \quad (5.30)$$

Let us now go back to the Bloch-Redfield equation (5.20), under the new light of the idea of dynamical semigroup and see what other approximation we need to perform in order to insure that the dynamics generated in (5.20) is effectively in a quantum dynamics semigroup. It is possible to reduce the Bloch-Redfield equation to a Lindblad form but some stronger assumption regarding the bath is required, the so called rotating wave approximation (RWA), otherwise the γ_n are not positive.

The first approximation for the RWA is to assume that the spectrum of H_S is discrete, we may then rewrite any A_α in (5.18) as

$$A_\alpha(\omega) = \sum_{e-e'=\omega} \Pi(e)A_\alpha\Pi(e'), \quad (5.31)$$

where $\Pi(e), \Pi(e')$ are the projector onto the eigenspace with eigenvalues e, e' , and the sum runs over all the energy eigenvalues of H_S with a fixed energy difference ω . Consequently we have that

$$[H_S, A_\alpha(\omega)] = -\omega A_\alpha(\omega), \quad (5.32)$$

$$[H_S, A_\alpha^\dagger(\omega)] = -\omega A_\alpha^\dagger(\omega), \quad (5.33)$$

We may rewrite the interaction Hamiltonian using (5.31)

$$H_I = \sum_{\alpha, \omega} A_\alpha(\omega) \otimes B_\alpha, \quad (5.34)$$

if we write H_I in the interaction picture we get

$$H_I(t) = \sum_{\alpha, \omega} e^{-i\omega t} A_\alpha(\omega) B_\alpha(t), \quad (5.35)$$

$$B_\alpha(t) = e^{iH_B t} B_\alpha e^{-iH_B t}. \quad (5.36)$$

$$(5.37)$$

Inserting (5.35) into the master equation (5.20) we get

$$\frac{d}{dt}\varrho_S(t) = \int_0^\infty ds \text{Tr}_B \{ H_I(t-t')\varrho(t)\varrho_B H_I(t) - H_I(t)H_I(t-t')\varrho_S(t)\varrho_B \} + h.c., \quad (5.38)$$

$$= \sum_{\omega, \omega'} \sum_{\alpha, \beta} e^{i(\omega-\omega')t} \Gamma_{\alpha\beta}(\omega) (A_\beta(\omega)\varrho_S(t)A_\alpha^\dagger(\omega') - A_\alpha^\dagger(\omega')A_\beta(\omega)\varrho_S(t)), \quad (5.39)$$

where

$$\Gamma_{\alpha\beta}(\omega) = \int_0^\infty ds e^{i\omega s} C_{\alpha\beta}(s), \quad (5.40)$$

where the $C_{\alpha\beta}(s)$ are again the bath correlation functions. The RWA approximation consist in the elimination of all the term for which $\omega' \neq \omega$ from the double sum in (5.38). The reason behind this choice is that the relaxation time of the bath τ_B is assumed much larger than the timescale of the evolution of the system $\sim |\omega' - \omega|^{-1}$. This means that the terms for which $\omega' \neq \omega$ will oscillate very rapidly during the time τ_B over which ϱ_B varies. This approximation is called for obvious reasons Rotating Wave Approximation. In RWA the master equation becomes

$$\frac{d}{dt}\varrho_S(t) = \sum_{\omega} \sum_{\alpha\beta} \Gamma_{\alpha\beta}(\omega) (A_\beta(\omega)\varrho_S(t)A_\alpha^\dagger\Gamma_{\alpha\beta}(\omega) - A_\alpha^\dagger(\omega)A_\beta(\omega)\varrho_S(t)) + h.c., \quad (5.41)$$

this last equation may be written as a Lindblad form, and it is also possible to prove that Γ_α may be split into an imaginary and real part, where the imaginary part contributes to the Unitary Hamiltonian dynamics and it is called Lamb-shift as it modifies the energy levels as the Lamb effect in quantum electro dynamics calculations [76]. The real part is positive and plays the role of γ_α in the Linbdlad equation [14].

For the RWA it is possible to prove that if the bath is at the equilibrium, and the density matrix ϱ_B for the bath at the equilibrium obeys the Boltzmann-Gibbs distribution with respect to the Hamiltonian H_B , then also the only asymptotic equilibrium density matrix for the system is

$$\varrho_{\text{eq}} = \frac{e^{-\beta H_S}}{Z}. \quad (5.42)$$

To prove (5.42) we use the Kubo-Martin-Schwinger relation that relates the correlation function, in fact for $C_{\alpha\beta}(t)$ there holds

$$C_{\alpha\beta}(t) = \langle B_\alpha^\dagger(t)B_\beta(0) \rangle = \langle B_\beta^\dagger(0)B_\alpha(t+i\beta) \rangle, \quad (5.43)$$

from there we get

$$\Gamma_{\alpha\beta}(-\omega) = e^{-\beta\omega}\Gamma_{\beta\alpha}(\omega), \quad (5.44)$$

and for the equilibrium density ϱ_{eq} there holds,

$$\varrho_{\text{eq}}A_\alpha(\omega) = e^{\beta\omega}A_\alpha(\omega)\varrho_{\text{eq}}, \quad (5.45)$$

$$\varrho_{\text{eq}}A_\alpha^\dagger(\omega) = e^{\beta\omega}A_\alpha^\dagger(\omega)\varrho_{\text{eq}}. \quad (5.46)$$

Ten years ago some studies were carried out aiming to generalize the Lindblad form in the case of time dependent semigroup generators [89].

They chose a dynamical map of this form

$$\Lambda = \sum_j W_j(t - t_0) \varrho(t_0) W_j^\dagger(t - t_0), \quad W_j(0) = c_j \text{Id}, \quad (5.47)$$

the requirement that $\sum_j W_j^\dagger(t) W_j(t) = 1$ at any time t guarantees the conservation of the trace.

The general form may be written as

$$\frac{d}{dt} \varrho(t) = L(t) \varrho(t), \quad (5.48)$$

$$L(t) = L_H(t) + L_D(t), \quad (5.49)$$

$$L_H(t) M = -i[H(t), M], \quad (5.50)$$

$$L_D(t) M = \frac{1}{2} \sum_{l,k} d_{k,l} \{ [B_k M, B_l^\dagger] + [B_k, M B_l^\dagger] \}. \quad (5.51)$$

where we have assumed that each $W_m(t)$ can be expanded in a fixed basis $W_m(t) = \sum_k c_{mk}(t) B_k$, and $d_{kl} = \sum_m c_{mk}(t) c_{ml}^*(t)$. The main issue within this approach is that the existence of a generator $\mathcal{L}(t, t_0)$ for the dynamical map $\Lambda(t, t_0)$ is not always possible [89].

More recently [96], starting from the point that the Lindblad form describes the most general generator of a dynamical semigroup only in the time independent case, proved that it is possible to preserve the positivity also when the λ_n in (5.23) are not positive if either they or the operators L_n are time dependent. The proof is based on the fact that if L is a generator of a dynamical semi-group, then L needs to be translational invariant, i.e $L(t, t_0) = L(t - t_0)$, but this is not the case if L becomes time dependent.

5.4 Numerical Methods

From a numerical point of view it is convenient to rewrite the differential equation for the reduced density matrix ϱ_S as follows:

$$\frac{d\varrho_S(t)}{dt} = -i[H, \varrho_S(t)] + \mathcal{D}(\varrho_S(t)) = \mathcal{L}(\varrho_S(t)). \quad (5.52)$$

\mathcal{D} is called the dissipator and depends on which approach is chosen, and on the interaction Hamiltonian. Both \mathcal{D} and \mathcal{L} are operators acting on an operator, the density matrix, for this reason they are sometimes called *superoperators* in the literature. From now on we will not consider anymore the density matrix for the bath degrees of freedom and consequently we drop the sub-notation S on the quantities in (5.52).

As a first example we take a simple but very used model coming from a simplified

Redfield equation [71, 96]. If H_I is chosen to be a single product of a system and a bath operator in (5.18): $H_S = A \otimes B$, we get a simplified expression of in the Schrödinger picture

$$\frac{d\rho}{dt} = -i[H, \rho] - \{A\Lambda\rho - \rho\Lambda^\dagger A + \Lambda\rho A + A\rho\Lambda^\dagger\}, \quad (5.53)$$

where Λ depends on the correlation function of A , as

$$\Lambda = \int_0^\infty dt' \langle A(t')A(0) \rangle e^{-iHt'} B e^{iHt'}. \quad (5.54)$$

Once the system is written as (5.52) we may see that it is possible to get a solution for $\rho(t)$ via different methods. A direct approach is to solve (5.52) as a matrix exponential [43],

$$\rho(t) = e^{-i\mathcal{L}t} \rho, \quad (5.55)$$

the only difference with a usual Liouville equation is that now \mathcal{L} is not Hermitian. Among the methods that have been suggested for the evaluation of a non-Hermitian matrix exponential when solving (5.55) there are the Arnoldi method presented in Chapter 3, and the Chebyshev polynomial expansion [35]. We remark here that extra care needs to be observed when applying the Chebyshev expansion for (5.55) as the matrix is not Hermitian, as generally the series diverges for nonreal arguments. However it has been numerically shown [5] that the series may still converge for small imaginary part of the eigenvalues of \mathcal{L} .

We mention here that it is possible to write a symplectic integrator algorithm for an analogous classical canonical system, for the general Liouville–von Neumann equation both for closed and open systems. We may define two coupled canonical variables

$$\begin{aligned} Q(t) &= \rho(t), \\ P(t) &= \dot{\rho}(t), \end{aligned} \quad (5.56)$$

and Hamiltonian G , to avoid confusion in the notation

$$G(Q, P) = \frac{1}{2}[P^T P + Q^T W Q], \quad (5.57)$$

where $W = -\mathcal{L}^2$. We may then write down the equations of motion for Q and P and we get

$$\dot{P} = -WQ(t), \quad (5.58)$$

$$\dot{Q} = P(t), \quad (5.59)$$

with this last set of equations we may use any symplectic algorithm that has been developed in the literature for the classical case, see [36, 52] for some examples of these algorithms. For more details about this method see [33, 9], for a specific applications to the Redfield equation see [43, 42].

Another possible approach treats differently the unitary and the dissipative terms. It is possible to solve via usual methods the unitary term of (5.52), to get a propagator for the dissipative term \mathcal{D} and combine them via a splitting technique [77], we solve separately

$$\frac{d\varrho}{dt} = -i[H_S, \varrho], \quad (5.60)$$

$$\frac{d\varrho}{dt} = \mathcal{D}(\varrho). \quad (5.61)$$

The first line is immediately solved as in the closed system case: $\varrho(t) = U(t)\varrho_0U^\dagger(t)$. For the second equation everything depends on \mathcal{D} , if it comes from a Lindblad form or from a RWA approximation it is linear with respect to ϱ .

In this case it has been suggested in the literature to use a (explicit) midpoint rule [77], solving directly

$$\varrho_{n+1} = \varrho_n + \delta t \mathcal{D}\left(\frac{1}{2}(\varrho_{n+1} + \varrho_n)\right) = G(\delta t)\varrho_n, \quad (5.62)$$

we may then combine the two methods and get a symmetric total evolution operator

$$\varrho_{n+1} = G\left(\frac{1}{2}\delta t\right) e^{-iH\delta t} \varrho_n e^{iH\delta t} G\left(\frac{1}{2}\delta t\right). \quad (5.63)$$

The main advantage of such approach is that it in the limit of small approximations it recovers the unitary nature of the propagator for the isolated system.

When dealing with the Redfield equation, \mathcal{D} is time indepent in (5.52) as it is a Markovian approximation of the memory kernel. Recently a Runge–Kutta(RK) method has been applied both for a Markovian and for a non–Markovian type of dynamics where \mathcal{D} contains a memory kernel as in (5.15) [48]. The two joint equations for the dynamics are

$$\frac{d\varrho}{dt} = -i[H_S, \varrho] + \mathcal{D}(\varrho(t)), \quad (5.64)$$

$$\mathcal{D}(\varrho(t)) = \int_0^t K(t, t')\varrho(t, t')dt', \quad (5.65)$$

$$(5.66)$$

where K is the memory kernel. If we apply a generalized RK scheme we get

$$\varrho_{n+1} = \varrho_n - i\delta t \sum_{j=1}^m b_j \mathcal{L}(t_n + c_j \delta t, P_{n,j}, Z_{n,j}), \quad (5.67)$$

$$P_{n,j} = \varrho_n - i\delta t \sum_{l=1}^m a_{jl} \mathcal{L}(t_n + c_l \delta t, P_{n,l}, Z_{n,l}), \quad (5.68)$$

$$Z_{n,j} = q_n(t_n + c_j \delta t) + \delta t \sum_{l=1}^m a_{lj} \mathcal{D}(t_n + c_j \delta t, t_n + c_l \delta t) P_{nl}, \quad (5.69)$$

$$q_n(t) = \delta t \sum_{l=0}^{n-1} \sum_{k=1}^m b_k \mathcal{D}(t, t_l + c_k \delta t) P_{lk}. \quad (5.70)$$

a_{ij} , b_j and c_j are the RK parameters and depends on the order and the number of stages of the chosen RK method. The comparison of the numerical results with a four stages fourth-order RK for a simple system where in good agreement with theoretical data in both the Markovian and the non-Markovian system [48].

5.5 The Augmented Dynamics Relaxation Approach

In this section we present the new approach we have been developing. Starting from the point of view that the Lindblad form is not a necessary condition in the case of time dependent coefficients [89, 96], nothing prevents us to try to develop a method that preserves the characteristics we need for the density matrix, while retaining greater flexibility than the Lindblad form would allow. The final aim would then to use this greater flexibility to the introduce some physical features of the bath.

Recalling the initial problem we may generalise it as follows: we have an initial equation of motion for ϱ

$$\dot{\varrho} = g_0(\varrho), \quad (5.71)$$

where generally $g_0(\varrho) = -i[H_0, \varrho]$, H_0 and ϱ being the Hamiltonian and the density matrix of the system we want to simulate. We suppose also that we know the equilibrium value ϱ_{eq} we want to reach.

We may formulate this problem by adding a set of external dynamical variables ξ that depends on ϱ . The augmented system then becomes

$$\begin{aligned} \dot{\varrho} &= g(\xi, \varrho), \\ \dot{\xi} &= f(\xi, \varrho), \end{aligned} \quad (5.72)$$

where for the external variables y there holds $g(\xi = 0) = g_0$ and $f(\xi, \varrho)$ describes the dynamics of the augmented variables. Let us recall the requirements we want to fulfill for the dynamics of ϱ :

- there exists only one equilibrium point of the augmented system (ϱ_{eq}, ξ_{eq}) i.e.

$$\begin{aligned} g(\xi_{eq}, \varrho_{eq}) &= 0, \\ f(\xi_{eq}, \varrho_{eq}) &= 0, \end{aligned} \tag{5.73}$$

- the trace of $\varrho(t)$ is preserved;
- the positivity of $\varrho(t)$ is preserved;
- $\varrho(t)$ is Hermitian.

Ideally we would like to turn the augmented terms into g to “turn off” once the equilibrium is reached i.e.: $\lim_{t \rightarrow \infty} g(\xi, \varrho) = g_0(\varrho)$, but it might not be possible to have also this extra requirement. We have complete freedom for both g , in terms of the dependence on ξ , and f . The aim of this method is to exploit this freedom and to use it to mimic for instance, a certain physical effect that we know influence most the relaxation of the system, or to have the dynamics of the extra variables to mimic some features of the environment. We may summarize this attempt with a question: if it is possible to build up a sequence of unitary propagators $U_n = e^{-iH(\xi_n)\Delta t}$ such that the final evolution of $\varrho(t)$ has a dissipative nature. The main difference of this attempt with either the Bloch–Redfield theory, or with the Lindblad form is that with this Augmented Dynamics Relaxation (ADR) the Hamiltonian structure of the dynamics is fully preserved. We are not adding any extra term like the relaxation core \mathcal{D} , whether with a memory kernel in a Mori–Zwanzig [64, 99] type of equation or with a Markovian approximation like in the Bloch–Redfield case or the sum over the trace–class operators in the Lindblad form. For this reason, the dynamics described by (5.72) is piece–wise unitary and so the positivity condition, the Hermitian condition and the conservation of the trace for ϱ at anytime are immediately fulfilled. For the same reason also the positivity of ϱ at anytime is not a problem.

The only remaining issue is the study of the stability points of the augmented system. Obviously it is extremely difficult to fully analyze that, for this reason as first step we try to verify the method for a simple system.

5.6 Augmented Dynamics Relaxation on a Toy System

The simplest system that can be studied in this framework is a two–state quantum system coupled to a bath. For simplicity, we set the unperturbed Hamiltonian of the system to be diagonal:

$$H = \begin{bmatrix} \omega & 0 \\ 0 & -\omega \end{bmatrix}. \tag{5.74}$$

The equilibrium value we want to get for ϱ is

$$\varrho_{eq} = \begin{bmatrix} e^{-\beta\omega} & 0 \\ 0 & e^{\beta\omega} \end{bmatrix}, \quad (5.75)$$

for the evolution we have that $\varrho(t) = U(t)\varrho_0U^\dagger(t)$ where

$$U(t) = e^{-iHt}. \quad (5.76)$$

Looking term-by-term at the equation of motion for the density matrix we have:

$$\dot{\varrho}_{[1,1]} = 0, \quad (5.77)$$

$$\dot{\varrho}_{[1,2]} = -2i\omega\varrho_{[1,2]}, \quad (5.78)$$

$$\dot{\varrho}_{[2,1]} = 2i\omega\varrho_{[2,1]}, \quad (5.79)$$

$$\dot{\varrho}_{[2,2]} = 0. \quad (5.80)$$

As expected this set of equations will never reach ϱ_{eq} .

Because of the conservation of the trace we have that $\varrho_{[2,2]} + \varrho_{[1,1]} = 1$; and since ϱ is Hermitian $\varrho_{[1,2]}^* = \varrho_{[2,1]}$. For this reason we may introduce a three-variable system that fully describes the dynamics of ϱ . We define

$$\rho_1 = \varrho_{[1,1]}, \quad (5.81)$$

$$R_2 = \text{Re}(\varrho_{[1,2]}), \quad (5.82)$$

$$I_2 = \text{Im}(\varrho_{[1,2]}). \quad (5.83)$$

In the general case to preserve the Hermitian nature of the Hamiltonian we may set

$$g(y, \varrho) = \begin{bmatrix} \omega + h_1(y, z) & +h_2(y, z) - ih_3(y, z) \\ h_2(y, z) + ih_3(y, z) & -\omega - h_1(y, z) \end{bmatrix}, \quad (5.84)$$

where $\xi = (y, z)$. (5.84) may be written in a compact form as a parametrized Hamiltonian with the help of the Pauli matrices

$$H(y, z) = (\omega + h_1)\sigma_z + h_2\sigma_x + h_3\sigma_y. \quad (5.85)$$

We may write the equation of motions for each degree of freedom

$$\dot{\rho}_1 = -2(h_3R_2 + h_2I_2), \quad (5.86)$$

$$\dot{R}_2 = 2(\omega_0 + h_1)I_2 + h_3(2\rho_1 - 1), \quad (5.87)$$

$$\dot{I}_2 = -2(\omega_0 + h_1)R_2 + h_2(2\rho_1 - 1). \quad (5.88)$$

For the evolution we choose a symmetric numerical method

$$\begin{aligned}\varrho_h &= U_0\left(\frac{h}{2}\right)\varrho_n U_0\left(\frac{h}{2}\right)^\dagger, \\ \xi_{n+1} &= y_n + hf(\varrho_h, \xi_n), \\ \varrho_{n+1} &= U_1\left(\frac{h}{2}\right)\varrho_h U_1\left(\frac{h}{2}\right)^\dagger.\end{aligned}$$

where $U_n(\Delta t) = e^{-iH(\xi_n)\Delta t}$. It is important to remark that the previous system is not a quantum–classical dynamics because we are not averaging over any system or bath degrees of freedom, so those particular challenges that could come from a quantum–classical approach [69, 7, 29] (e.g. infinite temperature behavior, not satisfaction of the detailed balance condition,...) are avoided from the beginning.

5.6.1 First Attempts

From (5.85) we see that, even for the simple two–states system there is an extreme freedom in the choice of the h_j and on $f(\xi)$, in this section we show the numerical results of some of these choices. To start this section we present some results we obtained with a “guessed” augmented dynamics, later we give some mathematical basis on how to choose it. However we stress that we have not found yet a satisfactory expression for the augmented dynamics which fulfills all the requirements of the previous section. The details for this guessed dynamics are

$$h_1 = 0, \quad (5.89)$$

$$h_2 = y, \quad (5.90)$$

$$h_3 = z, \quad (5.91)$$

$$\dot{y} = I_2 - (\rho_1 - \mu)^2 y, \quad (5.92)$$

$$\dot{z} = (\rho_1 - \mu) - z. \quad (5.93)$$

This result is particularly interesting as it shows that it is possible to describe an overall relaxation process as a sequence of parametrized Hamiltonian evolution steps. At the same time this result is not satisfactory as the steady states reached by R_2 is wrong.

In order to have a clearer picture of the behavior of the critical points we need to analyse the Jacobian.

The Jacobian of the augmented dynamics, with two variables $\xi = (y, z)$ reads

$$\begin{bmatrix} 0 & -2h_3 & -2h_2 & -2R_2\partial_y h_3 - 2I_2\partial_y h_2 & -2R_2\partial_z h_3 - 2I_2\partial_z h_2 \\ 2h_3 & 0 & 2(\omega_0 + h_1) & 2I_2\partial_y h_1 + (2\rho_1 - 1)\partial_y h_3 & 2I_2\partial_z h_1 + (2\rho_1 - 1)\partial_z h_3 \\ 2h_2 & -2(\omega_0 + h_1) & 0 & -2R_2\partial_y h_1 + (2\rho_1 - 1)\partial_y h_2 & -2R_2\partial_z h_1 + (2\rho_1 - 1)\partial_z h_2 \\ \partial_{\rho_1} f & \partial_{R_2} f & \partial_{I_2} f & \partial_y f & \partial_z f \\ \partial_{\rho_1} g & \partial_{R_2} g & \partial_{I_2} g & \partial_y g & \partial_z g \end{bmatrix}, \quad (5.94)$$

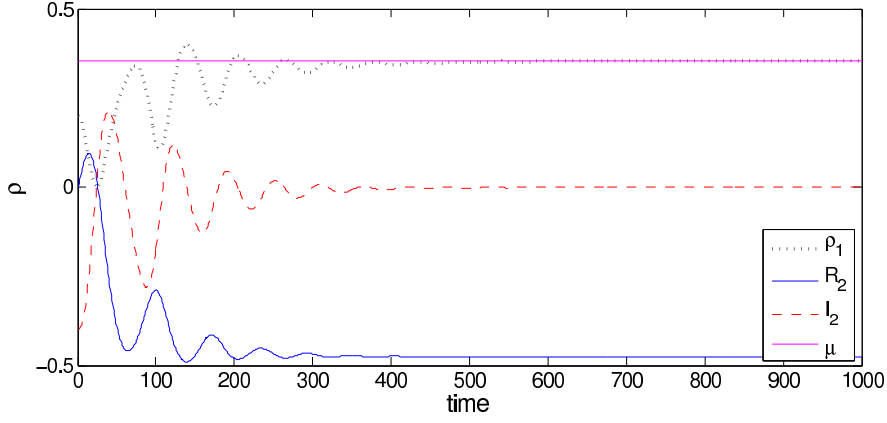


Figure 5.1: Dissipation on all the ϱ elements, wrong steady states for R_2 , μ is the equilibrium value for ρ_1 .

at the desired equilibrium ($\rho_1 = \mu$, $R_2 = I_2 = 0$), and making the reasonable assumptions that $h_1(\xi_{eq}) = h_2(\xi_{eq}) = h_3(\xi_{eq}) = 0$, (5.94) reads:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2\omega & \partial_y h_3 \tilde{\mu} & \partial_z h_3 \tilde{\mu} \\ 0 & -2\omega & 0 & \partial_y h_2 \tilde{\mu} & \partial_z h_3 \tilde{\mu} \\ \partial_{\rho_1} f & \partial_{R_2} f & \partial_{I_2} f & \partial_y f & \partial_z f \\ \partial_{\rho_1} g & \partial_{R_2} g & \partial_{I_2} g & \partial_y g & \partial_z g \end{bmatrix}, \quad (5.95)$$

where $\tilde{\mu} = 2\mu - 1$ and all the functions are evaluated at the equilibrium point. From (5.95) it is clear that the spectrum of this matrix at the equilibrium point will always contain at least an eigenvalue with 0 real part, so an asymptotic stability is impossible. This happens because of two reasons:

- at the equilibrium point most of the density matrix terms have to go to 0;
- $g(\varrho, \xi)$ is linear in ϱ because has to have the form $g(\varrho, \xi) = -iH(\xi)\varrho + i\varrho H(\xi)$;
- we are assuming $h_j = 0$ at the equilibrium to gain back the unperturbed Hamiltonian.

These factors together assure that there will be full rows of zeros in the Jacobian at the equilibrium. Due to the large number of parameters, and due to the fact that partial derivatives of unknown functions are involved it is difficult to perform a full analysis of (5.95), we can however make some general observations, and try to get a satisfactory solution of (5.95) using some simplifying assumptions.

From (5.95) it is clear that if we want the non-zero eigenvalues to have negative real part we need to have $\partial_y f + \partial_z g < 0$, and this is why in our guessed dynamics we put an exponential decaying term on both y and z (5.89). On the other end it is possible to prove that if we assume $\partial_{\rho_1} g = \partial_{R_2} g = \partial_{I_2} g = 0$, we get a quartic polynomial for the eigenvalues

$$\lambda^4 + \lambda^3(\partial_z g + \partial_y f) + \lambda^2\alpha + \lambda\beta + \gamma, \quad (5.96)$$

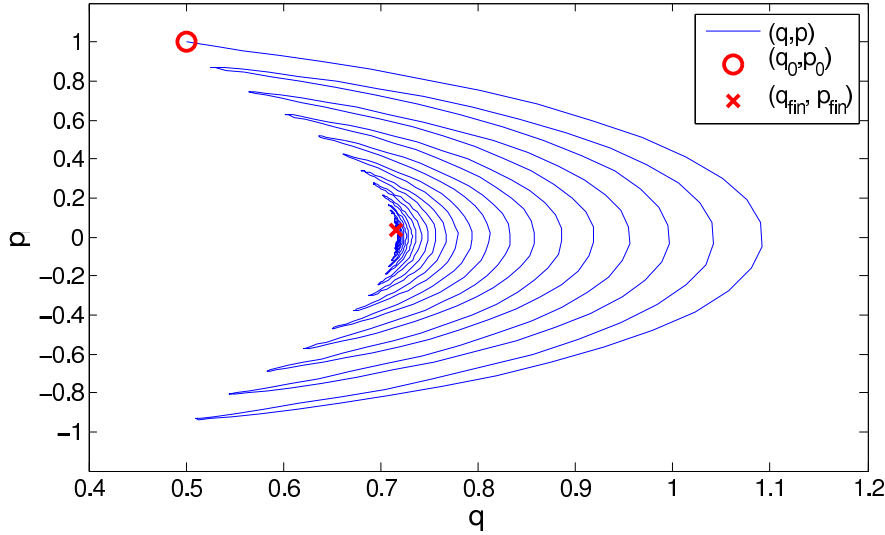


Figure 5.2: Phase Portrait for the parametrized pendulum.

where α and β are combinations of partial derivatives of (5.95).

The main issue with this simplification is that, to get all the roots of (5.96) in the left hand side plane we should have all positive coefficients, but $(\partial_z g + \partial_y f)$ has to be negative. Similar simplifications led to the same results.

The current direction of work is on the analysis of the full (5.95) without any assumptions, looking for equilibrium points which satisfy the requirements of the previous section. Any attempts of analysis with simplified versions of (5.95) has been so far unsuccessful.

From a qualitatively point of view, if we look at (5.86) we see that when R_2 and I_2 reach the equilibrium value, this also sets $\dot{\rho}_1$ to zero. In fact if we build the augmented dynamics in order to drive R_2 and I_2 to the equilibrium we then get a steady state for ρ_1 , as the derivative goes to zero as R_2 and I_2 go to zero, but the value of ρ_1^{eq} is not the desired one and depends on the initial condition. A similar behavior may be described for R_2 , I_2 with respect to the augmented variables, see Fig. 5.6.1. To explain better this behavior we take as an example a simple harmonic oscillator, where the frequency depends on the parameter y

$$\begin{pmatrix} \dot{q} \\ \dot{p} \end{pmatrix} = \begin{bmatrix} 0 & y \\ -y & 0 \end{bmatrix} \cdot \begin{pmatrix} q \\ p \end{pmatrix}. \quad (5.97)$$

We may ask whether it is possible to find a function $f(t) = \dot{y}$ such that given $(q_0, p_0) \neq (0, 0)$ the system dissipates energy and relaxes to $(0, 0)$.

In Fig. 5.6.1 we show the phase portrait of (q, p) for $f(t) = -0.1y - p$, we pick 0.1 as a prefactor to have a slow dissipation in that variable. It is clear that the parametrized frequency introduces a dissipation on the system, and we reach a steady state with $p^{\text{eq}} = 0$, but the steady state $q^{\text{eq}} \neq 0$ and depends on the initial choice of (q_0, p_0) . In fact we are draining energy from the system and when y reaches 0 then the system

freezes and remains there, the higher the energy of the initial state (q_0, p_0) the longer it takes to dissipate and this explains why we get a dependence on the initial state.

From this simple example we see from Fig. 5.6.1 that the dynamics of the parametrized system is extremely different from a dissipating (spiraling toward zero) oscillator.

A possible explanation of this dependence from the initial conditions comes from a perturbative expansion of the (5.72), in fact we may consider the component of the Hamiltonian which depends on the augmented variable as a time dependent perturbation $\epsilon V(t)$ to H_0 and write, using the Liouvillian,

$$\dot{\varrho}(t) = -i(L_0 + \epsilon L_V(t))\varrho(t). \quad (5.98)$$

We then expand $\varrho(t)$ and the initial value ϱ_0 about the equilibrium value ϱ_{eq} :

$$\varrho(t) = \varrho_{\text{eq}} + \Delta\varrho(t), \quad (5.99)$$

$$\varrho_0 = \varrho_{\text{eq}} + \delta\varrho_0. \quad (5.100)$$

$$(5.101)$$

With this change of variable we get an equation of motion for $\Delta\varrho(t)$

$$\dot{\Delta\varrho}(t) = -i(L_0 + \epsilon L_V(t))(\varrho_{\text{eq}} + \Delta\varrho(t)), \quad (5.102)$$

at the second order approximation we have

$$\dot{\Delta\varrho}(t) = -i(\epsilon L_V(t)\varrho_{\text{eq}} + L_0\Delta\varrho(t)), \quad (5.103)$$

where $L_0\varrho_{\text{eq}} = 0$. This last equation (5.103) is at the basis of the Linear-Response theory [87]. We may solve it and get an integral expression for $\Delta\varrho(t)$,

$$\Delta\varrho(t) = e^{-iL_0t}\delta\varrho_0 - i\epsilon \int_0^t e^{-iL_0(t-s)}L_V(s)\varrho_{\text{eq}}ds, \quad (5.104)$$

in this new form the steady state we want to get is $\Delta\varrho(t) = 0$, from (5.104) we see that, in order to get $\Delta\varrho(\tilde{t}) = 0$ for some \tilde{t} the choice of the augmented expression $L_V(t)$ depends on the initial condition $\delta\varrho_0$.

This dependence on the initial conditions gives us a clear indication that the system is not chaotic enough, in fact for a system to be chaotic we should observe a loss of dependence from initial conditions.

5.7 Discussion and open questions

As this whole chapter is about a work in progress, we underline here the partial results we have obtained so far and the open questions which have arisen, we will also provide some future directions of research.

The new ADR method consists on the introduction of an artificial parameter with

the aim of driving the augmented system to the desired equilibrium. We showed numerically that it is possible to drive the system to steady states via a time dependent variation of the Hamiltonian. We are also able to drive two of the three variables to the expected equilibrium values.

From one hand in this way the issues related to the unphysical behavior of the Bloch–Redfield method are overcome, and also the requirements are looser than those for the Lindblad form. If we are interested only on dissipation over particular degrees of freedom, such as for instance for a population preserving decay then ADR may be already applied, and we have shown numerically that it is possible to have a non exponential decay, see Fig.5.6.1.

At the same time there are still challenges to overcome, mainly:

- it is difficult to control the augmented system, even for a simple system and the analysis of the Jacobian (5.95) proved to be a difficult challenge;
- at this point we have not been able to determine a strategy to give some directions for the choice of the augmented dynamics in the general case;
- both numerical tests and a perturbation expansion show that there is a dependence on the initial conditions that needs to be analyzed;
- this great freedom may result in an augmented dynamics substantially distorted from the original one, modifying important features of the system like creating artificial steady states that do not exist in the original system.

The two main strands of future researches consist of the analysis of the existing method, mainly a study of the behavior of the equilibrium points in the parameter space, and on the exploration of possible extensions of ADR: for the analysis of the current method it might be necessary to apply bifurcation theory techniques for the study of the Jacobian (5.94) in the general case, with the aim of getting at least partial information (such as those we had for ∂g_z and ∂f_y), to guide the guess for the parameters.

In particular as observed before, we need to develop an augmented dynamics complex enough to observe a chaotic and dissipative behavior on the real system. In fact if the augmented dynamics is not complex enough, it is not possible to spread the energy of the system into the augmented degrees of freedom, which have to behave like a chaotic reservoir.

Because of that it would also be interesting to add an extra artificial particle and to use it to drive the system to the desired equilibrium, with the extra degrees of freedom it would be possible to create a sufficiently large chaotic reservoir in which the energy of the system would be allowed to spread, resulting in a decay on the steady states. At the same time dealing with a large number of degrees of freedom may result on extra difficulties for the control of such dynamics, to insure the decay of the system on the proper steady state.

Another possibility is to link ADR with the well known spin boson system. It is possible to prove that the interaction of an infinite harmonic bath on the system is like the effect of a stochastic term [50, 34]. The Hamiltonian for the spin boson system is

$$H(t) = -\frac{1}{2} [\Delta(t)\sigma_x + \epsilon(t)\sigma_z + \zeta(t)\sigma_z] \quad (5.105)$$

where $\Delta(t)$ and $\epsilon(t)$ are respectively the energy transfer and the biasing energy terms, while $\zeta(t)$ is the stochastic factor coming from the bath.

This equation is similar to the one for the augmented dynamics (5.85), the known issue of the spin boson approach is that ignoring the effects of the system on the bath drives the system to an “infinite temperature” equilibrium state, that is to a situation where the two states are equally populated ($\rho_1 = \frac{1}{2}$) [85, 30, 50]. It would be interesting to link the spin boson with our new method, where the parameters are affected by the system dynamics, trying to overcome the infinite temperature issue.

Conclusions

In this thesis we have presented several numerical algorithms for the solution of the Liouville–von Neumann equation. We divide this work into two main frames of research.

Closed Quantum Systems

In the context of closed quantum systems for nuclear spin dynamics we have studied both the autonomous and non–autonomous cases.

For the autonomous case we have performed the first analysis of the Zero–Track–Elimination (ZTE) method, and proved both numerically and analytically the weakness of such a method. It is not enough to know the behavior of a linear combination of periodic functions for a short initial time, especially if the initial time is not related to the lowest single oscillation, to identify all the modes; consequently the pruning step in ZTE may potentially discard low frequency oscillations. We have proposed two modifications of the method: we need to relate the initial check time with the smallest eigenvalue of the Liouvillian and secondly that ZTE may be safely used only in the case of well separated eigenvalues. We have also proved why despite the previous points, in the NMR case ZTE works. This is due to the fact that, in NMR, the only quantity that is used for the comparison between different methods is the signal (Free Induction Decay, FID). To take into account the relaxation process the FID is damped by an exponential; this damping term destroys the differences in the low frequency modes where the error of ZTE with respect to other canonical methods lies.

The main result of this thesis has been the development of a new method for the direct evaluation of the expectation values in quantum simulations. We exploited the fact that when comparing quantum simulations with experiments the quantities at stakes are the expectation values of observables. These objects are always scalar time dependent functions independent of the size of the systems. We have shown that via a direct application of the Chebyshev expansion to the equation for the expectations we get a new method called Direct Expectations via Chebyshev, or DEC, that exploits the reduction of the key quantities to a scalar function. The most expensive part of DEC is the the initial iteration procedure for the evaluation of the Chebyshev polynomials. For this part we developed an algorithm to calculate the exact number of terms in the expansion which will be needed throughout the whole simulation. This stopping criterion for the iterations is different from those presented in the literature based on error estimations. Numerical tests of DEC for nuclear spin dynamics show that DEC is up to an order of magnitude faster than a traditional Krylov based method, especially for large systems. When the system requires a short and very precise simulation, i.e. small total time but many steps, DEC gains even more in term of performances. DEC is a general method that may be applied to any quantum system described with the density matrix formalism.

For non–autonomous nuclear spin systems we have explored various splitting meth-

ods. A first type of method was developed exploiting the particular form of the time dependency: it is possible to write the Hamiltonian as a sum of time dependent scalar functions times fixed matrices. This method proved to be fairly accurate but become very expensive when the system size increases. This behavior comes from the fact that we need to diagonalize each split term once for all, and to the fact that at each step we perform a not too small (~ 10) number of matrix vector multiplications.

We explored also a second method, where we exploited the fact that, due to different magnitude among the type of interactions, the largest elements of the Hamiltonian lie on the diagonal. We therefore developed a diagonal splitting method (DS), where the the Liouvillian was divided between diagonal and non diagonal contributions, and the exponential of the non-diagonal matrix was evaluated via a Lanczos method. Due to the fact that this last matrix is sparser than the original Liouvillian it is possible to decrease the computational costs by 30%, if compared with Krylov-Lanczos techniques. We have also shown with numerical tests that the errors for this method remains comparable with Krylov-Lanczos techniques.

A possible future direction for work related to this section would be:

- a time dependent extension of DEC, that is, the exploitation of the Chebyshev expansion in the case of a time dependent Hamiltonian;
- for the splitting methods we have shown that for NMR simulations they may be used directly, as the errors are small and they perform better than Krylov-Lanczos methods when the stepsize is not too small. Nevertheless, a great deal remains to be explored, especially with the goal to find more clever ways to split the Hamiltonian rather than the simple diagonal plus non-diagonal component.

Open Quantum Systems

In the last chapter of the thesis we focused on the description of open quantum systems, particularly on the numerical methods that have been developed in the literature for the solution of the Liouville-von Neumann equation for the density matrix. At first we underlined the weaknesses of the two main theoretical approaches: the Lindblad form and the Bloch-Redfield equation. By exploiting the fact that the Lindblad form is not a necessary requirement in the case of time dependent coefficients, we developed an approach based on the addition of time dependent external parameters. The appeal of this new method is that it bridges between Lindblad and Bloch-Redfield, allowing more freedom in the choice of the dissipation than Lindblad and at the same time the unphysical behaviors that might appear with a Bloch-Redfield approach are avoided from the beginning.

We tested the augmented dynamics relaxation (ADR) method on a simple toy system, the results showed that it is possible to construct a dissipative system through a sequence of unitary (conservative) propagation steps. At the same time it is very difficult to find a proper expression for the augmented dynamics, and all our results

show a possible dependence on the initial data. This new approach is still a work in progress and has never been explored in the literature, but the aim to develop new ways to control the augmented dynamics, which will overcome the present issues.

It would be interesting to explore the possibility of introducing an artificial spin with a driven dynamics, this extra particle would be interacting with the bath and the dissipation would be transferred to the system through the interaction with this artificial particle. with the aim that through the interactions between the proper spins and the artificial one a dissipative process may arise.

As a final remark we underline a possible link between the two sections; we mention that recently the Chebyshev expansion has been applied for the solution of the Liouville–von Neumann equation for short simulation of open quantum systems [35]. It proved to be quite efficient and very accurate. Due to the fact that even for open quantum systems the quantities we are interested are the expectation values, it should be straightforward to apply DEC in this case, and possible attain better performances than the methods we presented in the last chapter.

Appendix A

Time Dependent Propagator

A.1 The Dyson's operator

The aim of this section is to give a proof for the Dyson formula. In the derivation of this formula we follow [25]. From the Schrödinger equation we may write a differential equation

$$\frac{d}{dt}U(t, t_0) = -iH(t)U(t, t_0), \quad (\text{A.1})$$

via a formal integration we get

$$U(t, t_0) - U(t_0, t_0) = -i \int_{t_0}^t dt' H(t')U(t', t_0), \quad (\text{A.2})$$

We can solve it by iteration (even if we do not have a general proof that the solution converges). If we also substitute $U(t_0, t_0) = 1$ we get

$$U(t, t_0) = 1 - i \int_{t_0}^t dt' H(t') + (-i)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' H(t')H(t'') + \dots, \quad (\text{A.3})$$

we rewrite the third term of this expansion reversing the order of integration as

$$\int_{t_0}^t \int_{t_0}^{t'} dt'' H(t')H(t'') = \frac{1}{2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' H(t')H(t'') + \frac{1}{2} \int_{t_0}^t dt'' \int_{t''}^t dt' H(t')H(t''). \quad (\text{A.4})$$

We can change the variables in the second term of the last expression as they are dummy variables and we get

$$\frac{1}{2} \int_{t_0}^t dt'' \int_{t''}^t dt' H(t')H(t'') = \frac{1}{2} \int_{t_0}^t \int_{t'}^t dt'' H(t'')H(t'), \quad (\text{A.5})$$

if we introduce the Heaviside function Θ we may recombine the two terms and get

$$\int_{t_0}^t \int_{t_0}^{t'} dt'' H(t')H(t'') = \frac{1}{2} \int_{t_0}^t dt' \int_{t_0}^t dt'' [H(t')H(t'')\Theta(t' - t'') + H(t'')H(t')\Theta(t'' - t')]. \quad (\text{A.6})$$

This last equation has the feature that contains the latest time at the farthest to the left. For this reason we introduce the time ordered operator T . For (A.6) we have

$$\int_{t_0}^t \int_{t_0}^{t'} dt'' H(t')H(t'') = \frac{1}{2} \int_{t_0}^t dt' \int_{t_0}^t dt'' T\{H(t')H(t'')\}, \quad (\text{A.7})$$

It is possible to repeat the same process to any other higher term of the sequence (A.3) and get for the general solution

$$U(t, t_0) = \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t dt_1 \dots \int_{t_0}^t dt_n T\{H(t_1) \dots H(t_n)\}. \quad (\text{A.8})$$

the last equation may be written as the exponential (1.40) assuming the convergence.

A.2 The Magnus expansion

Since the first appearing in 1954 [56] lots has been written on the Magnus expansion. The aim of this section is to state a couple of theorems that have been developed for the construction of the elements of the expansion and on the convergence of the series itself. In this section we mainly refer to the recent review on Magnus expansion [11].

Given a linear system of differential equations

$$\dot{y} = A(t)y, \quad y(0) = \text{Id}, \quad (\text{A.9})$$

the aim of the Magnus expansion is to find a function $\Omega(t)$ such that

$$y(t) = e^{\Omega(t)}, \quad (\text{A.10})$$

there are different ways to approximate $\Omega(t)$. We state here the theorem given by Magnus [56]

Theorem A.2.1. (*Magnus*) *Given $A(t)$ let $y(t)$ satisfy (A.9), then if some unspecified conditions of convergence are satisfied, we may write $y(t)$ as in (A.10) where*

$$\frac{d\Omega}{dt} = \sum_{n=0}^{\infty} \frac{B_n}{n!} \text{ad}_{\Omega}^n A, \quad (\text{A.11})$$

where B_n are the Bernoulli numbers and $\text{ad}_{\Omega}^n A$ is a linear operator defined as

$$\text{ad}_A B = [A, B], \quad \text{ad}_A^j B = [A, \text{ad}_A^{j-1} B]. \quad (\text{A.12})$$

If we integrate by iteration (A.11) we get an infinite series

$$\Omega(t) = \int_0^t A(t_1) dt_1 - \frac{1}{2} \int_0^t \left[\int_0^{t_1} A(t_2) dt_2, A(t_1) \right] dt_1 + \dots \quad (\text{A.13})$$

In Chapter 3 we have already written the first few terms of the Magnus expansion, it is possible to write an expression for the term at order n

$$\Omega_n(t) = \sum_{j=1}^{n-1} \frac{B_j}{j!} \int_0^t S_n^j(s) ds, \quad (\text{A.14})$$

where S_N^j is defined iteratively

$$S_n^j = \sum_{m=1}^{n-j} [\Omega_m, S_{n-m}^{j-1}], \quad S_n^1 = [\Omega_{n-1}, A], \quad S_n^{n-1} = \text{ad}_{\Omega_1}(A). \quad (\text{A.15})$$

For the convergence it is possible to prove that [11]

Theorem A.2.2. *Given the system (A.9) in a Hilber space \mathcal{H} and let $A(t)$ be bounded in \mathcal{H} . Then the Magnus series given by $\Omega(t) = \sum_{k=1}^{\infty} \Omega_k(t)$ with $\Omega_k(t)$ given by (A.14)*

converges in the interval $t \in [0, \tau)$, with τ obeying

$$\int_0^\tau \|A(s)\| ds < \pi. \tag{A.16}$$

and $\Omega(t)$ satisfies $y(t) = e^{\Omega(t)}$.

Appendix B

Perturbation Theory

We present here the demonstration of two results we used in Chapter 2, specifically the fact that the only contribution of an electromagnetic pulse to a spin system comes from the in phase half contribution, and the secular approximation we used to treat the Hamiltonian.

B.1 The Pulse

The electromagnetic pulse is given as an oscillating magnetic field along the x direction: $B_{\text{RF}} = 2B_1 e_x \cos(\omega_{\text{rf}} t)$. we may rewrite it as a sum of two rotating magnetic fields:

$$2B_1 e_x \cos(\omega_{\text{rf}} t) = B_1 (e_x \cos(\omega_{\text{rf}} t) + e_y \sin(\omega_{\text{rf}} t)) + B_1 (e_x \cos(\omega_{\text{rf}} t) - e_y \sin(\omega_{\text{rf}} t)), \quad (\text{B.1})$$

We apply then this magnetic field as a perturbation to a single spin problem, with $H_0 = -\frac{\gamma B_0}{2} I_z = -\frac{\omega_0}{2} I_z$. We write the time dependent perturbation as

$$V(t) = -\frac{\gamma B_1}{2} (e^{i\omega_{\text{rf}} t} I_x + e^{-i\omega_{\text{rf}} t} I_y), \quad (\text{B.2})$$

For the solution of this system we follow [74] specifically Chap. 5. The change of populations (w_α, w_β) between the state $|\alpha\rangle$ and $|\beta\rangle$, for this problem may be described with the Rabi's formula:

$$w_\beta = \frac{\gamma^2 B_1^2}{\gamma^2 B_1^2 + (\omega_{\text{rf}} - \omega_0)^2 / 4} \sin^2 \left[\left(\gamma^2 B_1^2 + \frac{(\omega_{\text{rf}} - \omega_0)^2}{4} \right)^{1/2} t \right]. \quad (\text{B.3})$$

Due to the fact that B_1 is in the range $1 - 200 \text{ kHz}$, so at least three-four orders of magnitude less than the Larmor frequency ω_0 [53], we have that $\gamma B_1 / \omega_0 \ll 1$. From (B.3) we see that the largest contribution to the transition comes from the resonance condition $\omega_{\text{rf}} \simeq \omega_0$. But if $+\omega_{\text{rf}}$ indicates the resonant component of B_1 , then for the remaining non-resonant part $-\omega_{\text{rf}}$ we have that if we substitute $-\omega_{\text{rf}}$ into w_β we obtain a contribution with small magnitude and fastly oscillating, we may then discard it as negligible.

B.2 The Secular Approximation

In this part of the appendix we sketch a proof for the secular approximation we have used to treat the Hamiltonian for the NMR system. We suppose that the Hamiltonian (H) may be split in two part, one (A) much larger than the other (B). We assume both A, B to be Hermitian, for this reason we may write down an orthonormal basis set from the eigenvectors $|\psi_n\rangle$ of A , like the Zeeman basis set. In general when $[A, B] \neq 0$, a matrix representation of B in the eigenset $|\psi_n\rangle$ is dense. However if the spectrum of A presents well separated groups of eigenvalues, then we can approximate B as a block-diagonal matrix following the pattern of near-degenerate eigenvalues of the spectrum of A . The idea is that if two eigenstates are well separated in A then we may approximate

We may write the secular approximation of B as

$$B \simeq B_0 = \sum_n b_n |\psi_n\rangle\langle\psi_n| + \sum'_{m \neq n} b_{mn} |\psi_m\rangle\langle\psi_n|, \quad (\text{B.4})$$

with $b_{mn} = \langle\psi_m|B|\psi_n\rangle$ and the primed sum only includes the near-degenerate states, i.e. omitting states for which

$$b_{mn} \ll |\lambda_m - \lambda_n| \quad (\text{B.5})$$

where λ_m is the eigenvalue associated with $|\psi_m\rangle$.

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