POLITECNICO DI TORINO

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Quantum exact response theory based on the Dissipation Function

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Summary

The exact response theory based on the Dissipation Function applies to general dynamical systems. In recent years, it has offered excellent results in various applications, from the field of non-equilibrium molecular dynamics to dynamical systems relevant in biological context and beyond. In this thesis, we derive its quantum translation. We first presented a brief summary of the most used quantum response theories. In many quantum dynamics, it has not yet been possible to overcome the perturbative approach, which is an approximation. Future extensions of our work could prove important in this regard. Firstly, we applied the quantization rule to the classical Dissipation Function. Then, we derived a quantum expression for calculating the expectation value of the observables over time, in a form analogous to that of the classical Dissipation Function response theory. To do this, we worked in finite-dimensional Hilbert spaces, as in the rest of the thesis. We tested the validity of the new formalism by applying it to qubit systems, which are of fundamental importance in quantum mechanics and at the basis of quantum computing. The dissipation operator used is not Hermitian. In an attempt to make it so, we derived a second expression, equivalent to the first. In addition to the Hermitian dissipation operator, the contribution of an antihermitian operator also appears in this second expression. Next, we studied the role that these dissipation operators have in the time evolution of the density operator. In conclusion, we tried to exploit the new formalism to solve Lindblad equations, which describe dissipative quantum dynamics, suggesting possible future extensions for this work.

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Chapter 1

Response theories in statistical and quantum mechanics

Statistical mechanics is the branch of mathematical physics that uses statistics and probability theory to study the mechanical and thermodynamic behaviour of systems composed of a large number of particles. It was born at the end of the XIX century thanks to the important contributions of its three founding fathers: L. Boltzmann, J. C. Maxwell and J. W. Gibbs.

Nature is made up of different scales. Let us look at a drop of water, observing more closely with the appropriate measurement systems, we discover a molecular structure and then an atomic structure. Moving away, we can see a river, then the earth and the solar system. Each scale has its own characteristics and a physical theory that explains them. These theories are different from each other and, going from large to small scales, we move from the theory of general relativity to classical Hamiltonian mechanics to quantum mechanics. Keeping these considerations in mind, we can understand the purpose for which statistical mechanics was born: to provide an understanding of macroscopic, thermodynamic observables in terms of the atoms at the microscopic scale, which obey the few fundamental laws of mechanics. The revolutionary idea that led to its birth is to introduce the concept of statistical ensemble, which is a large collection of virtual, independent copies of the system in various microscopic states. In other words, the statistical ensemble is a probability distribution over all possible microscopic states of the macroscopic system. Measures of pressure, temperature, magnetic susceptibility always entail an average of the sought quantity in macroscopic time intervals. If the system is at thermodynamic equilibrium, the measurements of these macroscopic observables are calculated with ensemble averages. The equivalence between these two types of

averages is guaranteed by the ergodic theory.
These are the initial foundations of statistical mechanics; from here numerous, effective and beautiful extensions of the theory have been developed. However, the theory of statistical physics in the years of its birth presented a series of controversies, the predicted results were in disagreement with experimental data. Subsequent discoveries in quantum physics resolved many of these controversies and brought great improvements to the theory of statistical physics.

In the first quarter of the XX century, several experiments were carried out which highlighted a series of inexplicable phenomena within the framework of classical physics. Following experiments on black body radiation, Max Planck came to state that the energy associated with electromagnetic radiation is transmitted in discrete units, called 'Quanta'. The value E of an energy quantum depends on the frequency ν of the radiation according to the formula $E = h\nu$, where h is the Planck's constant. Einstein managed to give a correct interpretation of the photoelectric effect by explaining it with the use of quanta, later called photons. The quantum nature of light was therefore revealed. Niels Bohr proposed an exact atomic model including the energy quantization principle. These are just a few important examples of experiments that confirmed the quantum nature of matter. These new quantum ideas caused, however, a growing number of anomalies, so a new physical theory capable of explaining the new phenomena with coherence was needed. This necessity led to a new mathematical formalism in which quantum ideas found their complete expression with the birth of quantum mechanics. Some of the most important mathematicians and physicists who contributed to the mathematical formulation of quantum mechanics are Heisenberg, Born, Dirac, Schrödinger, Von Neumann and Einstein. Two different formulations were born, 'Matrix Mechanics', formulated by Heisenberg, Jordan and Born in 1925 and 'Wave Mechanics' developed a few months later by Schrödinger. Only later, through Dirac's notation, their perfect equivalence will be discovered.

Quantum mechanics did not yet exist at the end of the XIX century, when statistical physics was born. However, statistical mechanics theory has been developed of such generality that it was found to adapt easily to the later quantum mechanics, leading in this way to the resolution of several open problems and apparent inconsistencies. So the introduction of quantum mechanics to statistical physics brought very important improvements in various applications, definitively consecrating the power of the XIX century's statistical formalism. Furthermore, this mathematical framework is so powerful that this type of description can be extended and adapted to any system far outside the fields of thermodynamics. The tools of statistical physics apply to every complex system that can be thought of as a 'macroscopic' entity made up of many 'microscopic' elements. Today, statistical mechanics finds applications in numerous very different areas: not only in the more classical fields of physics, chemistry and information theory but also in neuroscience, sociology, biology up to the newest applications in neuroscience, computer science and artificial intelligence.

Statistical physics initially focused on the study of macroscopic systems at thermodynamic equilibrium. However, the majority of systems of scientific interest are not at equilibrium, it was immediate to recognize the potential of statistical mechanics to describe them. Research in this direction led to the birth of non-equilibrium statistical physics. In this thesis, we will work precisely in this field, focusing on response theories, which study the behaviour of systems displaced from equilibrium due to an external perturbation. We will see that response theories can be of different types, in particular approximate or exact.

In this chapter, we will initially present the basic concepts and mathematical foundations of statistical and quantum mechanics. We will then summarize the developments of quantum response theory, starting from the older Kubo's approach, which is still valid and widely used even today, up to the most recent developments. We will briefly introduce the fluctuation theorems and finally present a recent classical exact response theory based on the Dissipation Function, highlighting its characteristics and quickly showing an application. We will see that this theory was born in the fields of Fluctuation Relations and molecular dynamics, but its validity is more general, it will in fact be presented in the context of classical dynamical systems. The main objective of this thesis is to develop the quantum translation of this classical theory to build a quantum response theory based on the Dissipation Function, and analyse its results, its characteristics, strengths and weaknesses and the potential innovations it could bring.

1.1 Fundamentals of statistical and quantum mechanics

Statistical Mechanics

The Hamiltonian formulation is the basis of quantum and statistical mechanics [1]. A Hamiltonian system is any dynamical system whose equations of motion can be derived from the Hamiltonian function $\mathcal{H}(q_i, p_i)$ as

$$\begin{cases} \dot{q}_k = \frac{\partial \mathcal{H}}{\partial p_k} \\ \dot{p}_k = -\frac{\partial \mathcal{H}}{\partial q_k} \end{cases} \tag{1.1}$$

q_i and p_i are called canonical variables.
These equations describe the evolution of the system in the 2N-dimensional phase

space

$$\mathcal{M} = (q_1, ..., \ q_N, \ p_1, ..., \ p_N).$$

However, the system (1.1) can be extremely complex, depending on the Hamiltonian function and the number of variables involved. The classic example, the one that was first treated in statistical mechanics, is the monoatomic ideal gas. One might consider that each time trajectory of each atom of the gas is in principle the best description one could hope. This description is well represented by (1.1). However, the number of atoms is of the order of Avogadro Number, $N_A = 6{,}022 \cdot 10^{23}$. Thinking better, even if one could access 10^{23} trajectories, what is he supposed to do with them? Also, one should know 10^{23} initial conditions, which is hardly an information we have access to. The idea behind statistical mechanics is to move on to a probabilistic treatment.

A physical observable is defined as any quantity that is in some way measurable either directly, with the appropriate measuring instruments, or indirectly, with calculation. Mathematically speaking, a generic observable $A = A(q_k, p_k, t) \in \mathbb{R}$ is a real function of canonical coordinates and time. Our system can be thought as a point Γ, called microstate, moving in time in the abstract 2N-dimensional phase space $\mathcal{M}$ according to (1.1). By introducing a probability measure μ_t on the phase space, one can calculate the expectation value of the macroscopic observables exploiting the microscopic dynamics. This probability measure is defined by thinking in terms of ensemble of systems 'suitably randomized'. If μ also admits a density function $f(q_i, p_i, t) \in \mathcal{M}$, the expectation value of an observable $A(q_i, p_i)$ is calculated as:

$$\langle A \rangle (t) = \int_{\mathcal{M}} A(q_i, p_i) f(q_i, p_i, t) dq_i dp_i.$$

For the purposes of this thesis, we are not interested in how an ensemble measure μ_t is constructed. It is sufficient for us to underline that, once the system has been defined through the Hamiltonian $\mathcal{H}$, a certain probability is assigned to each of its microstates Γ, assigning zero probability to inadmissible ones.

Returning to the gas example, macroscopic measurements are quantities that involve time averages on macroscopic timescale, $\overline{A}^t$. At thermodynamical equilibrium, an ideal gas is described by stationary ensembles $f(\Gamma)$ (microcanonical, canonical or grand-canonical), constant over time. The equivalence between the ensemble averages and the temporal ones,

$$\langle A \rangle = \int_{\mathcal{M}} A(q_i, p_i) f(q_i, p_i) dq_i dp_i = \lim_{t \to \infty} \frac{1}{t} \int_0^t A\Big(q(s), p(s)\Big) ds = \overline{A}^t,$$

is investigated by the ergodic theory. The latter still constitute an active and complex research area today. In the case of a gas at thermodynamical equilibrium, it is more than reasonable to take the limit $t \to \infty$, considering the separation of the time scales. The time needed to take a measurement in the laboratory, very short for us, is infinitely long on the microscopic scale. The equivalence between the two types of averages is valid.

The same reasoning is applicable to a very wide range of systems, even non-equilibrium ones. Anyway, the ergodicity of the system should always be demonstrated, which is a very difficult thing. Therefore, it is often simply assumed in statistical physics and investigated only in the ergodic theory research field; also in this thesis we will never deal with this question.

Let's consider a general dynamic $\dot{\Gamma} = G(\Gamma)$, Hamiltonian or not. The solution at time t, starting from an initial condition Γ is represented by the map $\Phi^t : \mathcal{M} \rightarrow \mathcal{M}$: $\Gamma(t) = \Phi^t \Gamma$. As the dynamics move the points of $\mathcal{M}$, in a sense, it moves the sets $E \subset \mathcal{M}$ as well, therefore one may say that the measure of E is the measure of the set of points that were somewhere else a time t earlier. This set is called preimage of E under the transformation Φ^t, and is denoted by:

$$\Phi^{-t}E = \{\Gamma \in \mathcal{M} : \Phi^t \Gamma \in E\}.$$

A thermodynamic system can be described by an ensemble in phase space only if its state is stationary and it is at thermodynamic equilibrium. However, if one forget about this and hypothesize the validity of this type of description in more general regimes, it is possible to draw important considerations [2]. One may imagine that probability is conserved in time and is transported in phase space $\mathcal{M}$, like the mass of fluids in real space. The probability density $f(\Gamma, t)$ evolves over time in the phase space like a perfect fluid. Proceeding with this formal analogy, one can derive the phase space continuity equation for $f(\Gamma, t)$, which is called Liouville Equation,

$$\frac{\partial f}{\partial t} = -\nabla_\Gamma \cdot (f\dot{\Gamma}). \tag{1.2}$$

Using the total derivative, one can write:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + G(\Gamma) \cdot \nabla_\Gamma f = -f \nabla_\Gamma \cdot G(\Gamma) = -f\Lambda.$$

The definition of the so-called phase space variation rate,

$$\Lambda \equiv \nabla_\Gamma \cdot G(\Gamma), \tag{1.3}$$

allows one to rewrite the Liouville equation as $\frac{d}{dt} lnf = -\Lambda$. Defining the Liouville operator,

$$\mathcal{L} = -i\Big(\nabla_\Gamma \cdot G(\Gamma) + G(\Gamma) \cdot \nabla_\Gamma\Big),$$

the solution of the Liouville equation (if the Liouville operator is time independent) can be formally written as

$$f_t(\Gamma) = e^{-i\mathcal{L}t} f_0(\Gamma). \tag{1.4}$$

For Hamiltonian systems, one has:

$$\Lambda(\Gamma) = \sum_{i=1}^{2N} [\frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial H}{\partial q_i}] = 0. \tag{1.5}$$

Hamiltonian dynamics is thus a sufficient condition for the validity of the Liouville Theorem, which states that $\frac{df}{dt} = 0$.

Understanding how a physical system responds to an external perturbation is an important question with great practical implications. The above considerations may offer the solution to this problem. However, the abstract $\mathcal{M}$ phase space is obviously immensely different from the familiar 3-dimensional space. On a practical level, it is very difficult mathematically to find the solution of eq. (1.2); operator (1.4) is often too complicated to handle. Furthermore, the perturbation could be time-dependent, implying an even higher degree of complexity. The most used techniques are therefore perturbative ones [3]. Assuming the perturbation is small, perturbative response theories are developed. We will present these in detail in the next section, for quantum systems. We will also see that, in classical physics, this approximate method is starting to be overcome; in particular, an approach based on the Dissipation Function is exploited to offer the solution of the Liouville equation in a much more manageable form.

Quantum mechanics

In quantum mechanics the physical states of a system are described by wavefunctions $\psi(x, t) \in \mathscr{H}$ [4], where t is the time variable and x the spatial one. The other big difference from classical physics is that now observables are no longer scalar functions but operators, eventually infinite-dimensional [5]. The evolution of $\psi(x, t)$ over time is governed by the Schrödinger equation,

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \mathcal{H}\psi(x,t), \quad \psi(x,0) = \psi_0(x). \tag{1.6}$$

$\hbar$ is the Plank constant h divided by 2π. $\mathcal{H}$ is the Hamiltonian operator and the wavefunction $\psi(x, t)$ is an element of the Hilbert space $L^2(\mathbb{C})$ (in general it can be an element of any Hilbert space, but the choice of $L^2(\mathbb{C})$ is more suitable for understanding the introductory basics). $\psi(x, t)$ has unitary norm and probabilistic interpretation,

$$\psi(x,t) \in \mathbb{C}, \quad \|\psi(x,t)\|^2 = (\psi, \psi) = 1.$$

When the Hamiltonian is time independent the stationary solutions are in the form

$$\psi(x,t) = e^{-\frac{i}{\hbar}Et}\psi(x),$$

where $\psi(x)$ is the eigenvector related to the eigenvalue problem $\mathcal{H}\psi(x) = E\psi(x)$, $E \in \mathbb{R}$ is the corresponding energy eigenvalue. Linearity is a peculiar characteristic of the quantum world, intimately linked to the principle of superposition. Therefore, the most general solution of the Schrödinger problem is a linear superposition of different energy eigenfunctions of the form

$$\psi(x,t) = \sum_n C(E_n) e^{-\frac{i}{\hbar}E_n t} \psi_{E_n}(x), \quad \psi(x,t) = \int_D dE C(E) e^{-\frac{i}{\hbar}Et} \psi_E(x)$$

The first formula refers to Hamiltonians characterized by a discrete spectrum of eigenvalues while the second one refers to Hamiltonians with a continuous spectrum. The time dependence can be considered part of the coefficient. Therefore, in the following, when not relevant for the purposes discussed, we will omit the type of dependence of ψ.

Chosen a basis $\mathcal{B}$ for the $L^2(\mathbb{C})$ space,

$$\mathcal{B} = \{\phi_k, k \in [1, \infty]\},$$

it is known that wave functions ψ and infinite-dimensional vectors $|v\rangle$ are in one-to-one correspondence, thanks to the functional analysis theorem of Fisher-Riesz [6]:

$$\psi = \psi_v(x) = \sum_k v_k \phi_k(x) \Rightarrow |\psi\rangle = |v\rangle = \sum_i v_i |i\rangle = [..., v_{i_{n-1}}, v_{i_n}, ..]'.$$

For the sake of simplicity, we have considered a basis with a discrete index j even if, in many situations, the index can be continuous. In this thesis, however, we will deal exclusively with discrete-spectrum quantum problems. The Dirac picture abandons the formalism based on the wave-function representation of physical states to adopt the vector formalism suggested by the Fisher-Riesz theorem. In this picture $|\psi\rangle$ is called ket-vector and it is a column vector. It is usual to introduce the corresponding bra-vector

$$\langle\psi| = [..., v^*_{i_{n-1}}, v^*_{i_n}, ..],$$

which is a row vector. In this way, the scalar product between two vectors can be represented as

$$(a, b) = \langle a|b\rangle = \sum_j \sum_k a^*_j b_k \langle j|k\rangle,$$

using an orthonormal basis $|n\rangle$ (for which we have $\langle n_j|n_k\rangle = \delta_{jk}$) one finds

$$(a, b) = \langle a|b\rangle = \sum_{n_j} \sum_{n_k} a^*_{n_j} b_{n_k} \delta_{jk} = \sum_n a^*_n b_n.$$

The condition of unitary norm is preserved:

$$\langle\psi|\psi\rangle = \sum_k |v_k|^2 = 1,$$

$|v_k|^2$ is the probability to find the system in the state ϕ_k.

The adjoint of a generic operator A, is defined as the operator $A^\dagger$ such that the following equivalence holds:

$$(\psi, A\psi) = (A^\dagger\psi, \psi).$$

An operator A is Hermitian if $A^\dagger = A$. Physical observables are represented by Hermitian operators. In the Dirac formalism, an arbitrary operator A thus corresponds to a (infinite dimensional) matrix

$$A_{i,j} = (\phi_i, A\phi_j), \quad A = \sum_i \sum_j |i\rangle A_{ij} \langle j|,$$

and the condition of hermitianity translates into

$$A^\dagger = A \iff A_{ij} = A^*_{ji} \;\; \forall i, j.$$

In quantum mechanics we can only have information about expectation values of physical observables. For an observable represented by the operator A, the expectation value is given by:

$$\langle A\rangle = (\psi, A\psi) = \langle\psi|A|\psi\rangle.$$

The constraint on the Hermitianity of observable operators has a very specific reason. The spectrum of the Hermitian operators is contained in $\mathbb{R}$ and the corresponding expectation values are therefore real, $\langle A\rangle \in \mathbb{R}$. For a non-Hermitian operator C, however, the spectrum may belong to $\mathbb{C}$, consequently the corresponding expectation value could be a complex number, $\langle C\rangle \in \mathbb{C}$. Expectation values represent the quantities measured experimentally. They must be real numbers, the hermitianity constraint guarantees this.

The measurement of operator A selecting the value λ within the eigenvalue set of the relevant spectrum entails that the wavefunction of the system changes to the corresponding eigenfunction $|\psi_\lambda\rangle$.

The same physical state ψ can be equivalently represented using different basis. A very used choice is the basis formed by the eigenstates relative to the Hamiltonian operator,

$$\mathcal{H}\psi_n(x) = E_n\psi_n(x) \Rightarrow \psi_n(x) \rightarrow |E_n\rangle.$$

However, in general, the basis of any other Hermitian operator could be adopted, for example, one can choose the momentum operator:

$$p\phi_k(x) = \hbar k \phi_k(x) \Rightarrow \phi_k(x) \to |k\rangle.$$

Representations of physical states relevant to two different basis are connected by a unitary transformation. A matrix S is unitary if

$$S^\dagger S = S S^\dagger = Id.$$

Unitary transformations preserve the correct normalization of physical states that ensures the probabilistic interpretation is maintained even if the basis is changed.

Quantum mechanics is formulated using two equivalent pictures: the Schrödinger picture and the Heisenberg picture. In the Schrödinger formalism $|\psi\rangle$ is a time dependent vector, namely, its components c_m are time-dependent. One has, in the energy basis,

$$|\psi\rangle = \sum_m c_m(t)|m\rangle = \sum_m c_m(0) e^{-\frac{i}{\hbar} t E_m} |m\rangle.$$

Operators are instead time independent in this representation. Anyway, their expectation values are, in general, time-dependent:

$$\langle A \rangle_t = \sum_r \sum_s c_r^*(0) c_s(0) e^{\frac{i}{\hbar} t (E_r - E_s)} A_{rs}.$$

Based on the equation for the expectation value it is possible to define the Heisenberg representation A_t for the evolution in time of a given operator A:

$$\langle A \rangle_t = (\psi(x,t), A\psi(x,t)) = (\psi_0 e^{-\frac{i}{\hbar}\mathcal{H}t}, A e^{-\frac{i}{\hbar}\mathcal{H}t}\psi_0) = (\psi_0, e^{+\frac{i}{\hbar}\mathcal{H}t} A e^{-\frac{i}{\hbar}\mathcal{H}t}\psi_0).$$

Therefore, in the Heisenberg picture operators are time-dependent and defined as

$$A_t = e^{+\frac{i}{\hbar}\mathcal{H}t} A e^{-\frac{i}{\hbar}\mathcal{H}t}, \tag{1.7}$$

while quantum states $|\psi\rangle$ are now fixed in time. In this picture, the commutator plays an essential role, it is defined as:

$$[A, B] \equiv AB - BA.$$

An operator A_t satisfies the so-called Heisenberg equation,

$$\frac{d}{dt} A_t = \frac{1}{i\hbar}[A_t, \mathcal{H}] + \partial_t A. \tag{1.8}$$

Despite the interpretative differences, the two pictures are equivalent as the expectation values of any operator always coincide. The Heisenberg picture presents a strong similarity with classical mechanics through equation (1.8). Indeed, a basic tool in Hamiltonian formulation (1.1) are the Poisson Brackets, defined as

$$\{A, B\} \equiv \sum_k \frac{\partial A}{\partial q_k}\frac{\partial B}{\partial p_k} - \frac{\partial B}{\partial q_k}\frac{\partial A}{\partial p_k}.$$

Thanks to the Poisson brackets one can express the evolution of a generic observable $A(q_k, p_k, t)$, in accordance with the dynamics (1.1) as

$$\frac{dA}{dt} = \{A, \mathcal{H}\} + \partial_t A. \tag{1.9}$$

The similarity of the Heisenberg equation (1.8) with the latter plays a crucial role in the quantization process of classical systems. It is the basis of the quantization rule, a criterion for expressing the quantum analogue of classical mechanics physical problems. Quantization rule states that the observables are replaced by their corresponding operators and the Poisson brackets by the commutator as follows:

$$\begin{array}{ccc} \multicolumn{3}{c}{\text{Classical system} \rightarrow \text{Quantum system}} \\ p,\ x,\ \mathcal{H},\ A & \rightarrow & \hat{p},\ \hat{x},\ \hat{\mathcal{H}},\ \hat{A} \\ \{\ \cdot\ ,\ \cdot\ \} & \rightarrow & \frac{1}{i\hbar}[\ \cdot\ ,\ \cdot\ ] \end{array} \tag{1.10}$$

By applying this criterion to the classical equation (1.9) one exactly finds the Heisenberg equation (1.8), but the real proof of the validity of this rule is due to the incredible results it has offered over the years to date.

The density operator

In quantum mechanics, a system is completely determined by its state $|\psi\rangle$ at the initial time, then the Schrödinger equation (1.6) describes its deterministic evolution over time. In statistical physics and whenever the state is not perfectly known, an ensemble of states description is used. The ensemble of states $\{|\psi_j\rangle, p_j\}$ takes into account that the system is in state $|\psi_j\rangle$ with probability p_j. Now, it becomes more convenient to describe the system by defining the density operator ρ [7]:

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|. \tag{1.11}$$

It is a simple generalization of what has already been described previously: if the system state is perfectly known the density operator is

$$\rho = |\psi\rangle\langle\psi|, \text{ i.e. } p_k = 1,\ p_j = 0\ \forall j \neq k,$$

and it is said that the system is in a 'pure state', otherwise it is in a 'mixed state'. The density operator ρ has three important properties:

- it is Hermitian: $\rho^\dagger = \rho$;
- it has a unitary trace: $Tr(\rho) = 1$;
- it is semi-definite positive: $\langle\psi|\rho|\psi\rangle \geq 0 \ \forall\psi \in \mathscr{H}$.

These three properties are essential to associate the meaning of probability density with this operator. In general, any matrix fulfilling these three properties can be interpreted as a valid density matrix. The introduction of ρ enables one to express $\langle A\rangle_t$ much more simply, using the well known trace operator:

$$\langle A\rangle = Tr(\rho A).$$

Therefore, the density operator ρ is a more general concept than that of state $|\psi\rangle$ and allows one to describe both pure states and ensembles of states with a single mathematical tool. It is now possible to treat mixed and pure states exactly in the same way. However, it is always necessary to keep in mind the differences in interpretation. Indeed, the probability density can play two different roles. In quantum mechanics the knowledge of the state $|\psi\rangle$ represents the maximum information that can be had about the system. When ρ represents a pure state, the knowledge about the system is maximum, the use of probability describes the exclusively quantum indeterminacy on the measurement. When ρ represents instead a mixed state the use of probability describes both classical and quantum indeterminacy on the measurement. To understand whether an arbitrary density matrix describes a pure state or a mixed one, the quantity $Tr(\rho^2)$ is analysed. This quantity has an important property: if the Hilbert space of the system is of dimension N then

$$\frac{1}{N} \leq Tr(\rho^2) \leq 1$$

(and in an infinite dimensional space the latter becomes $0 \leq Tr(\rho^2) \leq 1$). This quantity is important because it provides a measure of the degree of purity: ρ describes a pure state if and only if $Tr(\rho^2) = 1$; on the other hand, for $Tr(\rho^2) = \frac{1}{N}$ the ignorance about the system is maximum, the state is maximally mixed (this corresponds to a maximum of entropy).

From the way ρ was defined, it is clear that it is independent of time in Heisenberg picture. Instead, in Schrödinger picture it evolves over time according to Von Neumann (Quantum Liouville) equation:

$$\frac{\partial}{\partial t}\rho_t = \frac{1}{i\hbar}[\mathcal{H}, \rho_t]. \tag{1.12}$$

In particular, if the Hamiltonian is time independent, its evolution over time can be expressed as

$$\rho_t = e^{-\frac{it}{\hbar}\mathcal{H}}\rho_0 e^{\frac{it}{\hbar}\mathcal{H}}. \tag{1.13}$$

The similarity with the operators observable in the Heisenberg picture is evident, but it is important to underline a difference: the density operator ρ evolves 'in reverse time' (note the minus sign) compared to all the other operators. This is not a surprising fact if we remember that the former evolves only in Schrödinger pictures meanwhile operators only in Heisenberg picture. For convenience, the time evolution operator $U(t)$, also called time-propagator, is defined:

$$U(t) \equiv e^{-\frac{it}{\hbar}\mathcal{H}}, \quad U^{\dagger}(t) = e^{+\frac{it}{\hbar}\mathcal{H}}. \tag{1.14}$$

Then, if the Hamiltonian is time independent, one can write

$$A_t = U^{\dagger}(t) A U(t), \quad \rho_t = U(t)\rho_0 U^{\dagger}(t). \tag{1.15}$$

Instead, if the Hamiltonian is time-dependent the definition of these time propagators is different, we will clarify this case in chapter 5.

The equivalence of the two pictures in the calculation of the observables expectation value $\langle A\rangle_t$ is now easily shown using the cyclic property of the trace:

$$\Big(\langle A\rangle_t\Big)_H = Tr(\rho_0 A_t) = Tr\Big(\rho_0 U^{\dagger}(t) A U(t)\Big) =$$
$$Tr\Big(U(t)\rho_0 U^{\dagger}(t) A\Big) = Tr(\rho_t A) = \Big(\langle A\rangle_t\Big)_S$$

Subsequently, therefore, we will never specify the picture in which we are working, since they are equivalent. We will highlight it only in particular cases to underline relevant considerations.

Mathematical tools

Quantum systems are often treated in infinite dimension. In this thesis we will work only in Hilbert spaces of finite dimension. For now, it is sufficient to highlight that the only operators we will work with are matrices of finite dimension.

Considering the form of the time propagator (1.14), it is clear that it will be very important to know how to work with exponential matrices [8], so we briefly recall their main properties.

The exponential of a matrix A is defined as

$$e^{A} \equiv \sum_{k=0}^{\infty} \frac{A^k}{k!}.$$

This series is absolutely convergent for any operator A such that $\|A\| \in \mathbb{R}$. From this definition it follows that the exponential e^D of a diagonal matrix D ($D_{ii} = d_i \in \mathbb{C},\ D_{i,j} = 0\ \forall i \neq j$) is itself diagonal and its elements are the exponential of the diagonal elements of D ($e^D_{ii} = e^{d_i}$). Let B be a linear operator and Q an invertible linear operator then it holds that

$$B = QAQ^{-1} \Rightarrow e^B = Qe^AQ^{-1}. \tag{1.16}$$

This is a very important property that allows to easily calculate the exponential of any matrix. If matrix B is diagonalizable then one can construct the unitary passage matrix P using the eigenvectors of B, $B = PDP^{-1}$. So it is necessary to calculate only the exponential of the diagonal matrix D and then $e^B = Pe^DP^{-1}$. If instead matrix B is not diagonalizable then it is possible to calculate e^B similarly using the Jordan block form [8], the process will only be a bit more complicated. Furthermore, the typical properties of the exponential are no longer valid, for example,

$$e^{A+B} \neq e^Ae^B;$$

but one finds the validity again if the two operators commute,

$$[S, T] = 0 \quad \Rightarrow \quad e^Te^S = e^{S+T}.$$

For two arbitrary operators the expression e^Ae^B can be also calculated with the formula of Baker-Campbell-Hausdorff [9]:

$$e^Ae^B = exp(A + B + \frac{1}{2}[A, B] + \frac{1}{12}[A, [A, B]] + \frac{1}{12}[B, [B, A]] + ...).$$

This formula, thanks to the properties of commutators, can lead to great simplifications in expressing the solution Z of the equation $e^Ae^B = e^Z$.
The property $(e^S)^{-1} = e^{-S}$ always continues to hold.

We have recalled all the concepts and tools that we will use in this thesis. In the next chapters we will always maintain this notation.
We can now introduce response theories in the quantum context. We are going to present an overview of the various quantum response theories used today.

1.2 Response theories

In this section we will provide a general summary of the most recent and used quantum response theories. This is necessary to identify the main methods used in the literature to deal with perturbed dynamics. We will analyse the domain of validity, strengths and weaknesses of the different approaches. In this way it will be possible to better identify the area of applicability of the quantum response theory that we are going to formulate. Furthermore, this overview will allow us to use the approaches present in the literature as a comparison to analyse the new

approach of this thesis.
We point out that in this section we present brief summaries of some articles on the topic. We will try to offer the most complete and general picture possible without going into excessive details. We will therefore present only the essential results of the various articles and will always maintain the notation used by the authors. The numerous results presented in a short space may sometimes appear unclear, we therefore reiterate that this is only a brief overview, to delve deeper into the details of what is presented here the reader is invited to move to the cited articles.

The approach most used in quantum response theory is certainly the perturbative one. We therefore begin with an overview of the quantum linear response theory.

1.2.1 Quantum linear response theory

Computing the response of an observable expectation value to a small time-dependent perturbation is one of the most successful ways to relate physical quantities to the underlying theoretical description of matter.
A very important article in this regard is that of Kubo [10]. He considers a Hamiltonian system $\mathcal{H}$ that was at thermodynamic equilibrium at infinite past, $t = -\infty$. An external force $K(t)$ is then applied. Let ρ be the density matrix representing the statistical ensemble, it will evolve over time according to the quantum Liouville equation (1.12).
The perturbed Hamiltonian is

$$\mathcal{H}_t = \mathcal{H} - AK(t) = \mathcal{H} + \mathcal{H}_{ext}(t), \tag{1.17}$$

with A being the dynamical quantity conjugate to the applied force K. In quantum mechanics the Liouville operators $\mathcal{L}$, $\mathcal{L}_{ext}$ and $\mathcal{L}_t$ are defined by the commutators with the corresponding Hamiltonians (1.17). The initial condition for the Liouville equation at time $t = -\infty$ is $\rho(-\infty) = \rho_e$, which indicates that the system was described by the equilibrium ensemble density distribution ρ_e. The perturbation is small therefore Kubo approximates the external effect on the density to the first order:

$$\rho(t) \simeq \rho_e + \Delta\rho(t) = \rho_e + \int_{-\infty}^{t} dt' e^{(t-t')\mathcal{L}} \mathcal{L}_{ext}(t')\rho_e.$$

The response of the system to the perturbation is observed with respect to the change of some physical quantity B:

$$\langle \Delta B(t) \rangle = Tr\Big(B\Delta\rho(t)\Big).$$

By using the cyclic property of trace, Kubo moves on to the form:

$$\langle \Delta B(t) \rangle = \int_{-\infty}^{t} dt' K(t') Tr\left(\rho_e \frac{1}{i\hbar}[A, B(t-t')]\right),$$

where $B(t) = e^{\frac{i}{\hbar}\mathcal{H}t} B e^{-\frac{i}{\hbar}\mathcal{H}t}$ is the operator evolved over time according to the unperturbed Hamiltonian $\mathcal{H}$. Therefore, he defined the response function as

$$\phi_{BA}(t) \equiv Tr\bigg(\rho_e \frac{1}{i\hbar}[A, B(t)]\bigg) = Tr\bigg(\frac{1}{i\hbar}[\rho_e, A]B(t)\bigg). \tag{1.18}$$

The response function represents the response of the system at the time t to an impulsive force applied on the system at $t = 0$. The latter enables one to write the linear response $\langle \Delta B(t) \rangle$ in a compact form, as superposition of delayed effects,

$$\langle \Delta B(t) \rangle = \int_{-\infty}^{t} ds K(s) \phi_{BA}(t - s). \tag{1.19}$$

The exact same approach can be applied in classical statistical mechanics, simply by replacing the quantum commutators with Poisson brackets, as in eq. (1.10), and the trace operator with the phase space integration. In classical mechanics $\phi_{BA}(t)$ is a correlation function between the two physical observables A and B; Kubo demonstrates, by introducing the quantum canonical correlation function (2.14), that this interpretation remains valid even in quantum mechanics. In general, eq. (1.19) is a very important result: the response to a small perturbation is determined by the equilibrium dynamics and by the time correlation function of the perturbation and the observable of interest, computed with respect to the known equilibrium ensemble.

The case of periodic force $K = \mathcal{R}K_0 e^{i\omega t}$ is of particular interest. In this case, the response is expressed as

$$\langle \Delta B(t) \rangle = \mathcal{R}\chi_{BA}(\omega) K_0 e^{i\omega t}; \quad \chi_{BA}(\omega) = \int_{0}^{\infty} \langle [A(0), B(t)] \rangle_e e^{-i\omega t} dt$$

$\chi_{BA}(\omega)$ is called admittance and is a very important quantity to derive the fluctuation-dissipation theorem from here. The latter states a general relationship between the response of a given system to an external perturbation and the internal fluctuation of the system in the absence of the disturbance. The linear response theory is therefore a generalization of it.

Kubo linear response theory gives formulas to compute dynamical susceptibilities for closed quantum systems “not far apart from thermal equilibrium”. The effect of the environment is considered small and is completely neglected. The system is then supposed to evolve isolated from the environment according to the Schrödinger equation. In more recent times, there has been increasing interest in various generalizations of Kubo response theory. Before presenting them, it is necessary to introduce Lindbladian equations and quantum superoperators.

Master equations are a general class of equations used to describe the time evolution of the probability density of a system that can be modelled as being in a probabilistic combination of states at any given time. Lindbladian (GKSL) equations are the most used form of Markovian master equations in quantum mechanics: they generalize the Schrödinger equation to open quantum systems [11]. Lindblad equation can be written as:

$$\dot{\rho} = -\frac{i}{\hbar}[\mathcal{H}, \rho] + \sum_i \gamma_i \Big(L_i \rho L_i^\dagger - \frac{1}{2}\{L_i^\dagger L_i, \rho\} \Big); \tag{1.20}$$

the interaction between the environment and the system is expressed by operators L_i. We will review them in more detail in chapter 6.

Quantum superoperators [12] are mathematical tools widely used in the most recent academic articles in this field. We won't use them so we will only mention them briefly to understand the notation of the next articles presented. They provide a unifying framework applicable to quantum and classical systems. In this picture, $\rho(t)$ is a vector in Liouville space and not anymore an operator in Hilbert space. The Lindblad equation can be written using the relative superoperator $\mathcal{L}$ simply as

$$\dot{\rho} = \mathcal{L}[\rho].$$

The structure of $\mathcal{L}$, for many specific cases, may allow for a simplified treatment, a clearer physical meaning and an immediate classical analogue of the problem.

P. Zanardi and L. C. Venuti extend Kubo linear response theory to nonequilibrium situations where the system's evolution is described by a time-local master equation [13], such as Lindblad equations. In this generalization, thermal equilibrium states are replaced by nonequilibrium steady states, and dissipative perturbations are considered in addition to the Hamiltonian ones. They express the dynamics using the superoperator $\mathcal{L}(t) = \mathcal{L}_0 + \zeta_1(t)\mathcal{L}_1$ and the evolution operators $\mathcal{E}(t)$ formalism: the Heisenberg evolved A is $A(t) \doteq \mathcal{E}_0^*(t)(A)$. Then, they consider the time-dependent expectation value of an observable A given by $a(t) = Tr[\mathcal{E}(t)(\rho)A]$:

$$\delta a(t) \doteq a(t) - Tr[\mathcal{E}_0(t)(\rho)A] = \int_0^\infty d\tau \chi_{AB}(t-\tau); \quad \chi_{AB}(t) \doteq i\theta(t) Tr\{[A(t), \rho]B\}$$

The authors assume that the initial state ρ is a steady state of the unperturbed $\mathcal{L}_0$. Introducing the scalar product $\langle A, B\rangle_\rho = Tr(\rho A^\dagger B)$ over L($\mathcal{H}$), they can write the linear dynamical susceptibility (LDS) in a compact form: $\chi_{AB}(t) = 2\theta Im\langle A(t), B\rangle_\rho$. If $\mathcal{L}_0$ is itself of Hamiltonian type, one recovers the standard results (1.19) for closed quantum systems.

In open-systems is no longer possible to write $\chi_{AB}(t)$ as a correlation function. Indeed, the LDS for unitary perturbations can at best be expressed as the difference of two correlation functions associated with two different dynamical flows:

$$\chi_{AB}(t) = -i\theta(t)[\langle A(t), B\rangle_\rho - \langle B^{\#}(t), A\rangle_\rho]$$

(where symbol $^{\#}$ is related to the Hermitian conjugated of $\mathcal{L}_0$, which requires mathematical attention). When $A = B$, if $\mathcal{E}_0^*(t)$ are Hermitian with respect to the scalar product $\langle \cdot, \cdot \rangle_\rho$, one has $\chi_{AA}(t) = 0 \;\; \forall A = A^\dagger$. This type of "diagonal" no linear-response for all observables is a uniquely open-system phenomenon: any nontrivial unitary dynamics gives rise to a nonvanishing χ_{AA} for some A.

An important object is the Fourier transform of the LDS:

$$\hat{\chi}_{A,\mathcal{L}_1}(\omega) \dot{=} \mathcal{F}[\chi_{A,\mathcal{L}_1}](\omega) = \int_0^\infty dt e^{i\omega t} Tr[e^{t\mathcal{L}_0}\mathcal{L}_1(\rho)A] = iTr\left(\frac{1}{\omega - i\mathcal{L}_0 + i\epsilon}\mathcal{L}_1(\rho)A\right)$$

The basic response relation in the ω domain reads $\hat{\delta a}(\omega) = \hat{\zeta}_1(\omega)\hat{\chi}_{A\mathcal{L}_1}(\omega)$. The imaginary part of the complex susceptibility (admittance) is known to be related to the dissipation of energy. This argument still holds in this generalized setting.

For a harmonic perturbation $\zeta_1(t) = cos(\Omega t)$, the value

$$M_{hr}(\Omega) \dot{=} \| \frac{1}{\Omega - i\mathcal{L}_0 + i\epsilon}\mathcal{L}_1(\rho)\|_1,$$

called maximal harmonic response, sets an upper bound to the response of any (normalized) observable to the perturbation: $sup_{\|A\|_1} |\delta a(t)^\Omega| \leq M_{HR}(\Omega)$.

Considering a time-independent small perturbation λ, the system will relax to the steady state of $\mathcal{L}(\lambda), \rho(\lambda)$. For a general observable A one has

$$\langle A \rangle_\lambda = Tr[\rho(\lambda)A] = Tr[\rho(0)A] + \lambda\chi^T_{A,\mathcal{L}_1} + O(\lambda^2).$$

The authors prove that

$$\hat{\chi}_{A\mathcal{L}_1}(0) - \chi^T_{A\mathcal{L}_1} = \int_0^\infty dt e^{-\epsilon t} Tr[P_0\mathcal{L}_1(\rho_0)B],$$

where P_0 is the projector operator into the kernel of $\mathcal{L}_0$. They conclude that in the case of non-degeneracy, for maps with a unique steady state, $\chi_{A\mathcal{L}_1}(0) = \chi^T_{A\mathcal{L}_1}$ are equal, whereas it is well known that this is not the case for the unitary (closed) case. The article also contains some applications of these results to Davies generators, single qubits and an analysis of a dynamical phase transition.

This dynamical response theory focuses mainly on the Markovian case. Non Markovian effect should be taken into account in many systems. For this purpose, Shen *et al.* develop a linear response theory for an open quantum system by taking the non-Markovian effect into account [14].

They assume that $H_{ext}(t)$ is turned on at $t_0 \to -\infty$ and that the total system is at thermal equilibrium in the absence of the external field ($\rho_0(0) = \rho_{eq}$):

$$\chi_{\mu\nu}(\omega) = \int_0^\infty dt e^{i\omega t}\chi_{\mu\nu}(0, -t) = \frac{i}{\hbar}\int_0^\infty dt e^{i\omega t} Tr\Big\{\hat{B}_\mu e^{-\frac{i}{\hbar}\hat{\mathcal{L}}_0 t}[\hat{A}_\nu, \rho_{eq}]\Big\}$$

Authors define $\zeta_\nu(t) \equiv Tr_B\Big\{\frac{i}{\hbar}e^{-\frac{i}{\hbar}\hat{\mathcal{L}}_0 t}[\hat{A}_\nu, \rho_{eq}]\Big\}$ to simplify the notation. In this way, they obtain the expression $\chi_{\mu\nu}(\omega) = Tr_S[\hat{B}_\mu\zeta_\nu(\omega)]$: in order to calculate the susceptibility $\chi_{\mu\nu}(\omega)$, it is enough to calculate $\zeta_\nu(\omega)$, the Laplace transform of $\zeta_\nu(t)$.

To derive a concrete equation, it is necessary to specify the environment. After a long derivation, working on the interaction in weak-coupling assumption, they find a general equation for $\zeta_\nu(t)$ which includes completely non-Markovian memory effects. Matrix $\zeta_\nu(\omega)$ contains important coefficients related to the interaction with the environment. In conclusion, $\zeta_\nu(\omega)$ plays a crucial role in determining the non-Markovian effect of the environment on the susceptibility $\chi_{\nu\mu}(\omega) = \sum_{n,m}\hat{B}_{\nu,nm}\zeta_{\nu,nm}(\omega)$. This formalism might open a new way to better understand the relations between the response function and the non-Markovianity.

Linear response theory of quantum systems has been explored further in recent years and achieved a more complete picture. Different formulations of the response function and different points of view have indeed enriched the theory. M. Konopik and E. Lutz derive three different forms of quantum response function [15]. All these variants yield the same response. However, the existence of different types of fluctuation-response theorem offers significant theoretical and experimental advantages: one can choose the best one depending on the application. The response of any observable A may then be calculated to linear order as

$$\langle A\rangle_\epsilon(t) = \langle A\rangle + \int_0^t ds\epsilon(s)R(t-s); \quad R(\tau) = Tr\{Ae^{\mathcal{L}_0\tau}\mathcal{L}_1\pi_0\}; \quad \langle\cdot\rangle \doteq Tr[\cdot\pi_0]$$

This provides the basis for their quantum extension of the three equivalence classes. The first response function is

$$R_1(\tau) = \langle A(\tau)B_1\rangle = \langle A(\tau)\frac{(\mathcal{L}_1\pi_0)}{\pi_0}\rangle,$$

it is expressed as a correlation function with an observable $B_1 = (\mathcal{L}_1\pi_0)/\pi_0$. It contains only state variables and no time derivatives. This form shows that for a thermal stationary distribution $\pi_0 = exp(-\beta H_0)/Z_0$ the quantum response vanishes when $[H_0, H_1] = 0$ (this is not necessarily the case for a nonequilibrium steady state). Its drawback is that the observable B_1 involves the stationary distribution π_0, which is not always explicitly known in concrete situations.

The second response function is

$$R_2(\tau) = -Tr(A(\tau)\mathcal{L}_0\pi_1) = -d_\tau\langle A(\tau)\pi_1/\pi_0\rangle.$$

In the limit of closed quantum systems at equilibrium it reduces to the Kubo quantum response function (1.19).

In order to bring $R_2(\tau)$ in a form similar to the classical case, authors first introduce a generalized Kubo transformation: $\overline{\partial_\epsilon \ln \pi_\epsilon|_0} \doteq \int_0^1 \pi_0^\lambda (\partial_\epsilon \ln \pi_\epsilon)|_0 \pi_0^{-\lambda} d\lambda$. Introducing the quantum analogue of the stochastic entropy $S_\epsilon \doteq \partial_\epsilon \ln \pi_\epsilon|_0$, they find:

$$R_2(\tau) = -d_\tau \langle A(\tau) \overline{\partial_\epsilon S_\epsilon|_0} \rangle = -\langle A(t) d_s \overline{\partial_\epsilon S_\epsilon(s)|_0} \rangle.$$

This variant is the only one where the response function is given as a correlation function with a time derivative of a state variable ($\overline{\partial_\epsilon S_\epsilon|_0}$).
There is an alternative way of writing $R_2(\tau)$ without using any correlation function:

$$R_2(\tau) = -d_\tau \partial_\epsilon \langle A(\tau) \rangle_\epsilon |_0,$$

which is the time derivative of the time-dependent susceptibility. This form often enables a simple evaluation of the response function.

The third form is

$$R_3(\tau) = \frac{i}{\hbar} Tr\{\pi_0 [H_1, A(\tau)]\} = -\langle \mathcal{L}_1 A(\tau) \rangle.$$

It is the unique one that does not explicitly involve the stationary distribution. Indeed, this response is given as an expectation value of operators that do not explicitly depend on π_0, π_1 or π_ϵ. R_3 vanishes when the time evolved observable $A(\tau)$ commutes with the perturbation Hamiltonian H_1.
Equilibrium response functions obey the detailed balance condition:$\langle AB(t) \rangle = \langle BA(t) \rangle$. By contrast, the non equilibrium steady-state response functions do not. All these considerations underline the profound disparity between equilibrium and nonequilibrium quantum response theories.

These theorems have been derived for finite-dimensional systems. However, many relevant physical processes, especially in the field of quantum information technologies, are described by systems of infinite dimension in the Gaussian regime. Mehboudi *et al.* find a linear response theory for quantum Gaussian systems [16]. They consider processes described by Gaussian quantum channels and derive the linear response of the covariance matrix. The characteristic function of a Gaussian system has, by definition, the following form: $\chi(\eta) = e^{\frac{1}{2}\eta^T \sigma \Omega \eta - d^T \Omega \eta}$. Gaussian systems are fully described by their first and second moments. Thus, Gaussian channels $\mathcal{M}$ can be completely identified by their action on the displacement vector d and on the covariance matrix σ:

$$\mathcal{M} : d \to Xd + f \quad \mathcal{M} : \sigma \to X \sigma X^T + Y$$

Without loss of generality, one restricts to zero-mean Gaussian states and one-parameter family of Gaussian quantum channels M_λ, where λ can represent the strength of an external magnetic field or temperature. Authors assume $\mathcal{M}_\lambda = \mathcal{M}_0 +$

$\lambda\mathcal{M}+O(\lambda^2)$, $\sigma_\lambda = \sigma_0+\lambda\zeta+O(\lambda^2)$ and Markovian scenario: $\sigma(t) = \mathcal{M}_{\lambda(t)}...\mathcal{M}_{\lambda(1)}\sigma_0$. The aim is to characterize the linear response of $\sigma(t)$ in terms of steady state correlations, that is elements of steady state covariance matrix. They obtain:

$$\sigma(t) = \sigma_0 + \sum_{s=1}^{t} \lambda(t-s)\phi(s);\ \phi(t) = -\Delta_t(X_0^t \zeta X_0^{Tt})$$

$$\delta t \to 0 :\ \sigma(t) = \sigma_0 + \int_0^t ds\lambda(t-s)\phi(s)\ ;\ \phi(t) = -\partial_t(X_0^t \zeta X_0^{Tt}).$$

In order to find the response function one simply needs to find the static linear response $\zeta \equiv \partial_\lambda \sigma_\lambda|_{\lambda=0}$ and the time evolution of ζ under the unperturbed channel X_0. For any arbitrary Gaussian Lindbladian equation, these two objects can be identified straightforwardly. When dealing with thermal states evolving under unitary dynamics, one recovers Kubo's linear response theory.

Now we have a clear and general picture of linear response theory in open quantum systems. However, dynamical systems of physics feature nonlinear character as well, moreover, the disturbance may not be assumed to be small. A good theory that goes beyond the linear approximation is therefore of great importance.

1.2.2 Beyond linear approximation

Kubo's approach and all the methods presented previously are often extended taking higher-order terms in the expansion of the perturbation. This approach offers greater precision but it is very cumbersome and expensive. In some situations it can lead to a better approximation. However, there are problems related to the convergence and uniqueness of the response; moreover, this is always an approximation and it may not capture anomalous behaviour, such as phase transitions. A quantum exact response theory does not yet exist but it would be of fundamental importance for studying open quantum systems. We will see that for classical systems these theories exist and are often derived from fluctuation theorems, the goal of this thesis is to formulate their quantum analogue to lay the foundation for a quantum exact response theory. However, a conceptually opposite approach also seems interesting: the use of stochastic methods of classical physics in the study of quantum dynamics.

Recently, B. Mukherjee *et al.* introduced the stochastic reset technique in the study of quantum systems [17]. V. Dubey *et al.* apply this approach to a qubit system $|\psi\rangle$ that is monitored continuously but with interactions with a qubit-detector $|\chi\rangle$. The total Hamiltonian is

$$H = \gamma_0 \sigma_x \otimes Id + \sqrt{\frac{\gamma}{\tau}} \pi_1 \otimes \sigma_y,$$

where σ_i are the Pauli matrices. Two phenomena are in competition: the Zeno effect and Rabi oscillation. When $\gamma_0 \to 0$, there is a collapse of $|\psi\rangle$ to state ψ_0 or ψ_1 (Zeno effect); meanwhile, when $\gamma = 0$ the free evolution leads to well known Rabi oscillation.

Every time a detector, always initialized to χ_0, is measured to be in the state χ_1 corresponds to a 'click'. N_t is a Poisson process which counts the number of clicks in $[0, t]$. The dynamics is described by a stochastic Schrödinger equation; the authors, exploiting the representation of the Bloch sphere, manage to move to a stochastic dynamics of classical nature:

$$d\theta_t = \Omega(\theta_t)dt + (\pi - \theta_{t-})dN_t. \quad \Big(\mathbb{E}[dN_t] = \alpha(\theta_t)dt\Big)$$

This dynamics can be naturally interpreted as a resetting process, with a resetting rate that depends on the instantaneous state. In this way they obtain analytic results for the distribution of number of detector events and the exact time-evolution of the probability distribution. They also find dynamics transitions confirmed experimentally. This method is promising but has the disadvantage of being applicable only to a narrow range of quantum systems, it is not always possible to exploit technicalities to move on to the "classical" stochastic dynamics.

Quantizing a classical exact response theory could be the right way to acquire much more generality in the typology of exactly describable open quantum systems. In the following, we therefore set out to present the classical exact response theory based on the Dissipation Function that we are going to quantize in this thesis; first we will introduce the fluctuation theorems, the field from which the Dissipation Function arises.

1.2.3 Fluctuation Theorems

Fluctuation theorems are fundamental generalizations of the second law of thermodynamics for small systems. While the entropy production Σ is a non-negative deterministic quantity for macroscopic systems, it becomes random at the microscopic scale owing to the presence of non-negligible thermal or quantum fluctuations. Detailed fluctuation theorems quantify the probability of occurrence of negative entropy production events via the relation

$$\frac{P(\Sigma)}{P(-\Sigma)} = exp(\Sigma).$$

Fluctuation relations were discovered in the '90s and the main contributions are due to Evans, Cohen, Searles, Gallavotti, Crooks and Jarzynski [18]. The generic validity of fluctuation theorems arbitrarily far from equilibrium makes them particularly useful in nonequilibrium physics. They can be a good basis for a quantum exact response theory just as dissipation-fluctuation theorems underlie linear response theory.

D. Andrieux and P. Gaspard derive a universal quantum work relation for isolated time-dependent Hamiltonian systems in a magnetic field, which is a good starting point for formulating a quantum response theory [19].
The system is described by a Hamiltonian operator $H(t, B)$, with B magnetic field. Authors consider an arbitrary time-independent observable A with a definite parity under time reversal ($\Theta A \Theta = \epsilon_A A,\ \epsilon_A = \pm 1$). The Functional relation Theorem states that

$$\langle e^{\int_0^T dt\lambda(t)A_F(t)} e^{-\beta H_F(T)} e^{\beta H(0)} \rangle_{F,B} = e^{-\beta \Delta F} \langle e^{\epsilon_A \int_0^T dt\lambda(T-t)A_R(t)} \rangle_{R,-B}; \qquad (1.21)$$

$\Delta F = F(T) - F(0)$ is the difference of the free energies, $\lambda(t)$ is an arbitrary function. This theorem allows them to recover the quantum Jarzynski equality as a special case for $\lambda = 0$. $e^{-\beta H_F(T)} e^{\beta H(0)}$ can indeed be interpreted in the quantum setting in terms of the work performed on the system during the forward process.
Authors highlight that one can obtain different correlation functions by taking functional derivatives of (1.21) with respect $\lambda(t)$. For example, using this approach, they managed to obtain the well-known Green-Kubo formula. (1.21) unifies in a common framework the work relations and the response theory, thereby opening the possibility to obtain further general relations which are valid also in the far-from-equilibrium regime.

However, this method, also in higher order version, is only an approximation and it fails to predict the real behaviour in certain anomalous phenomena. One can try to eliminate the approximation to get an exact response from a quantum fluctuation theorem. Another valid path is to exploit classical exact responses (obtained from fluctuation theorems in classical field) and quantize them, this is precisely the path we will explore in this thesis.

1.2.4 The classical Dissipation Function exact response theory

Even a small perturbation may result in a large modification of the state. Non-linear effects, especially at the nanometric scale, can cause drastic changes of states, like phase transitions. Linear response is not valid in these situations and also higher order expansion, in addition to being very cumbersome, may not work. An exact theory is instead expected to handle such situations.

Following the discovery of the fluctuation relations, response theory has been generalized so that small systems as well as large drivings can be treated. A general exact response theory, also known as TTCF (transient time correlation function), has been derived. The key ingredient of this theory is known as Dissipation Function, developed as the energy dissipation rate in Fluctuation Relations of classic nature [20].

G. Jepps and L. Rondoni provide a dynamical-systems interpretation for the Dissipation Function [2]. They consider a system whose microscopic phase $\Gamma \in \mathcal{M}$ evolves according to the equation of motion $\dot{\Gamma} = G(\Gamma)$, whose solution at time $t \in \mathbb{R}$ from initial condition Γ is represented by $S^t\Gamma$. Considering an arbitrary initial distribution f_0, its evolution under the dynamics is described by the generalized Liouville equation, eq. (1.2),

$$\frac{\partial f_t}{\partial t}(\Gamma) = -\nabla_\Gamma \cdot \Big(f_t G(\Gamma)\Big).$$

It is shown that the latter can be expressed as

$$\frac{\partial f_t}{\partial t}(\Gamma) = f_t \Omega^{f_t}(\Gamma); \quad \Omega^{f_t}(\Gamma) \equiv -[\Lambda(\Gamma) + G(\Gamma) \cdot \nabla_\Gamma ln f_t(\Gamma)]. \tag{1.22}$$

Ω^{f_t} is called Dissipation Function, this quantity corresponds, in thermodynamic systems, to generalized entropy production. Ω^{f_t} can be used to describe the evolution of the ensemble average $\langle \mathcal{O} \rangle_{f_t}$ in terms of averages with respect to the initial distribution f_0 as

$$\langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} + \int_0^t \langle (\mathcal{O} \circ S^s) \Omega^{f_0} \rangle_{f_0} ds. \tag{1.23}$$

This result allows expressing the system's response to an external perturbation in an exact, not approximate, way. It is an exact response formula. This expression offers several advantages. Firstly, it keeps the probability fixed and makes the observables to evolve over time. In general, $\langle \mathcal{O} \rangle_t$ can be equivalently obtained either evolving the microscopic observable or the probability density,

$$\langle \mathcal{O} \rangle_t = \int_{\mathcal{M}} \mathcal{O}(x) f_0(S^{-t}x) J^{-t} dx = \int_{\mathcal{M}} \mathcal{O}(S^t x) f_0(x) dx,$$

where J is the Jacobian of the coordinates change. It is therefore clear why evolving only observables over time, as in eq. (1.23), is a great advantage: probability requires the reversed dynamics, which is much more difficult to exploit. For eq. (1.23), the dynamics are assumed to be only invertible, which does not mean that they have to be time-reversal invariant, as often required in statistical mechanics.
Secondly, $\langle \mathcal{O} \rangle_t$ is calculated as the correlation function, computed with respect to the initial distribution f_0, of the evolving observable with the dissipative flux, represented by the Dissipation Function. This led to new physical interpretations

in many molecular-dynamics applications.
Furthermore, this expression has allowed treating hard non- equilibrium problems, at low drivings [21], drastically improving the signal-to-noise ratio, and providing a superior method with respect to direct averaging for such calculations. Not only the presence of the time integral, but above all the use of the equilibrium distribution, has the advantage of smoothing the $\langle \mathcal{O} \rangle_t$ signal and cleaning it from noise.
Moreover, Jepps and Rondoni provide a dynamical-system interpretation. They offer new perspectives into second-law inequality, but interpreted in terms of relative entropies, independent of any putative thermodynamic context. They also study the role of the dissipation function to describe relaxations towards equilibrium. T-mixing is a necessary condition for the Fluctuation Relations to hold in non equilibrium steady states [20]. They find that the notion of T-mixing, through its connection with the dissipation function ($\Omega T-$mixing),

$$\langle \Omega^{f_0}(\mathcal{O} \circ S^t) \rangle_{f_0} \to \langle \Omega^{f_0} \rangle_{f_0} \langle \mathcal{O} \circ S^t \rangle_{f_0} = 0 \quad \text{for } t \to \infty,$$

provides an avenue for describing relaxation towards equilibrium, in terms of observable behaviour along the neighbourhood of a single phase space trajectory.

The main objective of this thesis is to write the quantum translation of the classical expression (1.23). It is interesting to understand its role and its domain of applicability in quantum mechanics. The hope is that it can bring progress also in quantum response theory, where we have seen that for many systems only approximate and perturbative approaches can so far be used.
Now we are going to present an application of expression (1.23) to show the potential it could also have in quantum physics.

L. Rondoni *et al.* compare new exact theory (1.23) with linear response theory [22] in an application on Kuramoto dynamics: a prototype of many particle systems exhibiting synchronization, a phenomenon ubiquitous in physics and biology. In this application the simplicity and great advantages that (1.23) offers, compared to other approaches, will be immediately evident.

The Kuramoto dynamics can be written as

$$\dot{\theta}_i = \omega_i + KR(\theta) sin(\Phi(\theta) - \theta_i), \quad \text{with} \quad \theta = (\theta_1, ..., \theta_N) \in \mathcal{M}.$$

θ is the phase vector and ω_i are the natural frequencies. For their purpose authors rewrite it as $\dot{\theta} = W + V(\theta)$, where W is the equilibrium unperturbed dynamics and V the non-equilibrium perturbation. They calculate the phase space volumes variation rate (1.3),

$$\Lambda = \nabla_\theta \cdot V = K(1 - NR^2).$$

They consider $\mathcal{S}^t : \mathcal{M} \to \mathcal{M}$ the flow determined by the ODE system $\dot{\theta} = V(\theta)$ and $d\mu_0(\theta) = f_0(\theta) d\theta$ the probability measure on $\mathcal{M}$. They assume μ_0 invariant under the unperturbed dynamics W, at time $t = 0$ the dynamics is perturbed and the perturbation V remains $\forall t > 0$. Equation (1.23) expresses the average $\langle \mathcal{O} \rangle_t$ in terms of a correlation function computed with respect to f_0, the non-invariant density, which is only invariant under the unperturbed dynamics. The full range of applicability of this theory is still to be identified. However, it obviously applies to smooth dynamics, such as the Kuramoto dynamics.

In this article authors focus on the case of identical oscillators: $W = \omega \mathbf{1}$. For this Kuramoto dynamics, $\dot{\theta} = W + V(\theta)$, one has:

$$f_0 = (2\pi)^{-N}; \quad \Omega^{f_0,V} = \frac{K}{N} \sum_{i,j}^{N} cos(\theta_j - \theta_i) - K \in C^{\infty}.$$

A very interesting quantity for studying the convergence of the system is precisely the observable $\mathcal{O} = \Omega^{f_0,V}$; from (1.23) one has the response formula for $\langle \Omega^{f_0,V} \rangle_t$.

It is well known that the solutions of this system converge, as $t \to \infty$, either to a complete frequency synchronized state $\theta_i = \varphi \; \forall i$, denoted by (N,0), or to a state (N-1,1): $\theta_i = \varphi, \theta_{i^*} = \varphi + \pi$. The authors demonstrated by means of (1.23) that $(N-1, 1)$ has 0-measure and that

$$lim_{t \to \infty} \langle \Omega^{f_0,V}(S^t \theta) \rangle = K(N-1) \; \forall \theta \neq (N-1{,}1).$$

$K(N-1)$, maximum of $\Omega^{f_0,V}$ in $\mathcal{T}^N$, corresponds exactly to (N,0)-synchronization.

In conclusion, they compare the exact response formalism with the standard linear response. With an expansion calculation in the variable ϵ they obtain a generalized linear dissipation formula:

$$\overline{\langle \mathcal{O} \rangle_{t,\epsilon}} = \langle \mathcal{O} \rangle_0 + \epsilon \int_0^t \langle (\mathcal{O} \circ S_0^{\tau}) \Omega^{f_0,V_p} \rangle_0 d\tau.$$

Comparing this with (1.23) they find that $\forall \epsilon > 0$ the difference of the two responses is small at small times, but it diverges linearly as time passes:

$$\langle \Omega^{f_0,V_\epsilon} \rangle_{t,\epsilon} = \overline{\langle \Omega^{f_0,V_\epsilon} \rangle_{t,\epsilon}} + o(\epsilon^2) t.$$

The exact response characterizes the synchronization transition, while the linear response does not.

We can conclude that exact expressions are necessary, not only in the presence of large perturbations, as obvious, but also for small perturbations, in the presence of resonance phenomena. Furthermore, many theoretical results can be derived from the exact expression before they can be numerically computed in simulations. This theory holds in presence of arbitrarily large perturbations and applicable to both Hamiltonian and dissipative deterministic particle systems. L. Rondoni and L. Iannella also extended its validity to time-dependent stochastic perturbations [23].

In the following, we will develop its quantum translation, we think this approach could form a good basis for a quantum exact response theory. Then, we will analyse the new formalism obtained from different points of view.

Chapter 2

Quantum translation of the Dissipation Function response theory

In this chapter, we will develop the quantum translation of the classical exact response theory (1.23). We will take the article [2] as a basis and will try to carry some of the considerations offered in this article also into the quantum world. First, we will apply the quantization rule to the Dissipation Function, defining its corresponding operator. Then, we will derive the quantum exact response expression, based on this new operator, in a form analogous to (1.23).

Here and throughout the rest of the thesis, we will work in finite-dimensional Hilbert spaces: quantum operators are simple matrices. Usually, many quantum systems are treated in infinite dimension, but our choice gives us several advantages with respect to our purposes. It will allow us to focus on the construction of the new formalism, avoiding complex technicalities of functional analysis. Furthermore, we will have the possibility to easily test the validity of the results obtained through numerical simulations. This choice is less limiting than it appears. Systems expressible in finite-dimensional Hilbert spaces are very important research objects today. Qubits, basic information units in quantum computing, belong precisely to this class of systems.

2.1 Definition of the dissipation operator

The Dissipation Function can be used and defined in various different ways. An important and very interesting result is its use in calculating the evolution of the ensemble average $\langle \mathcal{O} \rangle_t$ in terms of averages with respect to the initial (equilibrium) distribution f_0 with the formula (1.23). Our principal aims are to find a good definition in quantum mechanics for the Dissipation Function and then try to derive an exact formula for observables expectation values $\langle \mathcal{O} \rangle_t$ similar to the classical one.

In this section, we will apply the quantization rule to the Dissipation Function. To do this, we first recall its classical definition. In the previous chapter, we presented the Dissipation Function in the context of dynamical systems [2]. Considering a system whose microscopic phase $\Gamma \in \mathcal{M}$ evolves according to the equation of motion $\dot{\Gamma} = G(\Gamma)$, whose solution is represented by $S^t\Gamma$, the Dissipation Function is defined as

$$\Omega^{f_t}(\Gamma) \equiv -[\Lambda(\Gamma) + G(\Gamma) \cdot \nabla_\Gamma ln f_t(\Gamma)].$$

In this form, it plays an important role in expressing the generalized Liouville equation, as shown in eq. (1.22). However, the Dissipation Function arises in the different context of fluctuation theorems. Its integral form is the one with the greatest physical interpretability in non-equilibrium thermodynamics. The integral in time, between $t = 0$ and $t = s$, of the Dissipation Function in this context is

$$\Omega^{f_0}_{0,s} = \int_0^s \Omega^0(S^u\Gamma)du \equiv ln\left(\frac{f_0(\Gamma)}{f_0(S^s\Gamma)}\right) - \Lambda_{0,s}(\Gamma) = ln\frac{f_0(\Gamma)}{f_{-s}(\Gamma)}; \tag{2.1}$$

this definition form may be better than others for applying the quantization rule.

In classical mechanics and in the theory of dynamical systems, the Dissipation Function is well-defined even for complex dynamics. To construct the quantum analogue, however, it is appropriate to start from very simple dynamics and only then generalize to more interesting dynamics. We will move in steps, we will introduce a small generalization only after having ascertained the correctness and coherence of what we discovered in the previous step. We start from a Hamiltonian quantum dynamics which is time independent:

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_{ext}. \tag{2.2}$$

Then, the phase space expansion rate (1.3) is null, $\Lambda = 0$.

Let's start with some correspondences between classical and quantum entities observing (1.23). $f_0(\Gamma)$ is clearly in analogy with the initial density operator $\rho(\Gamma,0)$. Quantum densities depend on time and phase point Γ, but in a less explicit way than in the classic case due to the equivalence between the Schrödinger and Heisenberg pictures and being operators. To emphasize the quantistic nature of the density operator ρ compared to a time-dependent scalar function in phase space, we will not make explicit the dependence on Γ. Therefore, we have that $f_0(\Gamma)$ is in correspondence with ρ_0, $\mathcal{O} \circ S^s$ with $\mathcal{O}_s$, the observable operator in Heisenberg picture evolved over time, eq. (1.7). For the density matrix ρ_s, evolved over time according to the quantum Liouville equation (1.12), the problem is more delicate: it should match with $f(\Gamma, s)$, but with zero expansion rate could be in analogy also with $f(S^s\Gamma,0)$. Furthermore, if we want to pull something quantum out of equation (2.1), this last substitution seems immediate.

One of the main purposes of this thesis is to find a good definition for the quantum operator relating to the Dissipation Function. In quantum mechanics, the definition of a generic operator A is affected by the so-called ordering problem, which is unsolved. For example, the same classical function $x_1^2 p_1$ can be written in three ways

$$x_1\hat{p}_1x_1 = x_1^2\hat{p}_1 - i\hbar x_1, \quad x_1^2\hat{p}_1, \quad \hat{p}_1x_1^2 = x_1^2\hat{p}_1 - 2i\hbar x_1,$$

which are three different quantum operators. Writing symmetrized expressions (to obtain Hermitian operators) does not solve the problem, since many symmetrized equivalent forms are available. The validity of a definition can only be checked a posteriori. To limit this type of problem as much as possible, we choose to start the quantization process from equation (2.1). We could start from other classical definitions that are more convenient and easier to quantize, such as

$$\frac{\partial f_t(\Gamma)}{\partial t} = \Omega^{f_t}(\Gamma) f_t(\Gamma). \tag{2.3}$$

However, the form (2.1) is the most used definition in the literature in classical mechanics, as it is better physically interpretable. In the quantization operation it is therefore appropriate to remain as faithful as possible to this definition, which we could consider, in a certain sense, the "original one". In this way, we could have more hope of obtaining an operator physically interpretable as dissipation. However, in equation (2.1) there is a density that has evolved backwards in time, $f_{-s}(\Gamma)$, in view of the next quantization operation it is better to rewrite it by taking the value $t = -s$ in $\Omega_{0,t}$, thus obtaining

$$\Omega_{0,-s}^{f_0} = ln\frac{f_0(\Gamma)}{f_s(\Gamma)} = lnf_0(\Gamma) - lnf_s(\Gamma).$$

Now we can apply the quantization rule to the latter. In conclusion, the quantum analogue of definition (2.1), could be:

$$\Omega_{0,-s}^{\rho_0} = ln\rho_0 - ln\rho_s. \tag{2.4}$$

Here we note that in quantum mechanics the property of the logarithm is no longer valid:

$$ln\left(\frac{A}{B}\right) \neq ln(A) - ln(B);$$

because, if it were valid, it would lead to a contradiction:

$$AB^{-1} \neq B^{-1}A \Rightarrow ln(A) - ln(B) = ln(AB^{-1}) \neq ln(B^{-1}A) = ln(A) - ln(B).$$

However, it is lawful to apply that logarithm property to the classical definition first and apply the quantization rule later, like we just did. In this way, expression (2.4) seems to be well justified. This ambiguity has similar roots to those of the unsolved ordering problem. Indeed, as already mentioned previously, there are many different ways to define this operator, for example, we could have chosen to define the quantum analogue as

$$\Omega^{\rho_0}_{0,-s} = ln\Big(\frac{\rho_0}{\rho_s}\Big).$$

A good definition will have good mathematical properties and will offer exact physical predictions. We choose the quantum expression (2.4). Starting from this point, to obtain the definition of the quantum dissipation function we can use the fundamental theorem of integral calculus, taking the incremental limit for $s \to 0$, we have:

$$\Omega^0 = \lim_{s\to 0} \frac{ln\rho_0 - ln\rho_s}{-s} = \lim_{s\to 0} \frac{ln\rho_s - ln\rho_0}{s}. \tag{2.5}$$

Then we could write

$$\Omega^0 = \frac{d}{dt} ln\rho_t|_{t=0} = \rho_0^{-1} \frac{\partial}{\partial t}\rho_0. \tag{2.6}$$

Perhaps we were not rigorous enough, but the result obtained coincides with what is known in classical mechanics. Indeed, looking at equation (2.3) presented previously, also in classical mechanics we have

$$\Omega^{f_0}(\Gamma) = f_0^{-1}(\Gamma)\frac{\partial f_0(\Gamma)}{\partial t}.$$

Reassured by this analogy, we consider equation (2.6) valid. We can use the Von Neumann equation (1.12) to express $\partial_t \rho_0$, thus obtaining the final expression. We therefore define the quantum dissipation operator as follows.

Definition 2.1.1. *Let ρ_0 be the initial density operator and $\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$ the time-independent Hamiltonian operator. The non-hermitian dissipation operator can bedefinedd as*

$$\Omega^0 \equiv \frac{1}{i\hbar}\rho_0^{-1}[\mathcal{H}, \rho_0]. \tag{2.7}$$

This is the first definition found for the quantum analogue of the classical Dissipation Function, to underline its quantum nature we will call it 'dissipation operator'. For notational convenience, we have replaced the superscript ρ_0 with 0. It is necessary to emphasize once again that the definition of the quantum analogue

of the Dissipation Function is not unique. We will see later that this definition is good, as it will allow us to derive naturally an exact response formula that works in physical applications.
However, better definitions could exist, as this one has two problems. Firstly, dissipation operator (2.7) is not hermitian. The spectrum of a non-hermitian operator belongs to the set of complex numbers $\mathbb{C}$, consequently one has

$$\langle \Omega^0 \rangle \in \mathbb{C}.$$

With a non-Hermitian Ω^0, the association with physical observables becomes much more difficult. The first thing that comes to mind is to symmetrize it to make it Hermitian. We will explore this approach in chapter 4.

The second problem concerns the invertibility of ρ_0. Whenever ρ_0 represents a pure state, then it is not invertible. More generally, it is not invertible whenever it is not of full rank (i.e. whenever it is not bijective). However, there are different ways to deal with these cases. A first approach consists in reducing the dimension of the Hilbert space. Another one is to assign very small probability p_ϵ to every zero-probability state. ρ_0 becomes invertible, in this way we can exploit Ω^0 and subsequently analyse the limit for $p_\epsilon \to 0$. In chapter 3, we will show that this last approach still offers not bad numerical results.
We also highlight that this invertibility problem is well known to exist even in classical mechanics. The equilibrium density f_0 is not always invertible. Let us consider, for example, the dynamic $\dot{v} = -\gamma v$; this can describe, for instance, the speed of a body dampened by friction. Whatever the initial probability distribution in phase space, the equilibrium distribution is concentrated in the single fixed point $v = 0$. Even in this classic case, there is therefore this problem of invertibility of the equilibrium distribution f_0.
This can be more simply seen as a delimitation of the validity regime: the dissipation operator formalism perfectly describes mixed states, while for pure states it is better to adopt other methods.

In summary, with $\Lambda = 0$, we found:

$$\text{Classical: } \Omega^{f_0}(\Gamma) = -G(\Gamma)\nabla_\Gamma ln f_t(\Gamma) \quad \to \quad \text{Quantum: } \Omega^0 = \frac{1}{i\hbar}\rho_0^{-1}[\mathcal{H}, \rho_0].$$

We have expressed the Hamiltonian as $\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$; however the definition of the dissipation operator and all the results we will find later are actually valid for every time-independent Hamiltonian $\mathcal{H}$ of any kind, given any (invertible) initial density ρ_0.

$$\text{Applicability in general} : \mathcal{H}, \quad \rho(0) = \rho_0. \tag{2.8}$$

There is no mathematical necessity to distinguish $\mathcal{H}_0$ and $\mathcal{H}_{ext}$ in $\mathcal{H}$. The choice to highlight this particular form, as in eq.(2.2), concerns exclusively the interpretation of the results and a better preparation for future extensions. Form (2.2) highlights a perturbation. This, for simple mathematical convenience, should be thought of as being turned on at the initial instant, $t = 0$, and kept constant over time, i.e.

$$\mathcal{H}(t) = \mathcal{H}_0 + \theta(t)\lambda\mathcal{H}_{ext},$$

with $\theta(t)$ Heaviside function. $\mathcal{H}_0$ represents the equilibrium dynamics described by the invariant ensemble density ρ_0, equilibrium density operator with respect to $\mathcal{H}_0$:

$$[\mathcal{H}_0, \rho_0] = 0.$$

Observables expectation values are therefore constant over time with respect to this equilibrium dynamics $\mathcal{H}_0$. $\mathcal{H}_{ext}$ introduces a perturbation: ρ_0 is no longer invariant and the observables expectation values will return to being time-dependent. In classical physics, the achievement of a new steady state could be studied precisely in relation to the relaxation to equilibrium of certain observables [2]. One can think of carrying the same considerations for quantum systems; highlighting the perturbation in $\mathcal{H}$ is a good starting point from this perspective.

Anyway, we will see that if we do not highlight this distinction between $\mathcal{H}_0$ and $\mathcal{H}_{ext}$, considering the general dynamics (2.8), the new formalism will work in the same way. In this more general context, Ω_0 could be better associated with the mathematical distance between ρ_0 and ρ_{eq}, a measure of entropy. This result has already been demonstrated for classical dynamical systems [2] and may have a quantum analogue.

In summary, we highlight the disturbance as in (2.2) to reiterate that the ideal location of our work is in the field of response theory. The new formalism we are building can be a good basis for deriving in future an exact response formula for time-dependent perturbations or open systems. This is a very ambitious expectation since, as already noted previously, there is no exact response theory for these cases yet. However, it is not just an unfounded hope since this type of exact response based on the Dissipation Function already exists in classical mechanics.

We carry out some other considerations relating exclusively to the dissipation operator just defined. Firstly, it is mathematically usable in practical applications, meaning it is not an overly abstract operator. Secondly, in classical physics the dissipative flux [24] is defined as

$$J(\Gamma) = -\lambda\{\mathcal{H}_{ext}, \mathcal{H}_0\};$$

applying the quantization rule to the latter we obtain

$$\hat{J} = -\frac{\lambda}{i\hbar}[\mathcal{H}_{ext}, \mathcal{H}_0].$$

Expression (2.7) should be proportional to $\hat{J}$ but, in general, this is not immediate. Anyway, we can carry out this analysis for particular cases. For instance, if ρ_0 is the equilibrium canonical distribution for $\mathcal{H}_0$, one has

$$\rho_0 = \rho_{eq} = \sum_n \frac{e^{-\beta E_n^0}}{\mathcal{Z}} |\psi_n^0\rangle\langle\psi_n^0| = \frac{e^{-\beta\mathcal{H}_0}}{\mathcal{Z}}.$$

Obviously, ρ_0 commutes with $\mathcal{H}_0$: $[\mathcal{H}_0, \rho_0] = 0$. Taking advantage of these considerations we can conclude that Ω^0, in this particular case, presents some proportionality with the dissipative flux $\hat{J}$:

$$\Omega^0 = \frac{\lambda}{i\hbar}\left(\frac{e^{-\beta\mathcal{H}_0}}{\mathcal{Z}}\right)^{-1}[\mathcal{H}_{ext}, \frac{e^{-\beta\mathcal{H}_0}}{\mathcal{Z}}] = \frac{\lambda}{i\hbar} e^{+\beta\mathcal{H}_0}[\mathcal{H}_{ext}, e^{-\beta\mathcal{H}_0}] =$$
$$\frac{\lambda}{i\hbar} K(\mathcal{H}_0)[\mathcal{H}_{ext}, F(\mathcal{H}_0)] \propto -\frac{\lambda}{i\hbar}[\mathcal{H}_{ext}, \mathcal{H}_0] = \hat{J} \Rightarrow \Omega^0 \propto \hat{J}.$$

$K(\mathcal{H}_0)$ and $F(\mathcal{H}_0)$ are two matrices dependent on $\mathcal{H}_0$. We have not investigated the type of proportionality in detail. This is beyond the scope of our thesis and can be a starting point for other research in this direction. In any case, some proportionality seems to exist, this strengthens the possibility of associating the dissipation observable with the operator Ω.

We limited ourselves to defining Ω at the initial instant $t = 0$. In chapter 5 we will study its temporal evolution. However, we highlight here that thanks to the maintained generality, remember (2.8), any instant $t = t^*$ can be considered as initial of the quantum dynamics: the dissipation operator is therefore well-defined at any time instant.

The main aim of this thesis is to study the role of the dissipation operator in the exact calculation of $\langle\mathcal{O}\rangle_t$. Now we are going to use definition (2.7) to carry out precisely this analysis.

2.2 Derivation of the quantum exact response expression

In this section, we will exploit the dissipation operator (2.7) to derive the quantum analogue of the classical expression (1.23) for the calculation of $\langle\mathcal{O}\rangle_t$. Before doing this, however, let's introduce a series of interesting properties of the dissipation operator (2.7).

Proposition 2.2.1. *The expectation value of the dissipation operator calculated with respect to the density operator ρ_0 is always null,*

$$\langle\Omega^0\rangle_0 = 0.$$

Proof.

$$\langle \Omega^0 \rangle_0 = Tr\Big(\rho_0\big(\frac{i}{\hbar}\rho_0^{-1}[\mathcal{H},\rho_0]\big)\Big) = \frac{i}{\hbar}Tr(Id \cdot [\mathcal{H},\rho_0]),$$

now we can use first the linear property and then the cyclic property of the trace,

$$\frac{i}{\hbar}Tr(\mathcal{H}\rho_0 - \rho_0\mathcal{H}) = \frac{i}{\hbar}\Big(Tr(\mathcal{H}\rho_0) - Tr(\rho_0\mathcal{H})\Big) = \frac{i}{\hbar}\Big(Tr(\mathcal{H}\rho_0) - Tr(\mathcal{H}\rho_0)\Big) = 0$$

We conclude that $\langle \Omega^0 \rangle_0 = 0$. □

Another important property is the following.

Proposition 2.2.2. *The initial derivative of the dissipation operator expectation value is always positive,*

$$\frac{d}{ds}\langle \Omega^0 \rangle_s|_{s=0} \geq 0$$

Proof. We can show this statement by making the incremental limit explicit in the derivative operation.

$$\frac{d}{ds}\langle \Omega^0 \rangle_s|_{s=0} = \lim_{s\to 0}\frac{1}{s}[\langle \Omega^0 \rangle_s - \langle \Omega^0 \rangle_0] = \lim_{s\to 0}\frac{1}{s}[Tr(\rho_s\Omega^0) - Tr(\rho_0\Omega^0)] =$$

$$Tr\Big(\lim_{s\to 0}\frac{\rho_s - \rho_0}{s}\Omega^0\Big) = Tr\Big(\frac{\partial \rho_0}{\partial t}\Omega^0\Big).$$

Now we can use equation (2.6) to express $\frac{\partial \rho_0}{\partial t}$ in a much more convenient way,

$$\frac{\partial \rho_0}{\partial t} = \rho_0\Omega^0, \tag{2.9}$$

so the last expression becomes

$$Tr\Big(\rho_0\Omega^0\Omega^0\Big) = \langle (\Omega^0)^2 \rangle_0 \geq 0.$$

□

For now, we consider these two propositions to be purely mathematical properties, but we will see later that they could be essential to offer interpretations of the dissipation operator, in analogy to those of the classical dynamical systems [2]. In fact, the classical Dissipation Function satisfies the same properties.

Now we derive one of the main results of this thesis.

Proposition 2.2.3. *Let* ρ_0 *be the initial density operator and* $\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$ *the time-independent Hamiltonian operator. The expectation value at time* t *of a generic observable* $\mathcal{O}$ *can be calculated using the non-Hermitian dissipation operator* (2.7) *by means of the expression*

$$\langle \mathcal{O} \rangle_t = \langle \mathcal{O} \rangle_0 + \int_0^t \langle \Omega^0 \mathcal{O}_s \rangle_0 ds. \tag{2.10}$$

Proof. Let's derive a useful expression for $\frac{d}{ds}\langle\mathcal{O}\rangle_s$:

$$\frac{d}{ds}\langle\mathcal{O}\rangle_s = \lim_{h\to 0}\frac{1}{h}[\langle\mathcal{O}\rangle_{s+h} - \langle\mathcal{O}\rangle_s] = \lim_{h\to 0}\frac{1}{h}[Tr(\mathcal{O}\rho_{s+h}) - Tr(\mathcal{O}\rho_s)] =$$
$$\lim_{h\to 0}\frac{1}{h}[Tr\Big(\mathcal{O}U(s+h)\rho_0 U^\dagger(s+h)\Big) - Tr\Big(\mathcal{O}U(s)\rho_0 U^\dagger(s)\Big)].$$

The usual cycling property of the trace comes to our aid once again, we have that the latter is equal to

$$\lim_{h\to 0}\frac{1}{h}[Tr\Big(U^\dagger(s+h)\mathcal{O}U(s+h)\rho_0\Big) - Tr\Big(U^\dagger(s)\mathcal{O}U(s)\rho_0\Big)]. \tag{2.11}$$

We recall that, thanks to the group property of the operator $U(t)$, we can write

$$U(s+h) = U(h)U(s), \quad U^\dagger(s+h) = U^\dagger(s)U^\dagger(h).$$

Moreover, remembering that observables and density matrix evolve "at opposite times", expression (2.11) is equal to

$$\lim_{h\to 0}\frac{1}{h}[Tr\Big(U^\dagger(h)\mathcal{O}_s U(h)\rho_0\Big) - Tr\Big(\mathcal{O}_s\rho_0\Big)] =$$
$$\lim_{h\to 0}\frac{1}{h}[Tr\Big(\mathcal{O}_s U(h)\rho_0 U^\dagger(h)\Big) - Tr\Big(\mathcal{O}_s\rho_0\Big)] =$$
$$Tr\Big(\mathcal{O}_s \lim_{h\to 0}\frac{\rho_h - \rho_0}{h}\Big) = Tr\Big(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}\Big).$$

Now we can use, as already done previously, equation (2.9) to insert Ω^0:

$$Tr\Big(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}\Big) = Tr\Big(\mathcal{O}_s\rho_0\Omega^0\Big) = Tr\Big(\rho_0\Omega^0\mathcal{O}_s\Big) = \langle\Omega^0\mathcal{O}_s\rangle_0 \tag{2.12}$$

In conclusion we have:

$$\frac{d}{ds}\langle\mathcal{O}\rangle_s = \langle\Omega_0\mathcal{O}_s\rangle_0. \tag{2.13}$$

This last equation is very important because enable us to write the exact formula for the expectation value of an arbitrary observable at time t simply by integrating, thanks to the fundamental theorem of integral calculus, we have

$$\langle\mathcal{O}\rangle_t = \langle\mathcal{O}\rangle_0 + \int_0^t \frac{d}{ds}\langle\mathcal{O}\rangle_s ds = \langle\mathcal{O}\rangle_0 + \int_0^t \langle\Omega^0\mathcal{O}_s\rangle_0 ds$$

□

We highlight that, in proposition 2.2.3, $\mathcal{H}_0$ is considered the equilibrium dynamics, for which ρ_0 is the corresponding invariant equilibrium distribution. $\lambda\mathcal{H}_{ext}$

represents the Hamiltonian perturbation, which is arbitrarily large and time independent. It should be considered as turned on at the initial instant. The reasons for this distinction in $\mathcal{H}$ are the same as those stated previously, the validity of the expression is however more general, as in (2.8).

Let us analyse this statement. First, we note the good similarity with the analogous expression (1.23) in classical mechanics. Secondly, we highlight that $\langle \mathcal{O} \rangle_t$ can be calculated simply using the Heisenberg or the Schrödinger picture,

$$\langle \mathcal{O} \rangle_t = Tr(\rho_t \mathcal{O}) = Tr(\rho_0 \mathcal{O}_t) = Tr(\rho_0 e^{\frac{it}{\hbar}\mathcal{H}} \mathcal{O} e^{-\frac{it}{\hbar}\mathcal{H}});$$

indeed, also our equation (2.10) requires the knowledge of the exponential Hamiltonian $e^{\frac{it}{\hbar}\mathcal{H}}$. Proposition 2.2.3 can be seen as a different way to rewrite what is already known. This is true, but it does not mean that it is a trivial or irrelevant result. In general, finding different formalisms to rewrite the same result is often a great way to discover different points of view on a theory. The same problem can be very complicated in a certain formalism and much simpler in another. Knowing different formalisms gives more choice in which to use. Furthermore, finding a good, different point of view can be an important first step towards new discoveries. A clear example of this is represented by the equivalence of Heisenberg and Schrödinger pictures. They are two exactly equivalent ways of formalizing quantum mechanics. However, both are of essential importance, one never suppresses the other, they coexist. The Heisenberg picture has proven to be decisive in numerous discoveries thanks to its greater similarity to classical mechanics through the quantization rule and is the basis, for example, of the second quantization field theory. On the other hand, the Schrödinger picture is still important and used today as it is more convenient in other applications, is the basis of probabilistic interpretation and offers a better point of view for theoretically understanding quantum states.

Obviously, it is not enough to rewrite an equation to discover something new, it is necessary to find an original and promising way to do it. Equation (2.10) seems to possess these qualities thanks to its analogy with the classical expression (1.23). Let's try to make some initial suggestions on the advantages it could bring.

The quantum exact response formula could offer simplifications in ensemble problems. It is expressed in a very good form to fit, with the necessary extensions, quantum dynamics more complicated than a simple time-independent Hamiltonian. It can be a good starting point to adapt this discussion to time-dependent Hamiltonians and to more general dissipative dynamics. This could lead to revolutionary results, as these types of dynamics in quantum mechanics are only treated approximately. However, this will require hard research work to be able to introduce these extensions correctly.

Moreover, this formalism is based on the dissipation operator, in classical mechanics this is a physical observable linked to dissipation and is also widely studied from other points of view. Properties (2.2.1) and (2.2.2) will allow us to offer some interpretations of the dissipation operator in analogy with classical mechanics. It is true that in quantum mechanics, for constant Hamiltonians, the advantage typical of classical mechanics of evolving only the observables is lost. In fact, once $U(t)$ has been defined, one can indifferently make the observables or the density evolve, as in eq.(1.15). However, in quantum dissipative dynamics, a way to evolve only the observables, while maintaining the probability fixed, has not yet been found. Extending expression (2.10), it might be possible. Finally, the classical exact response based on the Dissipation Function is recent and still analysed today. The quantum translation may suggest new discoveries for both the corresponding classical theory and general quantum systems behaviours; or it could benefit from future new results of the classical approach.

In classical physics, $\langle AB\rangle_0$ is the correlation function of A and B calculated with f_0. In quantum mechanics, it can still be interpreted as a correlation function, however, it is necessary to highlight important differences. In general, Ω^0 and $\mathcal{O}$ doesn't commute and thus

$$\langle \Omega^0 \mathcal{O}_s\rangle_0 \neq \langle \mathcal{O}_s \Omega^0\rangle_0.$$

There may seem to be something wrong in the exact formula (2.10): we know that the expectation value is a real quantity only for hermitian observables; meanwhile it is not clear in general if operator $\Omega^0\mathcal{O}_s$ is Hermitian. However, if the proof is correct, we have remained faithful to the rules of quantum mechanics and $\langle \Omega^0 \mathcal{O}_s\rangle_0$ will always turn out to be a real quantity. We will see in the next chapter that this is also confirmed by several numerical tests. Therefore, we absolutely cannot use $\langle \mathcal{O}_s \Omega^0\rangle_0$ in the equation (2.10) because it would destroy the entire construction by providing incorrect results.

There are correlation functions with better properties (in the sense of closer to those of classical mechanics) than the one used previously. Two widely used correlation functions of this type are

$$\begin{aligned} \text{Symmetric correlation } \ \langle A;B\rangle_0 &= Tr\left[\rho_0\Big(AB+BA\Big)\frac{1}{2}\right], \\ \text{Kubo canonical correlation } \ \langle A_0;B_t\rangle_0^K &= \frac{1}{\beta}\int_0^\beta d\lambda Tr\Big[\rho_0 e^{\lambda H}A_0 e^{-\lambda H}\mathcal{B}_t\Big]. \end{aligned} \tag{2.14}$$

We would prefer to use them in equation (2.10) but we can't just apply a brutal substitution, this would destroy the entire derivation again. This substitution requires a demonstration which could lead to a different form for the formula. Indeed, eq. (2.13) may no longer hold for these new correlations keeping the same definition for the dissipation operator. However, in this case, it is not very important to look for a way to insert a different type of correlation into equation (2.10). If equation (2.10) works well then it is reasonable to keep it in this form, changing correlation type would not add anything significant. Anyway, it is worth underlining that some improvements for the dissipation operator definition are possible and a different type of correlation could be very useful in the attempt to derive a formula for $\langle \mathcal{O} \rangle_t$ using a different dissipation operator.

We also notice a very good behaviour with respect to the easiest observable of all, the constant function. Choosing $\mathcal{O} = 1$ we have that

$$\langle 1 \rangle_t = \langle 1 \rangle_0 + \int_0^t \langle \Omega^0 1 \rangle_0 ds = 1 + 0t = 1,$$

where in the second equality we used proposition 2.2.1. This result can be interpreted as a consistency condition: the probabilistic interpretation of the density operator is preserved, indeed we have just shown that the trace of the density operator remains constant over time using equation (2.10),

$$\langle 1 \rangle_t = Tr(1\rho_t) = 1.$$

In classical mechanics, the origin of the name Dissipation Function comes from the fact that this quantity corresponds precisely to the generalised entropy production: product of dissipative force and thermodynamic flux.
This is clear by comparing the classical expression (1.23) with those obtained using the TTCF for the time evolution of $\langle \mathcal{O} \rangle_t$, from an initial distribution f_0, for a thermodynamic system under the influence of an external field F_{ext} [2].

$$TTCF: \quad \langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} - \frac{V}{k_B T} \int_0^t \langle (\mathcal{O} \circ S^s) J \cdot F_{ext} \rangle_{f_0} ds. \tag{2.15}$$

Through this comparison, one can make the phenomenological association between Ω^0, f_0 and the energy dissipation due to the external field, whence the appellation ‘Dissipation Function’.

Another interesting interpretation is the one that Ω assumes in the more general context of dynamical systems. In this context,

$$\langle \Omega_{0,s}^{f_0} \rangle_{f_0} = \langle ln(f_0/f_{-s}) \rangle_0 \geq 0 \tag{2.16}$$

is a relative entropy $D(f_0 \| f_{-s})$, called also Kullback–Leibler divergence [2]. We therefore recover in equation (2.16) the second-law inequality, but interpreted in terms of relative entropies and independent of any thermodynamic context.

The first interpretation (2.15) is interesting for assigning the physical meaning of dissipation to Ω^0 in quantum thermodynamic systems. For this type of systems a good way to represent dissipation has not yet been found and therefore it is worth investigating this first way further.

Furthermore, equation (2.10) is also applicable to quantum non-thermodynamic systems. The second interpretation (2.16) could therefore make Ω^0 an observable with a very precise mathematical meaning. Thanks to properties 2.2.1 and 2.2.2 this second interpretation is still valid in quantum mechanics. In fact, combining them, we have that

$$\exists h > 0 : \langle \Omega^0_{0,s} \rangle_0 \geq 0 \quad for \;\; 0 < s < h. \tag{2.17}$$

Furthermore, the only density operators that are dissipation free, i.e. $\langle \Omega^0_{0,s} \rangle_0 = 0$, are those invariant with respect to the dynamics. A density operator ρ is invariant under the dynamics if $[\mathcal{H}, \rho] = 0$. In this sense, we can say that

$$\rho_0 \text{ is dissipation free} \iff \Omega^0 = 0.$$

In summary, in this chapter we have applied the quantization rule to the Dissipation Function, offering its possible quantum definition; we then used the new operator to derive expression (2.10) for the calculation of $\langle \mathcal{O} \rangle_t$, in analogy to the classic formula (1.23). We analysed the results obtained, highlighting their potential and weak points. It is now necessary to numerically test the validity of these results. This is what we are going to do in the next chapter, applying the new formula to simple quantum systems.

Chapter 3

Numerical tests for the quantum exact response expression

Even if we tried to remain rigorous in demonstrating the new formula (2.10), we could have unknowingly stumbled upon some conceptual errors. For example, we may not have well-defined the dissipation operator, or we may have used a property that is valid in classical mechanics but not in quantum mechanics. The new formula seems well demonstrated, but to fully ascertain its validity it is necessary to test it on theoretically well-known physical systems. In this thesis, we only consider finite-dimensional quantum operators. There are numerous quantum systems of this type of fundamental importance. In this section, we will apply equation (2.10) to quantum systems with only two energy levels, the simplest quantum systems possible. We will always work in a two-dimensional Hilbert space, and we will compare the results predicted by the new expression with those well known theoretically. Expression (2.10) has the advantage of being easily treatable numerically. We can therefore write a simple Matlab code to study its behaviour and analyse the predicted results.
In Appendix A, we report the final Matlab code used for the applications of this chapter, it also contains the implementation of the expression with the Hermitian dissipation operator that we will derive in the next chapter.

First, we recall the definition of Pauli matrices,

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \ \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{3.1}$$

which are of fundamental importance in quantum mechanics. The first physical

system to which we apply expression (2.10) is a spin particle in a magnetic field. This is a very well known system in the theory of quantum mechanics. We will therefore be able to compare the results predicted by the quantum exact response formula with results that are well known theoretically and certainly valid.
For mathematical convenience, we will always set $\hbar = 1$ and treat all physical quantities as dimensionless.

3.1 Applications to spin problems

Suppose that we initially have a spin $\frac{1}{2}$ particle in a magnetic field B_z directed along the $z-$axis. The dynamics of this physical system is described by the Hamiltonian

$$\mathcal{H}_0 = \mu_B B_z \sigma_z = \frac{\hbar\omega_0}{2}\sigma_z.$$

The system has reached a steady state, which is described, for example due to our partial ignorance of the system, by the following ensemble:

the particle is in spin up state $| \uparrow\rangle = (1,\ 0)'$ with probability $p_\uparrow$,
the particle is in spin down state $| \downarrow\rangle = (0,\ 1)'$ with probability $p_\downarrow$.

This is a quantum mixed state represented by the initial density matrix

$$\rho_0 = p_\uparrow | \uparrow\rangle\langle\uparrow | + p_\downarrow | \downarrow\rangle\langle\downarrow | = \begin{bmatrix} p_\uparrow & 0 \\ 0 & p_\downarrow \end{bmatrix}. \tag{3.2}$$

This density operator is invariant because $| \uparrow\rangle$ and $| \downarrow\rangle$ are eigenfunctions of $\mathcal{H}_0$ and we have

$$[\mathcal{H}_0, \rho_0] = 0.$$

Every observable in equilibrium dynamics $\mathcal{H}_0$ is constant over time. We can show this result by remembering that $[e^{i\mathcal{H}_0 t}, \rho_0] = 0$ since ρ_0 commutes with $\mathcal{H}_0$. One has

$$\langle\mathcal{O}\rangle_t = Tr(U(t)\rho_0 U^\dagger(t)\mathcal{O}) = Tr(U(t)U^\dagger(t)\rho_0\mathcal{O}) = Tr(Id\rho_0\mathcal{O}) = \langle\mathcal{O}\rangle_0.$$

By calculating this expectation value with equation (2.10), since $\Omega^0 = 0$, we always obtain $\langle\mathcal{O}\rangle_t = \langle\mathcal{O}\rangle_0$. We also note here that for every perturbation of the type

$$\mathcal{H} = \mathcal{H}_0 + \lambda\sigma_z,$$

ρ_0 is dissipation-free because $\Omega^0 = 0$ and therefore $\langle\mathcal{O}\rangle_t = \langle\mathcal{O}\rangle_0 \ \ \forall\mathcal{O}$, which is in perfect agreement with theoretically well-known results.

Let us now analyse more interesting perturbations. For example, we could turn off the magnetic field along z and turn it on along x. This perturbation can be represented by

$$\mathcal{H}_{ext} = \frac{\omega_x}{2}\sigma_x - \frac{\omega_0}{2}\sigma_z, \quad \lambda = 1,$$

then the final perturbed Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext} = \frac{\omega_x}{2}\sigma_x. \tag{3.3}$$

Now ρ_0 is not anymore invariant for $\mathcal{H}$. The solution of this problem is a well-known result of quantum mechanics. One has, for example for the observables $\mathcal{O} = \sigma_i$, the following theoretical results:

$$\langle\sigma_x\rangle_t = 0; \quad \langle\sigma_y\rangle_t = (p_\downarrow - p_\uparrow)sin(\omega_x t); \quad \langle\sigma_z\rangle_t = (p_\uparrow - p_\downarrow)cos(\omega_x t). \tag{3.4}$$

These results can be easily shown using the Heisenberg picture. Exploiting eq. (1.16), one can derive the following identity for Pauli matrices:

$$e^{i\alpha\sigma_k} = Id \cdot cos\alpha + i\sigma_k sin\alpha. \tag{3.5}$$

This result can be used to calculate operators σ_i evolved at the time t. By taking as example the observable $\mathcal{O} = \sigma_z$, we can calculate the Heisenberg evolved operator $\sigma_{z,t}$. For the perturbed Hamiltonian $\mathcal{H}$ we have

$$\sigma_{z,t} = e^{i\frac{\omega_x}{2}\sigma_x t}\sigma_z e^{-i\frac{\omega_x}{2}\sigma_x t} =$$

$$\begin{bmatrix} cos(\frac{\omega_x t}{2}) & isin(\frac{\omega_x t}{2}) \\ isin(\frac{\omega_x t}{2}) & cos(\frac{\omega_x t}{2}) \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} cos(\frac{\omega_x t}{2}) & -isin(\frac{\omega_x t}{2}) \\ -isin(\frac{\omega_x t}{2}) & cos(\frac{\omega_x t}{2}) \end{bmatrix} =$$

$$\begin{bmatrix} cos(\omega_x t) & -isin(\omega_x t) \\ +isin(\omega_x t) & -cos(\omega_x t) \end{bmatrix}.$$

While for σ_z evolved according to the equilibrium Hamiltonian $\mathcal{H}_0$ we would have

$$\sigma_{z,t} = e^{i\frac{\omega_0}{2}\sigma_z t}\sigma_z e^{-i\frac{\omega_0}{2}\sigma_z t} = \sigma_z e^{i\frac{\omega_0}{2}\sigma_z t}e^{-i\frac{\omega_0}{2}\sigma_z t} = \sigma_z,$$

because $[\sigma_z, e^{i\frac{\omega_0}{2}\sigma_z t}] = 0$.

According to the Heisenberg picture, the expectation value of σ_z at time t is simply $\langle\sigma_z\rangle_t = Tr(\rho_0\sigma_{z,t})$. Then, for the perturbed Hamiltonian dynamics we find

$$\text{In } \mathcal{H}: \quad \langle\sigma_z\rangle_t = Tr\left(\begin{bmatrix} cos(\omega_x t) & -isin(\omega_x t) \\ +isin(\omega_x t) & -cos(\omega_x t) \end{bmatrix}\begin{bmatrix} p_\uparrow & 0 \\ 0 & p_\downarrow. \end{bmatrix}\right) = (p_\uparrow - p_\downarrow)cos(\omega_x t).$$

It is interesting to highlight the difference with the equilibrium dynamics:

$$\text{In } \mathcal{H}_0: \quad \langle\sigma_z\rangle_t^{\mathcal{H}_0} = Tr(\rho_0\sigma_z) = p_\uparrow - p_\downarrow = \langle\sigma_z\rangle_0^{\mathcal{H}_0}.$$

With the same procedure we obtain the expressions for $\langle\sigma_x\rangle_t$ and $\langle\sigma_y\rangle_t$ reported in (3.4).

We can therefore begin to study validity of the quantum exact response formula (2.10) comparing its results with (3.4). We calculated $\langle\sigma_x\rangle_t$, $\langle\sigma_y\rangle_t$ and $\langle\sigma_z\rangle_t$ for the physical system $\mathcal{H}$ and initial density matrix ρ_0 just defined, using new expression (2.10). In figure 3.1 we plotted the predicted values for $\langle\sigma_y\rangle_t$ and $\langle\sigma_z\rangle_t$ as a function of time, choosing $p_\downarrow = 0.1$ and $p_\uparrow = 0.9$; $\langle\sigma_x\rangle_t$ is constant over time and equal to zero.
The results obtained coincide perfectly with the theoretical ones in (3.4).

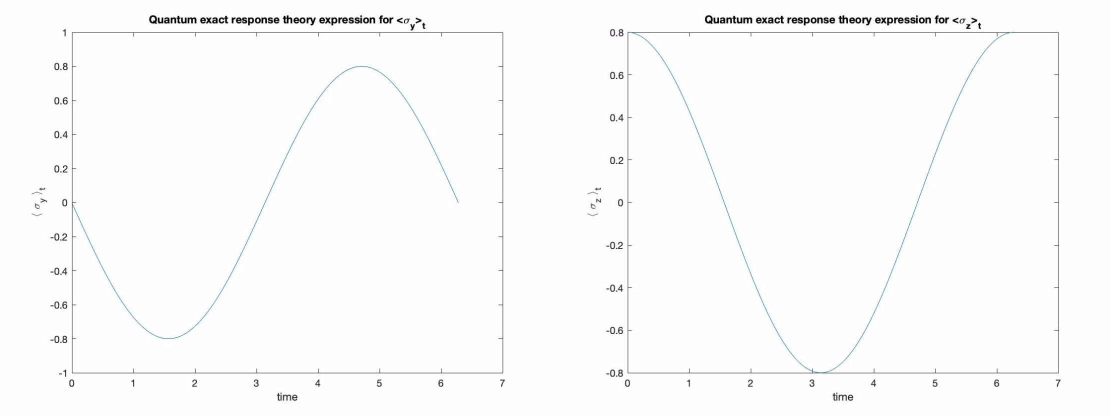

Figure 3.1: $\langle\sigma_y\rangle_t$ and $\langle\sigma_z\rangle_t$ calculated with quantum exact response expression (2.10). $t \in [0{,}2\pi]$, Hamiltonian (3.3), $p_\uparrow = 0.9$, $p_\downarrow = 0.1$ in (3.2), $\omega_x = 1$. Predictions are correct.

These results already constitute a very important confirmation of the validity of expression (2.10) for the calculation of $\langle\mathcal{O}\rangle_t$ using the non-Hermitian dissipation operator Ω^0 previously defined. If we had made some conceptual errors in the derivation, the predicted results would certainly not have been so good. Since we tested it on a single physical system, constructed in the simplest way possible, there could still be something conceptually wrong, but the correctness of the predicted results would then be a very unlikely coincidence. However, to remove any doubt it is necessary to test expression (2.10) on other different physical systems and more general cases. This is what we are going to do in the rest of this chapter, physically interpreting the results, and at the end of chapter 4, in a much more general way and from a purely mathematical point of view.

To carry out comparisons in the field of response theory we can always consider the spin particle in a magnetic field but changing the type of perturbation. It is interesting to compare the results obtained with those approximated by linear response theory. We keep the same Hamiltonians $\mathcal{H}_0$, $\mathcal{H}_{ext}$ but we vary the value of λ arbitrarily. In this way we obtain

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext} = \frac{\omega_0}{2}\sigma_z + \lambda(\frac{\omega_x}{2}\sigma_x - \frac{\omega_0}{2}\sigma_z) = (1-\lambda)\frac{\omega_0}{2}\sigma_z + \lambda\frac{\omega_x}{2}\sigma_x. \tag{3.6}$$

From a physical point of view, we are decreasing the z-direction component of the magnetic field, B_z, and increasing the x-direction component B_x, which was initially null. We will compare the results obtained with those predicted by the linear response theory. This will offer good approximate results only for small values of λ. For this purpose it is necessary to recall Kubo linear response formula (1.19) [10]. Kubo considers a perturbed dynamics of the type

$$\mathcal{H}_t = \mathcal{H} - K(t)\mathcal{A},$$

where $K(t)$ is a time dependent external force applied from the infinite past, $t = -\infty$, when the system was at thermal equilibrium, described by an equilibrium density matrix ρ_e, i.e. $\rho(-\infty) = \rho_e$. A is a dynamical quantity conjugate to the applied force K. For this system Kubo derives the linear response formula

$$\langle B\rangle_t = \langle B\rangle_{\rho_e} + \Delta\overline{B}(t), \quad \Delta\overline{B}(t) = \int_{-\infty}^{t} dt' K(t')\phi_{BA}(t-t'),$$
$$\phi_{BA}(t) = \frac{1}{i\hbar}\langle[A, B(t)]\rangle_{\rho_e};$$

where B is an arbitrary observable and $B(t) = e^{\frac{i}{\hbar}\mathcal{H}t}Be^{-\frac{i}{\hbar}\mathcal{H}t}$ is the Heisenberg-evolved operator according to the unperturbed dynamics $\mathcal{H}$ (different from the total dynamics $\mathcal{H}_t$, $\mathcal{H} \neq \mathcal{H}_t$). The dynamics we are considering in (3.6) is simpler than the latter and therefore Kubo's formula is certainly adaptable to our problem. We are taking a constant disturbance over time, we can consider it absent before time $t = 0$ and impulsively turned on at $t = 0$. We can rewrite Kubo formula with our notation and taking into account the simplifications. In the following scheme we have on the left Kubo's problem notation and on the right our notation

$$\mathcal{H}_t = \mathcal{H} - K(t)\mathcal{A} \to \mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$$
$$A \to -\mathcal{H}_{ext};$$
$$K(t) \to \lambda(t) = \theta(t)\lambda$$

where $\theta(t)$ is the Heaviside function. Kubo's formula can now be rewritten for our problem and simplified:

$$\Delta\overline{B}(t) = \int_{-\infty}^{t} dt'\theta(t')\lambda\phi_{B\mathcal{H}_{ext}}(t-t').$$

Thanks to the Heaviside function, the lower limit of integration is 0, indicating that our system is in equilibrium until time $t = 0$, the latter becomes

$$\Delta\overline{B}(t) = \int_0^t dt'\lambda\phi_{B\mathcal{H}_{ext}}(t-t').$$

Now it is convenient to change the integration variable, $t^* = t - t'$, obtaining

$$\Delta\overline{B}(t) = -\int_t^0 dt^*\lambda\phi_{B\mathcal{H}_{ext}}(t^*) = \int_0^t dt'\lambda\phi_{B\mathcal{H}_{ext}}(t')$$

The response function in our notation is

$$\phi_{B\mathcal{H}_{ext}}(t') = -\frac{1}{i\hbar}\langle[\mathcal{H}_{ext}, e^{\frac{i}{\hbar}\mathcal{H}_0 t}Be^{-\frac{i}{\hbar}\mathcal{H}_0 t}]\rangle_0 = -\frac{i}{\hbar}\langle[U_0^\dagger(t)BU_0(t), \mathcal{H}_{ext}]\rangle_0,$$

where we used the subscript 0 in $U_0(t)$ to distinguish the evolution operator relating to the equilibrium dynamics $\mathcal{H}_0$ from $U(t)$ of the total dynamic $\mathcal{H}$: $U_0^\dagger(t)\mathcal{O}U_0(t) \neq \mathcal{O}_t = U^\dagger(t)\mathcal{O}U(t)$. In conclusion, by setting $\hbar = 1$, we obtain

$$\langle\mathcal{O}\rangle_t = \langle\mathcal{O}\rangle_0 - i\lambda\int_0^t \langle[U_0^\dagger(t)\mathcal{O}U_0(t), \mathcal{H}_{ext}]\rangle_0 dt'. \tag{3.7}$$

Furthermore, the theoretical results are well known, the problem is easily solved in Heisenberg or Schrödinger picture,

$$\langle\mathcal{O}\rangle_t = Tr(\mathcal{O}_t\rho_0) = Tr(U^\dagger(t)\mathcal{O}U(t)\rho_0). \tag{3.8}$$

To express operator $\mathcal{O}_t$ we proceed as already shown in the derivation of results (3.4). The only difference is that now, for the exponential of the Hamiltonian operator $U(t) = e^{-i\mathcal{H}t}$, the previously used identity (3.5) is no longer valid because $\mathcal{H} \neq \alpha\sigma_i$. However, the exponential of the $\mathcal{H}$ operator can still be calculated as shown in the introduction chapter.

Therefore, we have calculated $\langle\sigma_i\rangle_t$ using the three expressions: non-Hermitian dissipation operator expression (2.10), Kubo linear expression (3.7) and Heisenberg picture expression (3.8) (which is the one surely correct). The calculations were carried out numerically with the Matlab code of Appendix B. We compared the results for different values of λ, ρ_0, time interval and observable $\mathcal{O}$. In figures 3.2 and 3.3 we show some graphs that well capture the behaviours of the three formulas for $\mathcal{O} = \sigma_y$, with initial equilibrium density matrix ρ_0 in the form (3.2). Qualitatively very similar results (as λ varies) were found for any Hermitian observable, and any initial density operator ρ_0 (in general form, not necessarily diagonal as in (3.2)). The qualitative analysis of the comparison remains the same.

In summary, for very small λ the linear approximation is good and the difference between linear and non-hermitian Ω^0 formulas is indistinguishable to the eye. As λ increases, the linear approximation becomes increasingly worse (as expected), while the Ω^0-response continues to offer results in agreement with those of the Heisenberg picture. Furthermore, the results of the linear theory worsen over long times, while the expression (2.10) does not have this defect.

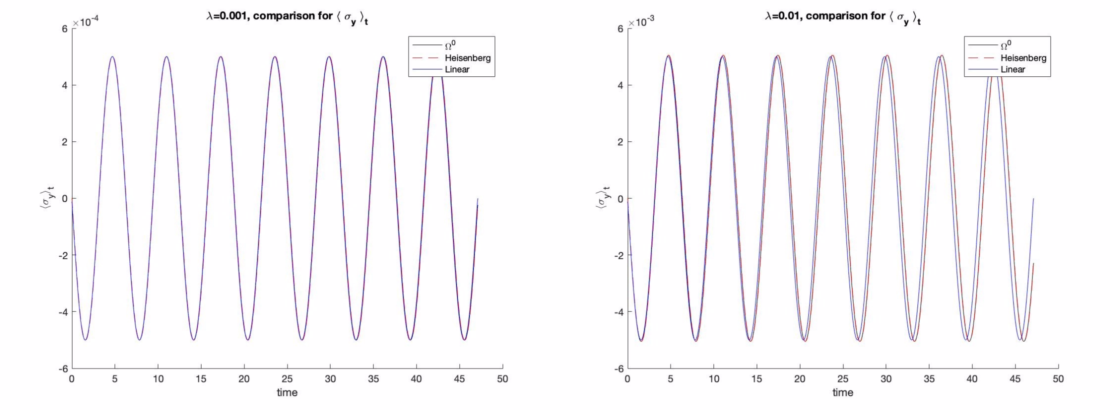

Figure 3.2: Comparison between linear (blue), Heisenberg (red) and dissipation (black) responses for $\langle\sigma_y\rangle_t$. (Left panel) $\lambda = 0.001$; (Right panel) $\lambda = 0.01$. $t \in [0,15\pi]$, $p_\uparrow = 0.75$, $p_\downarrow = 0.25$. $\omega_x = \omega_0 = 1$. The three responses coincide for $\lambda = 0.001$. For $\lambda = 0.01$ the difference begins to be noticed over long times. $\Omega-$expression (2.10) still coincides with the Heisenberg picture (the correct one), the linear response differs slightly over long times.

The linear response theory has offered numerous very important results and will continue to be a fundamental theory whenever the perturbation is excessively complex and inexpressible exactly. However, as already noted, it has clear limitations. With this comparison, we are absolutely not stating that the new theory is already better than the linear response theory. The $\mathcal{H}$ dynamics considered is so simple that it would not even make sense to study it with the linear approximation and our formula has not yet been generalized to more complex perturbations. However, expression (2.10) is a very good basis from which to extend this method to even slightly more complicated dynamics. If it were possible to achieve this, then we would obtain an exact response (certainly better than an approximate method) in dynamics for which a perturbative approach is still one of the most effective today.

In the next section we will continue to test expression (2.10) but we will abandon the form $\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$, characterizing response theories, to study the new formula behaviour on qubits. Qubits are quantum systems which are gaining ever greater importance with the progress of technology. The simplicity of this type of systems will still allow us to work in a two-dimensional Hilbert space using the dissipation

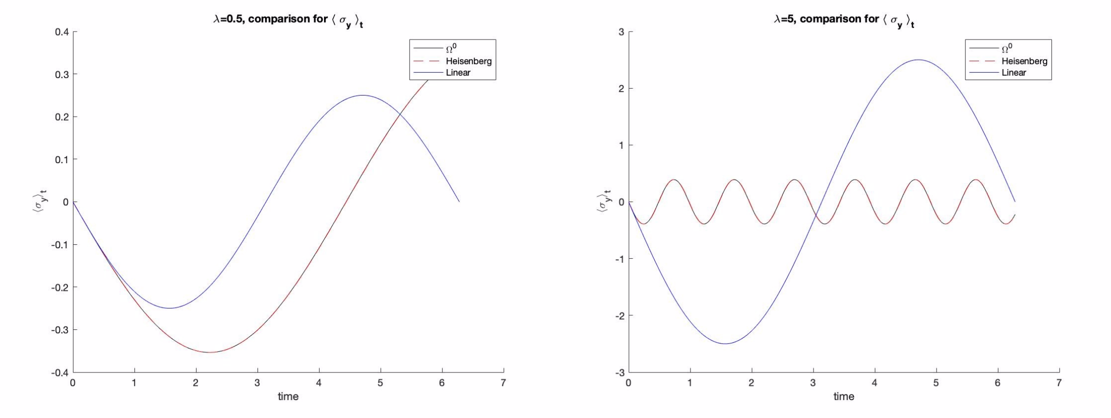

Figure 3.3: Comparison between linear (blue), Heisenberg (red) and dissipation (black) responses for $\langle\sigma_y\rangle_t$. (Left panel) $\lambda = 0.5$; (Right panel) $\lambda = 5$.
$t \in [0,2\pi]$, $p_\uparrow = 0.75$, $p_\downarrow = 0.25$. $\omega_x = \omega_0 = 1$. $\Omega-$expression (2.10) still coincides with the correct Heisenberg picture (the two curves overlap), the linear response does not.

operator method.

3.2 Qubits and Rabi oscillations

The previous system formed by the $\frac{1}{2}$ spin particle in a magnetic field B is a quantum system with 2 states, there are only two energy levels. Any quantum 2-state system is called qubit. They are systems of extraordinary importance as they constitute the basic unit of quantum information. Therefore, in quantum computing, a qubit is the quantum analogous of a classic bit. In this section we present some properties of the qubits, and then we will apply the new expression (2.10) to these types of systems.
A qubit admits two states: $|0\rangle$ and $|1\rangle$. According to the laws of quantum mechanics, it can be in a quantum superposition of states $|0\rangle$ and $|1\rangle$. It is a unitary vector $|\psi\rangle$ in the 2D Hilbert space $\mathscr{H} = |0\rangle \otimes |1\rangle$,

$$|\psi\rangle = a(t)|0\rangle + b(t)|1\rangle, \quad a(t), b(t) \in \mathbb{C}.$$

Qubits present a very interesting geometric representation: quantum states can be visualised using the Bloch sphere [25]. This seems initially strange, indeed probability amplitudes are complex quantities and 4 degrees of freedom would seem necessary for a correct representation. However, two degrees of freedom can be removed. The first is removed using the normalization constraint

$$|a(t)|^2 + |b(t)|^2 = 1.$$

The second remembering that the global phase of the state has no physically observable consequences, so one can arbitrarily choose a (or b) to be real. The quantum state can be represented using only two real coordinates, $\theta(t) \in \mathbb{R}$ and $\phi(t) \in \mathbb{R}$:

$$a = cos\frac{\theta}{2},\ b = e^{i\phi} sin\frac{\theta}{2},$$

$e^{i\phi}$ is the physically significant relative phase. The pure quantum state of a qubit is therefore represented by a point on the surface of the Bloch sphere, which has a unit radius. Once an axis passing through the centre is fixed, it identifies two poles, one corresponds to state $|0\rangle$ and the other to state $|1\rangle$. The measurement process destroys the coherent superposition state and the state collapses to one of the two poles. Thus, when we measure a qubit, we can obtain $|0\rangle$ with probability $|a|^2$ and $|1\rangle$ with probability $|b|^2$. Projectors are important observables relative to probabilities $|a(t)|^2$, $|b(t)|^2$, they are defined as

$$\pi_0 = |0\rangle\langle 0|, \quad \pi_1 = |1\rangle\langle 1|.$$

These are very important operators because their expectation value at time t gives the probability of finding the system in state 0 or 1 respectively,

$$p_0(t) = Tr(\rho_t \pi_0) = Tr(|\psi(t)\rangle\langle\psi(t)||0\rangle\langle 0|) =$$
$$Tr(\langle 0||\psi(t)\rangle\langle\psi(t)||0\rangle) = Tr(a(t)a^*(t)) = |a(t)|^2.$$

So far in this summary description of qubits we have focused on pure states, but even mixed states can be visualized on the Bloch sphere. The density operator ρ for a qubit system is always a 2x2 matrix that can be written as a linear combination of the identity and the Pauli matrices:

$$\rho = \frac{1}{2}(Id + \vec{a}\cdot\vec{\sigma}) = \frac{1}{2}\bigg(Id + a_1\sigma_x + a_2\sigma_y + a_3\sigma_z\bigg);\ |\vec{a}|^2 \leq 1$$

The coefficient $\vec{a}$ is named 'Bloch vector'. The norm of the Bloch vector contains information about mixedness. If the system is in a pure state $|a| = 1$ while if it is in a mixed state $|a| < 1$. Pure states are therefore points on the unit surface of the Bloch sphere while mixed states lie inside the sphere. When the Bloch vector is null, $|\vec{a}| = 0$, the system is in a totally mixed state $\rho = \frac{1}{2}Id$.

A qubit system always evolves according to a Hermitian Hamiltonian

$$\mathcal{H} = \vec{c}\cdot\vec{\sigma}_4,\ \text{where } \vec{\sigma}_4 = (Id, \sigma_x, \sigma_y, \sigma_z) \text{ and } \vec{c} = (c_0, c_1, c_2, c_3) \in \mathbb{R}^4. \tag{3.9}$$

For example, we choose

$$\mathcal{H} = \gamma\sigma_x. \tag{3.10}$$

If states $|1\rangle$ and $|0\rangle$ are eigenstates of the Hamiltonian (3.10), which we denote with $|\rightarrow\rangle$ and $|\leftarrow\rangle$ the behaviour is not very interesting to analyse. The expectation value of an arbitrary observable, and so also of the projectors π_0 and π_1 is constant in time. We therefore choose to study, from a physical point of view, the state of the system along the z-axis (up and down). In other words, the state $|0\rangle$ corresponds to the vector $|\uparrow\rangle = (1{,}0)$ and the state $|1\rangle$ to $|\downarrow\rangle = (0{,}1)$, which are not eigenvectors of the Hamiltonian (3.10). This system presents the so-called Rabi oscillations [26]. If the initial condition is the pure state $|\psi(0)\rangle = |1\rangle$, the probability of finding the qubit in the state $|0\rangle$ at time t is

$$p_0^1(t) = \langle\pi_0\rangle_t = sin^2(\gamma t), \tag{3.11}$$

where the superscript 1 indicates that the system is in state $|1\rangle$ at the initial time and the subscript 0 that we are measuring the probability that the system is in state $|0\rangle$ at time t. One can show equation (3.11) working in Heisenberg representation,

$$\langle\pi_0\rangle_t = Tr\Big(\rho_0 e^{i\gamma\sigma_x t}|0\rangle\langle 0|e^{-i\gamma\sigma_x t}\Big),$$

and now, using identity (3.5),

$$e^{i\gamma\sigma_x t} = Id \cdot cos(\gamma t) + i\sigma_x sin(\gamma t), \quad e^{-i\gamma\sigma_x t} = Id \cdot cos(\gamma t) - i\sigma_x sin(\gamma t).$$

In conclusion,

$$\langle\pi_0\rangle_t = Tr\Bigg(\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} cos(\gamma t) & isin(\gamma t) \\ isin(\gamma t) & cos(\gamma t) \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} cos(\gamma t) & -isin(\gamma t) \\ -isin(\gamma t) & cos(\gamma t) \end{bmatrix} \Bigg) =$$
$$Tr\Bigg(\begin{bmatrix} 0 & 0 \\ isin(\gamma t)cos(\gamma t) & -i^2 sin^2(\gamma t) \end{bmatrix} \Bigg) = sin^2(\gamma t).$$

If the qubit is in a mixed ensemble state at time 0,

$$|\psi(0)\rangle = \begin{cases} |0\rangle & \text{with probability } e_0 \\ |1\rangle & \text{with probability } e_1 \end{cases} \qquad e_0 + e_1 = 1,$$

the amplitude of the oscillations will decrease but the reference value around which it oscillates continues to be $\frac{1}{2}$. This can be shown by repeating the previous calculation for the new density matrix

$$\rho_0 = e_0|0\rangle\langle 0| + e_1|1\rangle\langle 1| = \begin{bmatrix} e_0 & 0 \\ 0 & e_1 \end{bmatrix}.$$

Alternatively, more simply, we can use the properties of probability theory. Combining the concept of statistical uncertainty and quantum uncertainty the expectation value becomes

$$\langle\pi_0\rangle_t = e_1 p_0^1(t) + e_0 p_0^0(t). \tag{3.12}$$

We just calculated $p_0^1(t)$. Thanks to the symmetry of the system it is then clear that $p_0^0(t)$ coincides with $p_1^1(t)$, which is the complementary probability of $p_0^1(t)$. In conclusion,

$$p_0^0(t) = p_1^1(t) = 1 - p_0^1(t)$$

and, substituting this in (3.12), we can write

$$\langle \pi_0 \rangle_t = e_1 p_0^1(t) + e_0(1 - p_0^1(t)) = e_0 + (e_1 - e_0) p_0^1(t).$$

We note that, if the initial state is a totally mixed state

$$\rho_0 = \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1| = \frac{1}{2} Id, \tag{3.13}$$

then the density operator is invariant, because the identity commutes with any operator, $[\rho_0, \mathcal{H}] = 0$. This last mixed state actually coincides with the maximum uncertainty, we know nothing about the qubit, and therefore it could be in one of the two states with equal probability, this initial uncertainty remains constant over time due to the oscillating dynamics represented by Hamiltonian (3.10).

Now we can study the behaviour of the quantum exact response formula with respect to Rabi-oscillations. This is a case where it is of no significance to distinguish between the form $\mathcal{H}_0 + \lambda \mathcal{H}_{ext}$ and $\mathcal{H}$. We are not considering any perturbation, the dynamics is non-dissipative, as already mentioned, however, the formula is certainly still valid. If the system is in the totally mixed initial state (3.13), then the density matrix is invariant and consequently the dissipation operator is null,

$$[\rho_0, \mathcal{H}] = 0 \Rightarrow \Omega^0 = 0.$$

For this system it makes no sense to talk about physical dissipation, but it could make sense to talk about "dissipation" with respect to probability densities. We can say that ρ_0, as a purely mathematical entity, is dissipation-free in the sense that the corresponding dissipation operator is zero. Formula (2.10) correctly predicts the following result

$$p_0(t) = \langle \pi_0 \rangle_t = \langle \pi_0 \rangle_0 = \frac{1}{2}.$$

We start analysing the case of initial density matrix in form (3.2). Every time that $e_0 \neq e_1$, we can say that the density operator ρ_0 is dissipative, in the sense that $\Omega^0 \neq 0$. Ω^t could measure in time the distance of ρ_t from a possible stationary distribution. The probability density of this system will never reach a steady state, the Schrödinger equation is deterministic and the probabilities continue to oscillate infinitely over time. However, it is good to remember that a mathematical model always has characteristic scales, outside which it can lose validity. If we let the system evolve for infinitely long times, the uncertainty on the qubit return to being maximum. In this sense, the density matrix (3.2) with $e_0 = e_1 = 0.5$ would be the stationary density ρ_{eq} and Ω^t can be considered a measure of the 'mathematical distance' of ρ_t from ρ_{eq}. This consideration should be better formalized and studied from a mathematical point of view, for now it is only an original and a little imaginative attempt of interpretation.

We have already noticed that our expression (2.10) has bad behaviour compared to pure states. The density matrix ρ_0 is not invertible. A somewhat hasty but effective way of dealing with this problem is to simply solve it by replacing the pure initial state $|1\rangle$ with an ensemble having very high probability weight for state $|1\rangle$:

$$\rho_0 = e_0|0\rangle\langle 0| + e_1|1\rangle\langle 1| \quad \text{with } e_1 \gg e_0.$$

Using the quantum exact response formula with this initial density matrix we find classical Rabi oscillations with height $A \simeq 1$. If instead we change the probability weights e_0, e_1 in (3.2), increasing e_0 and decreasing e_1 the amplitude predicted by the formula will gradually decrease until it vanishes for $e_0 = e_1 = \frac{1}{2}$. The height increase again by continuing to increase e_0 and will reach its maximum ($A \simeq 1$) for $e_0 \gg e_1$, indeed the problem is symmetric with respect to the two states. In figure 3.4 we have plotted the graph in time of Rabi oscillations predicted by expression (2.10), the amplitude and the frequency of the probability oscillations is perfectly captured. Our formula offers excellent results for qubit systems.

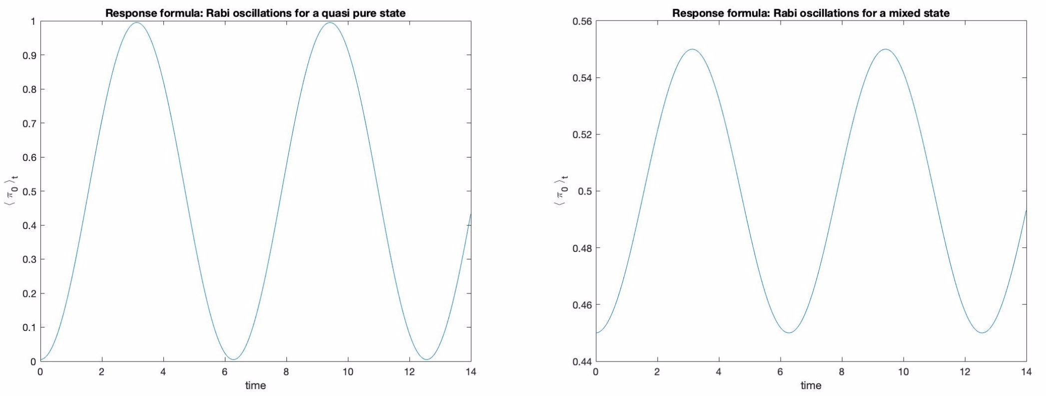

Figure 3.4: $\langle \pi_0 \rangle_t$ calculated with the exact quantum response expression (2.10). Left panel: ρ_0 quasi-pure state density matrix: $e_0 = 0.005$ and $e_1 = 0.995$. Right panel: ρ_0 mixed-state density matrix, $e_0 = 0.45$ and $e_1 = 0.55$. $t \in [0,14]$, $\gamma = 0.5$. Amplitude changes, frequency does not.

To conclude the analysis on qubits we choose an arbitrary Hamiltonian in the form (3.9), for example choosing $\vec{c} = (1, -0.5, 3, 1.2)$. The system can initially be in any state in the Bloch sphere, it is not necessarily an ensemble only of $|0\rangle$ and $|1\rangle$ states. Then we also randomly take the initial density matrix ρ_0, represented for instance by the point in the Bloch sphere identified by the Bloch vector $\vec{a} = (0.43, -0.31, -0.111)$. We numerically compare the probability oscillation $p_1(t) = \langle \pi_1 \rangle_t$ predicted by the new expression (2.10) with the correct value,

$$p_1(t) = \langle \pi_1 \rangle_t = Tr(e^{-i\mathcal{H}t} \rho_0 e^{+i\mathcal{H}t} \pi_1)$$

In figure 3.5 we plot the two corresponding graphs.

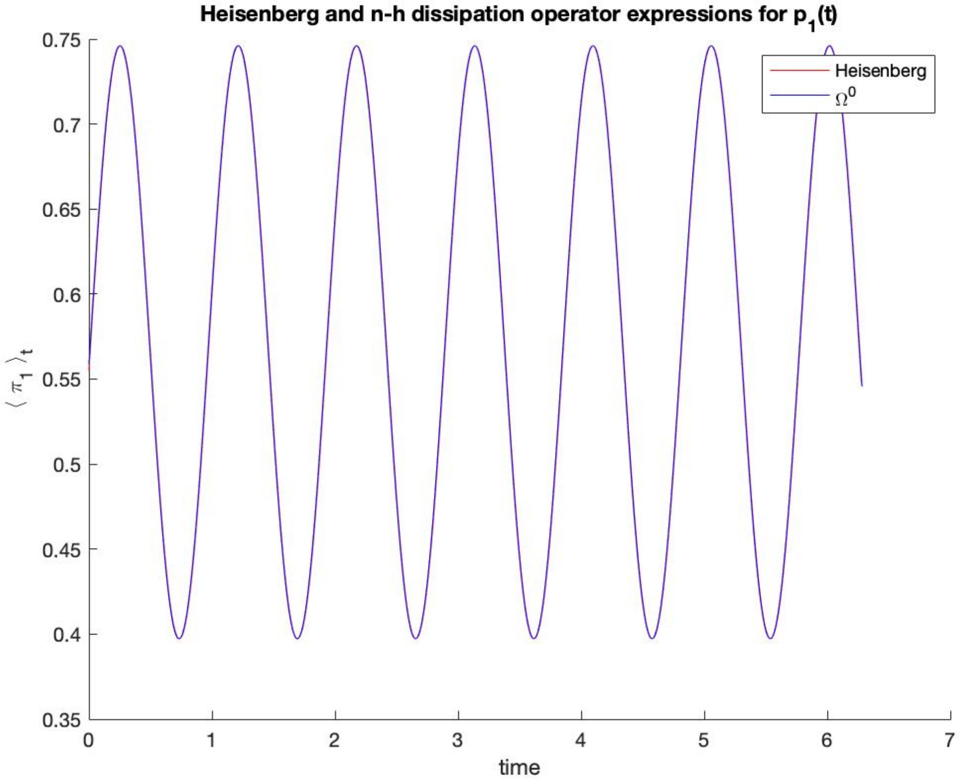

Figure 3.5: $\langle \pi_1 \rangle_t$ calculated: with dissipation operator formula (2.10) (in blue) and using the Heisenberg picture (in red). The two curves overlap and so the results are correct. $t \in [0,2\pi]$; ρ_0-Bloch vector $\vec{a} = (0.43, -0.31, -0.111)$; Hamiltonian defined by $\vec{c} = (1, -0.5, 3, 1.2)$.

The predicted results are correct and therefore the new expression (2.10) is certainly valid. However, a problem remains, the dissipation operator Ω^0 is non-Hemitian. We would like to choose it as observable, $\mathcal{O} = \Omega^0$, calculate its expectation value $\langle \Omega^0 \rangle_t$ with the new corresponding approach and associate this value with the physical observable of dissipation. Unfortunately, it is in general a complex number,

$$\langle \Omega^0 \rangle_t \in \mathbb{C},$$

and becomes very complicated to associate dissipation with this quantity. A possible choice is to associate the dissipation only with the real or imaginary part. This is a possible option but it is clear that, without further analysis, it is a hasty and unjustified choice.

A good way to solve this interpretative problem is to define a Hermitian dissipation operator, in this way it would certainly be a physical observable. In the next chapter, we are going to define such a Hermitian dissipation operator.

Chapter 4

Generalizations and analysis of the dissipation operator

Defining the dissipation operator in a Hermitian way would make the association with a physical observable more immediate, since its expectation value would always be a real quantity. In this chapter we will define a Hermitian dissipation operator. Then, we will use it to derive an exact response expression for calculating $\langle \mathcal{O} \rangle_t$. In this expression, however, it will not be possible to use only the new Hermitian dissipation operator, an antihermitian operator will naturally appear in the attempt to derive the formula. We will compare the new expression with that of chapter 2, eq. (2.10); finally, we will carry out other numerical tests focusing on the mathematical aspects in the applications of the two formulas.

4.1 The Hermitian dissipation operator

The classic procedure for making a non-Hermitian operator A self-adjoint is to symmetrize it in the following way,

$$A \to \tilde{A} = \frac{1}{2}(A + A^\dagger) \Rightarrow \tilde{A} = \tilde{A}^\dagger.$$

Thus, it is immediate to try this approach with the non-hermitian dissipation operator (2.7). Then we could redefine Ω^0 as

$$\Omega^0 \to \tilde{\Omega}^0 = \frac{1}{2}(\Omega^0 + (\Omega^0)^\dagger). \tag{4.1}$$

It is therefore necessary to calculate the adjoint of Ω^0.

Proposition 4.1.1. *The adjoint of the non-Hermitian dissipation operator* Ω^0 *is*

$$(\Omega^0)^\dagger = \frac{1}{i\hbar}[\mathcal{H}, \rho_0]\rho_0^{-1}.$$

Proof. Before using the properties of the adjoint operation it is best to make the commutator explicit to switch to a more convenient form for our purposes,

$$(\Omega^0)^\dagger = \Big(\frac{1}{i\hbar}\rho_0^{-1}[\mathcal{H},\rho_0]\Big)^\dagger =$$
$$\Big(\frac{1}{i\hbar}\rho_0^{-1}(\mathcal{H}\rho_0 - \rho_0\mathcal{H})\Big)^\dagger = \Big(\frac{1}{i\hbar}\rho_0^{-1}\mathcal{H}\rho_0 - \frac{1}{i\hbar}\mathcal{H}\Big)^\dagger.$$

The adjoint operation, for two arbitrary operators A, B and a complex number $\lambda \in \mathbb{C}$, has the following properties [6]

$$(A+B)^\dagger = A^\dagger + B^\dagger, \quad (\lambda A)^\dagger = \lambda^* A^\dagger, \quad (AB)^\dagger = B^\dagger A^\dagger, \quad (A^{-1})^\dagger = (A^\dagger)^{-1}.$$

Therefore, for the dissipation operator we have

$$(\Omega^0)^\dagger = -\frac{1}{i\hbar}(\rho_0^{-1}\mathcal{H}\rho_0)^\dagger + \frac{1}{i\hbar}(\mathcal{H})^\dagger = -\frac{1}{i\hbar}(\rho_0\mathcal{H}\rho_0^{-1} - \mathcal{H}).$$

In the last equality we used the Hermitianity property of operators $\mathcal{H} = \mathcal{H}^\dagger$ and $\rho_0 = \rho_0^\dagger$. Moreover, if ρ_0 is hermitian also its inverse ρ_0^{-1} must be hermitian.
We can rewrite the latter in a more convenient form,

$$-\frac{1}{i\hbar}(\rho_0\mathcal{H}\rho_0^{-1} - \mathcal{H}) = -\frac{1}{i\hbar}[\rho_0,\mathcal{H}]\rho_0^{-1} = \frac{1}{i\hbar}[\mathcal{H},\rho_0]\rho_0^{-1}.$$

In conclusion, we obtain

$$(\Omega^0)^\dagger = \frac{1}{i\hbar}[\mathcal{H},\rho_0]\rho_0^{-1}.$$

□

Knowing the adjoint operator of Ω^0 allows us to redefine the dissipation operator to make it Hermitian, the application of rule (4.1) leads to the following definition.

Definition 4.1.2. *We define the hermitian dissipation operator as*

$$\tilde{\Omega}^0 \equiv \frac{1}{2}(\Omega^0 + (\Omega^0)^\dagger). \tag{4.2}$$

Operator $\tilde{\Omega}^0$, defined in this way, can be expressed in different forms, all equivalent, for example as

$$\tilde{\Omega}^0 = \frac{1}{2i\hbar}\{\rho_0^{-1},[\mathcal{H},\rho_0]\},$$

where we used the anticommutator to obtain a compact form. We remind here that the anticommutator is defined as

$$\{A,B\} \equiv AB + BA.$$

Equivalently, after some calculations, we can write $\tilde{\Omega}^0$ in the form

$$\tilde{\Omega}^0 = \frac{1}{2i\hbar}(\rho_0^{-1}\mathcal{H}\rho_0 - \rho_0\mathcal{H}\rho_0^{-1}).$$

Now we want to study again the properties already demonstrated for the non-Hermitian dissipation operator, the ideal would be to find exactly the same properties as the non-Hermitian operator. In fact, we have seen previously that these acquire an important role in the classic case.

Proposition 4.1.3. *The expectation value of the Hermitian dissipation operator calculated with respect to the density operator ρ_0 is always null,*

$$\langle\tilde{\Omega}^0\rangle_0 = 0. \tag{4.3}$$

Proof. Thanks to analogous proposition (2.2.1), we just need to calculate the expectation value of $(\Omega^0)^\dagger$, indeed we simply have

$$\begin{aligned}\langle\tilde{\Omega}^0\rangle_0 = \frac{1}{2}\langle\Omega^0\rangle_0 + \frac{1}{2}\langle(\Omega^0)^\dagger\rangle_0 = \\ 0 + \frac{1}{2i\hbar}Tr([\mathcal{H},\rho_0]\rho_0^{-1}\rho_0) = \\ \frac{1}{2i\hbar}Tr(\mathcal{H}\rho_0 - \rho_0\mathcal{H}) = \frac{1}{2i\hbar}\Big(Tr(\mathcal{H}\rho_0) - Tr(\mathcal{H}\rho_0)\Big) = 0\end{aligned}$$

□

A key passage in the derivations of chapter 2 was the equality (2.9), which allows us to insert the dissipation operator in place of the time derivative of the initial density operator. Now we can use the Von Neumann equation to compare the (non hermitian) dissipation operator and its adjoint:

$$\begin{aligned}\Omega^0 &= \frac{1}{i\hbar}\rho_0^{-1}[\mathcal{H},\rho_0] = \rho_0^{-1}\frac{\partial\rho_0}{\partial t} \\ (\Omega^0)^\dagger &= \frac{1}{i\hbar}[\mathcal{H},\rho_0]\rho_0^{-1} = \frac{\partial\rho_0}{\partial t}\rho_0^{-1}.\end{aligned}$$

Therefore, we can replace $\frac{\partial\rho_0}{\partial t}$ in two ways, we highlight this by recalling that

$$\begin{aligned}\frac{\partial\rho_0}{\partial t} &= \rho_0\Omega^0, \\ \frac{\partial\rho_0}{\partial t} &= (\Omega^0)^\dagger\rho_0.\end{aligned} \tag{4.4}$$

This observation will prove essential in the following demonstrations.

We were unable to prove $\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0} \geq 0$, but in trying to do so we obtained an equality that comes very close to this goal.

Proposition 4.1.4. *The initial derivative of the hermitian dissipation operator expectation value satisfies the following equality*

$$\begin{aligned}\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0} &= \frac{1}{4}\Big(\langle(\Omega^0)^2\rangle_0 + \langle(\Omega^{0\dagger})^2\rangle_0\Big) + n(\mathcal{H},\rho_0);\\ n(\mathcal{H},\rho_0) &= \frac{1}{2\hbar^2}\Big(Tr(\mathcal{H}^2\rho_0) - Tr(\mathcal{H}\rho_0^2\mathcal{H}\rho_0^{-1})\Big)\end{aligned} \tag{4.5}$$

Proof. If we repeat the passages of proposition (2.2.2) we obtain

$$\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0} = Tr(\tilde{\Omega}^0\frac{\partial\rho_0}{\partial t}),$$

now it is immediate to use both forms of equation (4.4), the latter becomes

$$\begin{aligned}&\frac{1}{2}Tr((\Omega^0 + (\Omega^0)^\dagger)\frac{1}{2}(\rho_0\Omega^0 + (\Omega^0)^\dagger\rho_0)) =\\ &\frac{1}{4}Tr((\Omega^0)^2\rho_0 + (\Omega^{0\dagger})^2\rho_0 + \Omega^0(\Omega^0)^\dagger\rho_0 + (\Omega^0)^\dagger\Omega^0\rho_0) =\\ &\frac{1}{4}(\langle(\Omega^0)^2\rangle_0 + \langle(\Omega^{0\dagger})^2\rangle_0 + 2Tr(\rho_0\Omega^0(\Omega^0)^\dagger).\end{aligned}$$

Moreover, the last term can be rewritten in a form such that it would be negligible in many applications:

$$\begin{aligned}Tr(\rho_0\Omega^0(\Omega^0)^\dagger) &= -\frac{1}{\hbar^2}Tr(\rho_0\rho_0^{-1}[\mathcal{H},\rho_0][\mathcal{H},\rho_0]\rho_0^{-1}) =\\ &\frac{1}{\hbar^2}Tr\Big((\mathcal{H}\rho_0 - \rho_0\mathcal{H})(\mathcal{H}\rho_0 - \rho_0\mathcal{H})\rho_0^{-1}\Big) =\\ &\frac{1}{\hbar^2}Tr\Big((\mathcal{H}\rho_0\mathcal{H}\rho_0 - \mathcal{H}\rho_0^2\mathcal{H} - \rho_0\mathcal{H}^2\rho_0 + \rho_0\mathcal{H}\rho_0\mathcal{H})\rho_0^{-1}\Big).\end{aligned}$$

Using the cyclic property of the trace and the identity $\rho_0\rho_0^{-1} = \rho_0^{-1}\rho_0 = Id$ we have

$$\begin{aligned}&\frac{1}{\hbar^2}(Tr(\mathcal{H}^2\rho_0) - Tr(\mathcal{H}\rho_0^2\mathcal{H}\rho_0^{-1}) - Tr(\rho_0\mathcal{H}^2) + Tr(\mathcal{H}^2\rho_0)) =\\ &\frac{1}{\hbar^2}(Tr(\mathcal{H}^2\rho_0) - Tr(\mathcal{H}\rho_0^2\mathcal{H}\rho_0^{-1})).\end{aligned}$$

In conclusion, we find

$$\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0} = \frac{1}{4}\Big(\langle(\Omega^0)^2\rangle_0 + \langle(\Omega^{0\dagger})^2\rangle_0\Big) + \frac{1}{2\hbar^2}\Big(Tr(\mathcal{H}^2\rho_0) - Tr(\mathcal{H}\rho_0^2\mathcal{H}\rho_0^{-1})\Big)$$

□

This equality can be exploited to demonstrate the positivity of $\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0}$; it is reasonable to assume, considering its form, that $n(\mathcal{H},\rho_0)$ is negligible compared to the other two terms, both certainly positive. We do not exclude that it is possible to demonstrate that $n(\mathcal{H},\rho_0)=0$, if it were not, one can calculate the value of n in every application. Whenever $\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0}\geq 0$ is found, we would get (2.17) and the analogy with the relative entropy $D(f_0\|f_{-s})$ (Kullback-Leibler divergence) could be maintained.

Now we want to rewrite the exact response formula derivation using the new Hermitian operator. Clearly, it is not enough to replace the new operator in the previous expression (2.10), this would destroy the good derivation. So the new expression will inevitably be in a different form, but the hope is that, eventually by using a different type of correlation (2.14), the analogy with the classic formula will remain unchanged. The goal is thus to express $\langle\mathcal{O}\rangle_t$ as a function only of ρ_0, $\mathcal{O}_t$ and $\tilde{\Omega}^0$. This would allow us, in analogy to classical mechanics, to interpret the Hermitian operator $\tilde{\Omega}^0$ as the physical observable of dissipation. Unfortunately, we are not able to do this: a new operator appears in the expression for $\langle\mathcal{O}\rangle_t$.

Proposition 4.1.5. *Let* ρ_0 *be the initial density operator and* $\mathcal{H}=\mathcal{H}_0+\lambda\mathcal{H}_{ext}$ *the time-independent Hamiltonian operator. The expectation value at time t of a generic observable* $\mathcal{O}$ *can be calculated using the Hermitian dissipation operator* (4.2) *by means of the expression*

$$\langle\mathcal{O}\rangle_t=\langle\mathcal{O}\rangle_0+\int_0^t\left(\langle\tilde{\Omega}^0;\mathcal{O}_s\rangle_0+\frac{1}{2}\langle[\overline{\Omega^0},\mathcal{O}_s]\rangle_0\right)ds, \tag{4.6}$$

where $\overline{\Omega^0}$ *is the antihermitian operator* $\overline{\Omega^0}\equiv\frac{1}{2}\Big(\Omega^0-(\Omega^0)^\dagger\Big)$.

Proof. From the proof of (2.10) we have

$$\frac{d}{ds}\langle\mathcal{O}\rangle_s=Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}),$$

indeed, in all the previous passages we don't mention the dissipation operator. At this point, we would like to insert the (new) Hermitian dissipation operator $\tilde{\Omega}^0$. A good way to do this is to use both forms for $\frac{\partial\rho_0}{\partial t}$ in equations (4.4).

$$\begin{aligned}Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t})=\frac{1}{2}Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t})+\frac{1}{2}Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t})=\\ \frac{1}{2}Tr(\mathcal{O}_s\rho_0\Omega^0)+\frac{1}{2}Tr(\mathcal{O}_s(\Omega^0)^\dagger\rho_0)=\\ \frac{1}{2}Tr(\Omega^0\mathcal{O}_s\rho_0+(\Omega^0)^\dagger\rho_0\mathcal{O}_s).\end{aligned} \tag{4.7}$$

We can rewrite this last expression in several different ways. An interesting form for our purposes could be

$$\begin{aligned} Tr(\Omega^0\mathcal{O}_s\rho_0 + (\Omega^0)^\dagger\rho_0\mathcal{O}_s) = Tr\Big(\Omega^0\mathcal{O}_s\rho_0 + (\Omega^0)^\dagger(\mathcal{O}_s\rho_0 + [\rho_0, \mathcal{O}_s])\Big) = \\ Tr\Big((\Omega^0 + (\Omega^0)^\dagger)\mathcal{O}_s\rho_0\Big) + Tr\Big((\Omega^0)^\dagger[\rho_0, \mathcal{O}_s]\Big). \end{aligned} \tag{4.8}$$

Now we can simply use definition (4.2) to insert the hermitian dissipation operator in the equation, obtaining

$$2Tr\Big(\tilde{\Omega}^0\mathcal{O}_s\rho_0\Big) + Tr\Big((\Omega^0)^\dagger[\rho_0, \mathcal{O}_s]\Big), \tag{4.9}$$

this was precisely our aim. Due to the presence of $(\Omega^0)^\dagger$, the last expression still remains in a form that is not at all elegant. A good idea is therefore to repeat the same calculations done in (4.8) but using the commutator property for the first term in the trace:

$$Tr(\Omega^0\mathcal{O}_s\rho_0 + (\Omega^0)^\dagger\rho_0\mathcal{O}_s) = Tr\Big(\Omega^0\rho_0\mathcal{O}_s + \Omega^0[\mathcal{O}_s, \rho_0] + (\Omega^0)^\dagger\rho_0\mathcal{O}_s\Big).$$

With analogous passages to the previous ones we can arrive at the form

$$2Tr\Big(\tilde{\Omega}^0\rho_0\mathcal{O}_s\Big) + Tr\Big(\Omega^0[\mathcal{O}_s, \rho_0]\Big) \tag{4.10}$$

Now we want to combine equations (4.9) and (4.10), the hope is to express $Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t})$ using only the hermitian dissipation operator $\tilde{\Omega}^0$ and eliminate with calculations the presence of any other type of dissipation operator, such as Ω^0 and $(\Omega^0)^\dagger$. Starting from equation (4.7) we could write

$$Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}) = \frac{1}{4}(Tr(\Omega^0\mathcal{O}_s\rho_0 + (\Omega^0)^\dagger\rho_0\mathcal{O}_s) + Tr(\Omega^0\mathcal{O}_s\rho_0 + (\Omega^0)^\dagger\rho_0\mathcal{O}_s)).$$

Now we can use equation (4.9) in place of the first trace operation and equation (4.10) in place of the second one, obtaining

$$\begin{aligned} \frac{1}{4}\Big(2Tr\Big(\tilde{\Omega}^0\mathcal{O}_s\rho_0\Big) + Tr\Big((\Omega^0)^\dagger[\rho_0, \mathcal{O}_s]\Big) + 2Tr\Big(\tilde{\Omega}^0\rho_0\mathcal{O}_s\Big) + Tr\Big(\Omega^0[\mathcal{O}_s, \rho_0]\Big)\Big) = \\ \frac{1}{2}Tr\Big(\tilde{\Omega}^0\mathcal{O}_s\rho_0\Big) + \frac{1}{2}Tr\Big(\tilde{\Omega}^0\rho_0\mathcal{O}_s\Big) + \frac{1}{4}\Big(Tr\Big((\Omega^0)^\dagger[\rho_0, \mathcal{O}_s] + \Omega^0[\mathcal{O}_s, \rho_0]\Big)\Big) = \\ \frac{1}{2}Tr\Big(\tilde{\Omega}^0\mathcal{O}_s\rho_0\Big) + \frac{1}{2}Tr\Big(\mathcal{O}_s\tilde{\Omega}^0\rho_0\Big) + \frac{1}{4}\Big(Tr\Big((\Omega^0 - (\Omega^0)^\dagger)[\mathcal{O}_s, \rho_0]\Big)\Big). \end{aligned}$$

We can clearly use the symmetric correlation for terms with $\tilde{\Omega}^0$ but we are unable to completely replace Ω^0 and $(\Omega^0)^\dagger$ with the hermitian $\tilde{\Omega}^0$. However, we could still have arrived at an interesting form. Indeed, we can observe that $\Omega^0 - (\Omega^0)^\dagger$ is an antihermitian operator. More precisely, we could define the antihermitian part of Ω^0 as

$$\overline{\Omega^0} \equiv \frac{1}{2}\Big(\Omega^0 - (\Omega^0)^\dagger\Big).$$

In conclusion, we obtain

$$\frac{d}{ds}\langle \mathcal{O}\rangle_s = \langle \tilde{\Omega}^0; \mathcal{O}_s\rangle_0 + \frac{1}{2} Tr\Big(\overline{\Omega}^0[\mathcal{O}_s, \rho_0]\Big)$$

which can be rewritten as

$$\frac{d}{ds}\langle \mathcal{O}\rangle_s = \langle \tilde{\Omega}^0; \mathcal{O}_s\rangle_0 + \frac{1}{2}(\langle \overline{\Omega^0}\mathcal{O}_s\rangle_0 - \Big\langle \mathcal{O}_s\overline{\Omega^0}\rangle_0)$$

or, equivalently, as

$$\frac{d}{ds}\langle \mathcal{O}\rangle_s = \langle \tilde{\Omega}^0; \mathcal{O}_s\rangle_0 + \frac{1}{2}\langle [\overline{\Omega^0}, \mathcal{O}_s]\rangle_0.$$

This last form seems the best of these. Integrating as already done previously we obtain

$$\langle \mathcal{O}\rangle_t = \langle \mathcal{O}\rangle_0 + \int_0^t \left(\langle \tilde{\Omega}^0; \mathcal{O}_s\rangle_0 + \frac{1}{2}\langle [\overline{\Omega^0}, \mathcal{O}_s]\rangle_0\right) ds$$

□

This new expression is perfectly equivalent to the previous one in the calculation of $\langle \mathcal{O}\rangle_t$ for a generic observable $\mathcal{O}$. The real step forward is the Hermitianity property of $\tilde{\Omega}^0$. Now its expectation value is a real quantity

$$\langle \tilde{\Omega}^0\rangle_t \in \mathbb{R}.$$

Now $\tilde{\Omega}^0$ can be better interpreted physically as it is real. It could be associated with dissipation but the issue is delicate. The expression (4.6) is no longer in precise correspondence with the classical one (1.23). The classical Dissipation Function appears to have split into two components in the quantum analogue. It could be interesting to study the distinction between the two components and try to understand their role. We must not make the mistake of focusing a priori on the meaning of $\tilde{\Omega}^0$ and not caring about the commutator part $[\overline{\Omega}^0, \mathcal{O}_s]$.

However, the expression constructed with the Hermitian operator (4.6) offers exactly the same results as the one with the non-Hermitian operator (2.10). So we could have simply calculated $\langle \tilde{\Omega}^0\rangle_t$ using the non-Hermitian formula.
In fact, we will see that the result is coincident. On the one hand, this is a good thing because the results of the previous expression (2.10) were correct, therefore this new expression (4.6) is also valid. On the other hand, we realize that the new expression is a decomposition of the previous one and may not add anything relevant. Anyway, we presented both, future works will be able to further investigate

the differences and possible interpretations.

By analysing proposition 4.1.5 a posteriori, it could be better clarified what happens by deriving expression (4.6). Any operator A can be decomposed into the sum of a Hermitian and an antihermitian operator,

$$A = A + \frac{1}{2}A^\dagger - \frac{1}{2}A^\dagger = \frac{1}{2}(A + A^\dagger) + \frac{1}{2}(A - A^\dagger) = \tilde{A} + \overline{A}. \tag{4.11}$$

Applying this decomposition to Ω^0, after some calculations, we should arrive at the same equation (4.6) we just found. This way seems simpler, but we did not take it into consideration initially because our goal was to obtain a final formula containing only the Hermitian operator $\tilde{\Omega}^0$. Starting the derivation with decomposition (4.11) would have meant taking a step in the opposite direction to our aim, as we would have immediately introduced an unwanted operator ($\overline{\Omega^0}$). With the procedure used, instead, we hoped to combine the Hermitian operator $\tilde{\Omega}^0$, the initial density operator ρ_0 and the observable $\mathcal{O}_t$, cutting out any other dependencies through a good use of the properties of all the operators involved and the choice of appropriate correlations. We were unable to do so, and we also realize a posteriori that it is probably easier to demonstrate that it is impossible to exclude the antihermitian part, as it would somehow mean destroying the property of unitary evolution of ρ_t. To better understand this last statement, it is useful to analyse the time evolution of ρ according to the Von Neumann equation (1.12) and compare it with that of the dissipation operator (4.4). In the next chapter we carry out this analysis.
Here, it is interesting to highlight that all the dissipation operators derived so far can be expressed in a more compact form by defining the operator ω^0 as

$$\omega^0 \equiv \rho_0^{-1}\mathcal{H}\rho_0 \tag{4.12}$$

Indeed we have, by exploiting the decomposition (4.11),

$$\begin{aligned} \Omega^0 = \frac{1}{i\hbar}(\omega^0 - \mathcal{H}); \qquad (\Omega^0)^\dagger = \frac{1}{i\hbar}(\mathcal{H} - \omega^{0\dagger}); \\ \tilde{\Omega}^0 = \frac{1}{i\hbar}\overline{\omega^0}; \qquad \overline{\Omega^0} = \frac{1}{i\hbar}(\tilde{\omega}^0 - \mathcal{H}). \end{aligned} \tag{4.13}$$

We will see in the next chapter that the introduction of the hermitian operator $\tilde{\omega}^0$ will allow us to rewrite the time propagator $U(t)$ using exclusively these dissipation operators.

To conclude this chapter, we show numerical applications of the two expressions for $\langle \mathcal{O} \rangle_t$ derived so far;

4.2 Generic numerical tests

It is necessary to verify also from a numerical point of view that the new expression with Hermitian and antihermitian dissipation operators, equation (4.6), is equivalent to the previous equation (2.10) with only a non-Hermitian dissipation operator. In this section we will test this equivalence by applying the two formulas to physical problems, and we will also always compare the results obtained with the certainly correct ones, predicted in the Schrödinger/Heisenberg picture. In this section, we will continue to work with qubit systems but we will try to be as general as possible. Previously we had only dealt with simple observables, consisting of the three Pauli matrices σ_i and the 2 projectors π_i. Considering the linearity characterizing quantum mechanics, this is already a very good proof, since a generic Hermitian observable is a linear combination of the Pauli matrices and the identity. Anyway, now we are going to show the equivalence of the results predicted by the three approaches maintaining the maximum possible generality for a quantum problem in a 2-dimensional Hilbert space. To do this, we will consider each application from a purely mathematical point of view, never dwelling on the physical meaning of the results obtained. This comparison is implemented with the Matlab code reported in Appendix A.

All possible physical observables (Hermitian matrices in the 2D Hilbert space) are represented by the linear combination of the identity and Pauli matrices; the density operator from the Bloch vector. We have:

$$\begin{aligned} &\mathcal{H} = \vec{c}\cdot\vec{\sigma}_4, \qquad \mathcal{O} = \vec{q}\cdot\vec{\sigma}_4; \qquad \vec{c},\vec{q}\in\mathbb{R}^4. \\ &\rho = \frac{1}{2}(Id + \vec{a}\cdot\vec{\sigma}), \qquad \vec{a}\in\mathbb{R}^3,\ |\vec{a}|\leq 1. \end{aligned} \tag{4.14}$$

Firstly, we verify that the new expressions obtained, the one with non-Hermitian dissipation operator, eq. (2.10), and the one with Hermitian operator and antihermitian part, eq. (4.6), give the same correct results. We arbitrarily chose vectors $\vec{a}$, $\vec{c}$ and $\vec{q}$ and then we numerically simulated the obtained problem. We repeated the process for several different combinations of Hamiltonian, initial density, observable and time interval. In all cases, the two expressions offer perfectly equivalent results coinciding with the correct ones. Two examples of these numerous tests are shown in figure 4.1.

In numerous classical problems we have seen that it is very useful to evaluate the observable Ω. One of the main reasons for this formalism is indeed the possibility of being able to associate the dissipation operator with a physical observable. Furthermore, the second formula, eq (4.6), was introduced precisely in an attempt to associate a real value with $\langle\tilde{\Omega}^0\rangle_t$. We therefore choose the new operator as

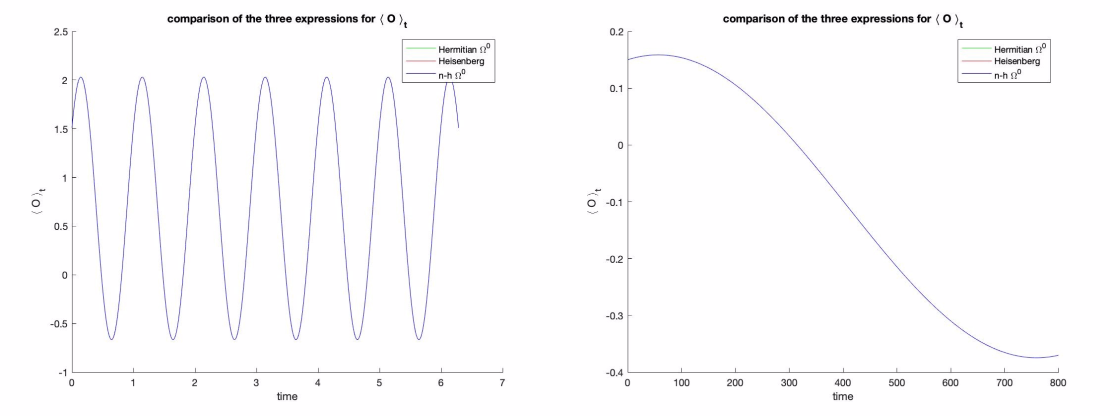

Figure 4.1: Two different tests. On the left: $\vec{a} = (0.3,0.3,-0.3)$; $\vec{c} = (4,0.8,0.5,3)$; $\vec{q} = (1,0.2,3,1.5)$; $t \in [0,2\pi]$. On the right: $\vec{a} = (0,0.1,-0.5)$; $\vec{c} = (10^{-3},10^{-3},2 * 10^{-3},0)$; $\vec{q} = (-0.1,-0.2,0,-0.5)$; $t \in [0,800]$. In green $\tilde{\Omega}^0$-expression, in blue Ω^0-expression, in blue Heisenberg-expression. The colours are indistinguishable as the three curves always overlap. Results are correct.

observable, $\mathcal{O} = \tilde{\Omega}^0$. Figure 4.2 shows the results obtained by calculating $\langle\tilde{\Omega}^0\rangle_t$ and $\langle\overline{\Omega}^0\rangle_t$. We realize that once the Hermitian dissipation operator was defined we could also calculate its expectation value with the first expression (2.10), without deriving a second one. Moreover, comparing these results with the $\langle\Omega^0\rangle_t$ calculation, we obtain the following confirmation:

$$\Re[\langle\Omega^0\rangle_t] = \langle\tilde{\Omega}^0\rangle_t \in \mathbb{R};\ -i\Im[\langle\Omega^0\rangle_t] = \langle\overline{\Omega}^0\rangle_t \in \mathbb{C}, \tag{4.15}$$

and, by construction, $\langle\overline{\Omega}^0\rangle_t$ is always a pure imaginary number.

It is natural to ask what difference there is between equation (2.10) and (4.6). Which of these two is the best form? First, we underline that it is a good thing that they give the exact same results for $\langle\mathcal{O}\rangle_t$, as they are confirmed results in the Heisenberg picture. However, it is not at all clear which of the two is better. Considering equivalence (4.15), the first form (2.10) seems better. It is much more similar to the classical expression (1.23). Furthermore, if it were possible to associate a physical meaning only with $\tilde{\Omega}$ or $\overline{\Omega}$, it would be sufficient to calculate the latter as real imaginary part of Ω. Anyway, the second form (4.6) is not to be thrown away at all. It can become very interesting if one wish to use the symmetric correlation, which is much more similar to the classical one in that $\langle A; B\rangle = \langle B; A\rangle$. Furthermore, a physical meaning could be associated, for example, not with $\overline{\Omega}$ but only with its commutator $[\overline{\Omega}, \mathcal{O}]$. Finally, this form could be more convenient for introducing non-Hamiltonian dynamics in future extensions.

It might seem to be more interesting to calculate other quantities, such as $\langle\Omega^t\rangle$, however we saw in chapter 1, that in the classical application to Kuramoto dynamics [22], the quantity $\langle\Omega^0\rangle_t$ is the one used to obtain all the information. As regards the calculation of $\langle\Omega^t\rangle_t$, we know that it is equal to 0 for the proposition 2.2.1: any instant can be considered as initial.

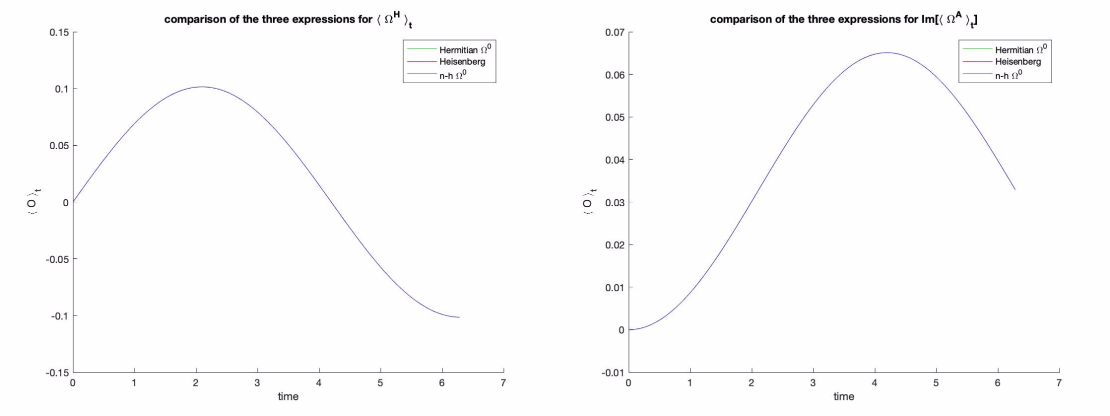

Figure 4.2: On the left: $\langle\tilde{\Omega}^0\rangle_t$ (Hermitian dissipation operator). On the right: $Im[\langle\overline{\Omega}^0\rangle_t]$ (antihermitian dissipation operator). They correspond respectively with the real and imaginary parts of $\langle\Omega^0\rangle_t$. $\vec{a} = (-0.2, -0.1, 0.4)$; $\vec{c} = (3, -0.1, 0.2, -0.3)$; $t \in [0, 2\pi]$.

With this numerical analysis we also noticed a curious property of the observable $(\Omega^0)^2$. In all tests carried out in 2D, this operator always appears in the following form

$$(\Omega^0)^2 = \begin{bmatrix} p & 0 \\ 0 & p \end{bmatrix} = p * Id, \qquad \text{with } p \in \mathbb{R}, \quad p \geq 0;$$

this is a very particular mathematical property, whose origin is not yet understandable. However, it is only a conjecture, if it were useful to exploit it, it should first be rigorously demonstrated. From this form follows that $(\Omega^0)^2$ would be a constant of motion: the identity commutes with any operator, therefore,

$$[(\Omega^0)^2, \mathcal{H}] = p[Id, \mathcal{H}] = 0 \Rightarrow \frac{d}{dt}(\Omega^0)^2 = 0.$$

Indeed, calculating its expectation value numerically, we find that

$$\langle(\Omega^0)^2\rangle_t = \langle(\Omega^0)^2\rangle_0 \quad \forall t$$

Moreover, a proportionality seems to emerge in relation to the eigenvalues of the Hamiltonian $\mathcal{H}$:

$$\langle(\Omega^0)^2\rangle_0 \propto |E_1(\mathcal{H}) - E_0(\mathcal{H})|.$$

It seems also have a proportionality with respect to non-diagonal elements in ρ_0: their presence greatly increases the value of $\langle(\Omega^0)^2\rangle_0$. We could state that

$$\langle(\Omega^0)^2\rangle_0 \propto \text{"Some kind of disorder between } \rho_0 \text{ and } \mathcal{H}\text{"}.$$

This result becomes less surprising if we remember proposition 2.2.2: the quantity $\langle(\Omega^0)^2\rangle_0$ coincides with the initial derivative of the dissipation operator expectation value. Consistently with what has been demonstrated, even in tests it is always positive or equal to 0. The association with disorder is linked precisely to the attempts, in classical systems, to relate Ω with forms of entropy. In conclusion, $(\Omega^0)^2$ might be an observable to analyse better.

An important observable is the Hamiltonian, whose expectation value represents the energy of the system. The two new expressions provide consistent results: we always find also numerically that the Hamiltonian is a constant of motion,

$$E = \langle\mathcal{H}\rangle_t = \langle\mathcal{H}\rangle_0. \tag{4.16}$$

By this we are not saying that the energy of the system always remains unchanged, before and after the perturbation. Let's clarify this point: the energy of the system before the perturbation is

$$E_0 = \langle\mathcal{H}_0\rangle_0$$

After the perturbation, the system is described by the new Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_{ext}$. Result (4.16) means that the energy E, after the perturbation, is a constant of motion. We can highlight this by writing

$$E_0 = \langle\mathcal{H}_0\rangle_0 \neq \langle\mathcal{H}\rangle_0 = E.$$

Furthermore, to strengthen our arguments developed in proposition 4.1.4, we have numerically calculated in many different applications (4.14) the quantity $Tr(\tilde{\Omega}^0\frac{\partial\rho_0}{\partial t})$ (which coincides with $\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0}$). In all cases this value has been shown to be positive or null,

$$\frac{d}{ds}\langle\tilde{\Omega}^0\rangle_s|_{s=0} \geq 0 \quad \text{(numerically)}.$$

In the next chapter we are going to investigate the role that dissipation operators (4.13) have in the time evolution of the density operator. This will help us understand why we were unable to derive an expression for the calculation of $\langle\mathcal{O}\rangle_t$ containing only the Hermitian dissipation operator. Furthermore, the next study will suggest possible extensions of this quantum response theory.

Chapter 5

Temporal evolution of ρ through the use of dissipation operators

In this chapter we study the role that the dissipation operators play in the time evolution of the density operator ρ_t. Firstly, we will review the derivation of the Von Neumann equation and of the solution expressed in the form with time propagators. We will present in detail all the properties of these time evolution operators. Secondly, we will analyse the solution ρ_t in the case of time dependent Hamiltonian $\mathcal{H}(t)$. To this end, we will introduce the time ordering operators. These will then be exploited to obtain the solution of the quantum Liouville equation written in a different form, through the use of the dissipation operator. Finally, we will use some of the dissipation operators, presented in (4.13), to rewrite the time propagators.

We start with a detailed review of the Von Neumann equation and time propagators in the case of constant Hamiltonian $\mathcal{H}$.

5.1 Time evolution of the density operator ρ

In quantum mechanics the density matrix evolves according to the Liouville Von-Neumann equation (1.12)

$$i\hbar\frac{\partial\rho}{\partial t} = [\mathcal{H}, \rho],$$

we are now considering the Hamiltonian constant over time. This equation is derived starting from the Schrödinger equation both for $|\psi_n\rangle$ and for $\langle\psi_n|$,

$$i\hbar\frac{\partial|\psi_n\rangle}{\partial t} = \mathcal{H}|\psi_n\rangle, \quad i\hbar\frac{\partial\langle\psi_n|}{\partial t} = -\langle\psi_n|\mathcal{H}.$$

These two expressions are then used to calculate $i\hbar\frac{\partial\rho}{\partial t}$ as follows

$$i\hbar\frac{\partial\rho}{\partial t} = i\hbar\frac{\partial}{\partial t}\left(\sum_n p_n|\psi_n\rangle\langle\psi_n|\right) = \sum_n p_n\left(i\hbar\frac{\partial}{\partial t}|\psi_n\rangle\langle\psi_n| + |\psi_n\rangle i\hbar\frac{\partial}{\partial t}\langle\psi_n|\right) =$$
$$\sum_n p_n\Big(\mathcal{H}|\psi_n\rangle\langle\psi_n| - |\psi_n\rangle\langle\psi_n|\mathcal{H}\Big) = \mathcal{H}\rho - \rho\mathcal{H} = [\mathcal{H}, \rho].$$

The procedure leads precisely to the Liouville-Von Neumann equation, the quantum analogue of the classical Liouville equation (1.2), which expresses the conservation of the probability density in phase space.

To derive time propagators (1.14), that describe the temporal evolution of a quantum system, one can reason in the following way. Assuming constant Hamiltonian $\mathcal{H}$, the wavefunction evolves in time according to the Schrödinger equation, one can define the evolution operator $U(t)$ as the operator that maps $\psi(0)$ in $\psi(t)$:

$$\psi(t) = U(t)\psi(0).$$

The equation that $U(t)$ must fulfil is

$$\begin{aligned} i\hbar\frac{\partial\psi(t)}{\partial t} = \mathcal{H}\psi(t) \Rightarrow i\hbar\frac{\partial}{\partial t}\Big(U(t)\psi(0)\Big) &= \mathcal{H}U(t)\psi(0) \\ \Rightarrow \left(i\hbar\frac{dU(t)}{dt} - \mathcal{H}U(t)\right)\psi(0) &= 0. \end{aligned} \tag{5.1}$$

The initial condition is derived from $\psi(0) = U(0)\psi(0)$ which implies $U(0) = Id$. In conclusion,

$$\frac{dU(t)}{dt} = -\frac{i}{\hbar}\mathcal{H}U(t), \quad U(0) = Id;$$

the solution of this problem is

$$U(t) = e^{-\frac{i}{\hbar}\mathcal{H}t}.$$

This can be shown also by substitution, making the definition of the exponential operator explicit,

$$\frac{dU(t)}{dt} = 0 - \frac{i}{\hbar}\mathcal{H} + \Big(-\frac{i}{\hbar}\Big)^2\mathcal{H}^2 t + \frac{1}{2}\Big(-\frac{i}{\hbar}\Big)^3\mathcal{H}^3 t^2 + ... =$$
$$-\frac{i}{\hbar}\mathcal{H}\left(Id + (-\frac{i}{\hbar})\mathcal{H}t + \frac{1}{2}\Big(-\frac{i}{\hbar}\Big)^2\mathcal{H}^2 t^2 + ...\right) = -\frac{i}{\hbar}\mathcal{H}U(t).$$

In the same way one can find

$$U^{\dagger}(t) = e^{+\frac{i}{\hbar}\mathcal{H}t},$$

in perfect coherence with the adjoint operation. As already mentioned in the introduction, these operators are used to evolve both the density matrix in the Schrödinger picture and the observables in the Heisenberg picture.

It is interesting, for our purposes, to better analyse the properties of time propagators. The time propagator is a one-parameter unitary group [5], this means that it fulfils the following four properties:

1. $U(t)$ is unitary $\forall t \in \mathbb{R}$:

$$U(t)U^{\dagger}(t) = U^{\dagger}(t)U(t) = Id.$$

2. $U(t)$ satisfy the group property:

$$U(t+s) = U(t)U(s), \ \forall t \in \mathbb{R}.$$

3. At the initial instant $t = 0$ coincides with the identity operator

$$U(0) = Id.$$

4. It satisfies the following strong continuity property:

$$\langle v|\Big(U(t) - Id\Big)|v\rangle \to 0 \quad if \ t \to 0.$$

These properties are essential for evolving correctly the density operator ρ over time while preserving its mathematical meaning of probability density. The first property can be rewritten to highlight that the inverse of the time propagator coincides with its adjoint,

$$U^{-1}(t) = U^{\dagger}(t), \tag{5.2}$$

this is precisely the definition of unitary matrix (operator). Unitary matrices represent bijections that preserve the hermitian product, property necessary to keep the norm of the wave function $|\psi\rangle$ constant over time and equal to 1, i.e. $Tr(\rho) = 1$, and thus to preserve the probabilistic interpretation. Let's take an arbitrary operator A, we want to study the necessary properties that the operator A must satisfy so that e^A is a unitary operator. The adjoint of the exponential operator $(e^A)^{\dagger}$ is equal to the exponential of the adjoint operator $A^{\dagger}$, $e^{A^{\dagger}}$, indeed,

$$(e^A)^{\dagger} = \left(\sum_{n=0}^{\infty} \frac{1}{n!}A^n\right)^{\dagger} = \sum_{n=0}^{\infty} \frac{1}{n!}(A^{\dagger})^n = e^{A^{\dagger}}.$$

Operators A and $-A$ commute, $[A,-A]=0$, so one has that

$$e^{A}e^{-A}=e^{-A}e^{A}=e^{A-A}=Id \Rightarrow \left(e^{A}\right)^{-1}=e^{-A}$$

By definition e^{A} is unitary if it respects the property (5.2), then

$$(e^{A})^{-1}=(e^{A})^{\dagger} \iff e^{-A}=e^{A^{\dagger}} \iff -A=A^{\dagger}. \tag{5.3}$$

In conclusion, e^{A} is a unitary operator if and only if A is an antihermitian operator. Equivalently, highlighting the imaginary unit i and remembering that $i^{\dagger}=-i$, one finds that e^{iS} is a unitary operator if and only if the operator S is Hermitian.

At any time t the solution of the Liouville equation can be seen as a unitary transformation in the phase space of the initial density operator ρ_0, in fact it is written as

$$\rho_t=e^{-\frac{it}{\hbar}\mathcal{H}}\rho_0 e^{\frac{it}{\hbar}\mathcal{H}}=U(t)\rho_0 U^{\dagger}(t). \tag{5.4}$$

The dynamics of type $\mathcal{H}=\mathcal{H}_0+\lambda\mathcal{H}_{ext}$ studied so far, can be considered constant over time since the perturbation $\mathcal{H}_{ext}$ is assumed to be activated at the initial instant and kept constant over time.

We want also analyse the case of time-dependent Hamiltonian $\mathcal{H}(t)$, both for future extensions and to analyse how to calculate the integral over time of a time-dependent operator. This is what we will present initially in the next section. Then, we will exploit the time ordering operators to write the Von Neumann solution via the dissipation operator. Furthermore, we will derive the time evolution of Ω^{t} in the case of constant Hamiltonian $\mathcal{H}$.

5.2 Time ordering and dissipation operator for the Von Neumann solution

Considering a time dependent Hamiltonian, Liouville's equation becomes $i\hbar\partial_t\rho_t=[\mathcal{H}(t),\rho_t]$. The new time evolution operator $\mathcal{U}(t)$ that determines the solution can be obtained by reasoning as previously in (5.1). In presenting this derivation we refer to the text [27]. One finds

$$\frac{d\mathcal{U}(t)}{dt}=-\frac{i}{\hbar}\mathcal{H}(t)\mathcal{U}(t);\;\; \mathcal{U}(0)=Id.$$

$\mathcal{H}(t)$ is now a time-dependent operator and therefore, in general, it does not commute valued in different time instants of the integration domain, $[\mathcal{H}(t_1),\mathcal{H}(t_2)]\neq$

0. The solution can be obtained by iteration in a complicated form:

$$\mathcal{U}(t) = \mathbf{1} - \frac{i}{\hbar}\int_0^{t_1} dt_1 \mathcal{H}(t_1) + \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{H}(t_1)\mathcal{H}(t_2) + \\ + \left(-\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_3} dt_3 \mathcal{H}(t_1)\mathcal{H}(t_2)\mathcal{H}(t_3) + ...$$

It is proven that this series of nested time integrals, called Neumann series, can be rewritten using the time ordering operator T_L as

$$\mathcal{U}(t) = T_L\left[exp\left(-\frac{i}{\hbar}\int_0^t \mathcal{H}(s)ds\right)\right] \quad for \quad t > 0 \tag{5.5}$$

Operator T_L orders the operators according to their times from later times to earlier times:

$$T_L\Big(A(t_1)B(t_2)...Z(t_n)\Big) = B(t_2)D(t_4)A(t_1)...Z(t_n) \quad if \ t_2 > t_4 > t_1 > t_n$$

The operator that does exactly the opposite operation is the anti-time ordering operator T_R:

$$T_R\Big(A(t_1)B(t_2)...Z(t_n)\Big) = B(t_2)A(t_1)...Z(t_n) \quad if \ t_2 < t_1 < t_n$$

The names 'time ordering' and 'anti-time ordering' seem counterintuitive thinking about the time axis, however it is enough to remember that operators at previous moments act first on a $|\psi\rangle$ vector, $C(2)B(1)A(0)|\psi\rangle$, it is therefore clear that T_L gives us the natural order and T_R the inverse one.
The explicit form of operator (5.5) is represented by the Dyson series,

$$\mathcal{U}(t) = \mathbf{1} - \frac{i}{\hbar}\int_0^{t_1} dt_1 H(t_1) + \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2 T_L\Big[H(t_1)H(t_2)\Big] + \\ + \frac{1}{6}\left(-\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 T_L\Big[H(t_1)H(t_2)H(t_3)\Big] + ...$$

which is proven to be equivalent to Neumann series.
We also highlight that in the previous sections we had already calculated integrals of operators. However, the time ordering problem did not exist as the trace operator was always involved, the result of the integral was therefore always a scalar number and never an operator.
Instead, the adjoint of (5.5) is

$$\mathcal{U}^\dagger(t) = T_R\left[exp\left(\frac{i}{\hbar}\int_0^t \mathcal{H}(s)ds\right)\right] \quad for \quad t > 0$$

In the following we will denote the exponential constructed with time ordering operator T_L and anti-time ordering operator T_R respectively with $e_L^{I(t)}$ and $e_R^{I(t)}$. The solution of the quantum Liouville equation in this case can be expressed as

$$\rho_t = \mathcal{U}(t)\rho_0\mathcal{U}^\dagger(t) \tag{5.6}$$

and the new time propagators still form a one-parameter unitary group.

In the case of constant Hamiltonian, time ordering operators are useless because $\mathcal{H}(t) = \mathcal{H}(s) = \mathcal{H} \ \ \forall t, s \in \mathbb{R}$ and so operators at different times always commute, $[\mathcal{H}(t), \mathcal{H}(s)] = 0$. Then, the Liouville solution (5.6) returns to the usual form

$$\rho_t = e^{-\frac{i}{\hbar}\mathcal{H}t}\rho_0 e^{\frac{i}{\hbar}\mathcal{H}t}.$$

It is possible to obtain the solution in a different form using the dissipation operator. Let's see this for the non-Hermitian dissipation operator. Ω^0 expresses the variation over time of the density operator at the initial instant $t = 0$,

$$\frac{\partial\rho_0}{\partial t} = \rho_0\Omega^0,$$

this equation does not give us any information about the density operator ρ_t at an arbitrary time $t \in \mathbb{R}$. However, we can consider any time t^* as the initial instant of the dynamics, and therefore define

$$\Omega^{t^*} = \frac{1}{i\hbar}\rho_{t^*}^{-1}[\mathcal{H}, \rho_{t^*}] \tag{5.7}$$

Once this consideration has been highlighted, it is clear that we can write

$$\begin{gathered}\frac{\partial\rho_t}{\partial t} = \rho_t\Omega^t \\ \rho(0) = \rho_0.\end{gathered} \tag{5.8}$$

Now, it is necessary to note that, in general, working with operators, two types of equations exist:

$$(i)\ \frac{dV(t)}{dt} = A(t)V(t); \qquad (ii)\ \frac{dV(t)}{dt} = V(t)A(t). \tag{5.9}$$

The initial condition is always $V(0) = V_0$. It is demonstrated that for $t > 0$ the time ordering operator solves equation (i) while the anti-time ordering operator solves equation (ii) [27]:

$$(i)\ V(t) = T_L\Bigg[exp\bigg(\int_0^t A(s)ds\bigg)\Bigg]V_0; \quad (ii)\ V(t) = V_0T_R\Bigg[exp\bigg(\int_0^t A(s)ds\bigg)\Bigg]. \tag{5.10}$$

The time ordering operators are reversed for $t < 0$.
Equation (5.8) is expressed in the form (ii), therefore the solution is

$$\rho_t = \rho_0 T_R \left[e^{\int_0^t \Omega^s ds} \right] \tag{5.11}$$

This is formally correct but it is not yet clear how Ω evolves over time. The definition of Ω^s, which is (5.7), contains ρ_s and therefore it is appropriate to find an alternative way to express Ω^s and be able to calculate the integral without using explicitly ρ_s. The ordering operator in (5.11) is necessary to clearly define the solution in this form through the use of the exponential, however, if the Hamiltonian is constant over time, it is therefore possible to use time propagators (1.14) (defined without any time ordering operator) to make Ω^s evolve over time. We thus find an interesting fact.

Proposition 5.2.1. *If the Hamiltonian $\mathcal{H}$ is time independent, then the dissipation operator defined at time s, Ω^s, coincides with the initial dissipation operator Ω^0 evolved backward in time,*

$$\Omega^s = U(s)\Omega^0 U^\dagger(s). \tag{5.12}$$

Proof. By definition we have

$$\Omega^s = \frac{1}{i\hbar}\rho_s^{-1}[\mathcal{H}, \rho_s].$$

We can express ρ_t using time propagators,

$$\Omega^s = \frac{1}{i\hbar}(U(s)\rho_0 U^\dagger(s))^{-1}[\mathcal{H}, U(s)\rho_0 U^\dagger(s)].$$

Let's remember now that for three arbitrary invertible operators A, B, C, we have $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$, applying this rule we can write

$$\Omega^s = \frac{1}{i\hbar}(U^\dagger(s))^{-1}\rho_0^{-1}U^{-1}(s)[\mathcal{H}, U(s)\rho_0 U^\dagger(s)].$$

Evolution operator are unitary operators and so, by applying equation (5.2), the latter becomes

$$\Omega^s = \frac{1}{i\hbar}U(s)\rho_0^{-1}U^\dagger(s)\Big(\mathcal{H}U(s)\rho_0 U^\dagger(s) - U(s)\rho_0 U^\dagger(s)\mathcal{H}\Big) =$$
$$\frac{1}{i\hbar}U(s)\rho_0^{-1}U^\dagger(s)\mathcal{H}U(s)\rho_0 U^\dagger(s) - \frac{1}{i\hbar}U(s)\rho_0^{-1}U^\dagger(s)U(s)\rho_0 U^\dagger(s)\mathcal{H};$$

the second term can be easily simplified by noting that

$$U(s)\rho_0^{-1}U^\dagger(s)U(s)\rho_0 U^\dagger(s) = Id.$$

Moreover, the evolution operators and the Hamiltonian commute,

$$U^\dagger(s)\mathcal{H}U(s) = \mathcal{H}U^\dagger(s)U(s) = \mathcal{H},$$

thus we can write

$$\begin{aligned}\Omega^s = \frac{1}{i\hbar}U(s)\rho_0^{-1}\mathcal{H}\rho_0 U^\dagger(s) - \frac{1}{i\hbar}U(s)U^\dagger(s)\mathcal{H}U(s)U^\dagger(s) =\\ \frac{1}{i\hbar}U(s)\Big(\rho_0^{-1}\mathcal{H}\rho_0 - U^\dagger(s)\mathcal{H}U(s)\Big)U^\dagger(s) =\\ \frac{1}{i\hbar}U(s)\Big(\rho_0^{-1}\mathcal{H}\rho_0 - \mathcal{H}\Big)U^\dagger(s) =\\ U(s)\Big(\frac{1}{i\hbar}\rho_0^{-1}[\mathcal{H},\rho_0]\Big)U^\dagger(s) = U(s)\Omega^0 U^\dagger(s).\end{aligned}$$

□

It is important to underline that the dissipation operator does not evolve over time like any observable in the Heisenberg representation, $U^\dagger(t)\mathcal{O}U(t)$. It instead evolves back in time, as a density operator, $\Omega^t = U(t)\Omega^0 U^\dagger(t)$. This feature could complicate the association of Ω^0 with a physical observable. It is a counterintuitive fact which is worth exploring further. This type of inverse-time evolution is not due to the order of the operators in the definition. For example, trying to redefine the dissipation operator as

$$\Omega^0_{new} = \frac{1}{i\hbar}\rho_0^{-1}[\rho_0,\mathcal{H}] \quad \text{or as} \quad \Omega^0_{new} = \frac{1}{i\hbar}[\mathcal{H},\rho_0]\rho_0^{-1},$$

(or in any other form obtained by exchanging the order of $\mathcal{H},\ \rho_0$ and ρ_0^{-1}) the dissipation operator would still evolve in the same way, in reversed time as in proposition 5.2.1. The true foundation of this type of evolution lies in the presence of the operators involved, $\mathcal{H}$ and ρ. The Hamiltonian operator $\mathcal{H}$, in the simple case we are examining for now, commutes with time propagators:

$$U(t) = e^{-\frac{i}{\hbar}\mathcal{H}t} \Rightarrow [\mathcal{H},U(t)] = [\mathcal{H},U^\dagger(t)] = 0 \ \ \forall t \in \mathbb{R}_+$$

while ρ and ρ^{-1} evolves at reversed times. Consequently, a dissipation operator defined in our way evolves in accordance with ρ_t, at reverse times. If we necessarily wanted a dissipation operator that evolves like any physical observable, then we would have to completely change the definition, avoiding the use of ρ.

This result generates ambiguity in the calculation of the expectation value of Ω: $\langle\Omega^0\rangle_t$ and $\langle\Omega^t\rangle_0$ do not coincide. However, proposition 5.2.1 may not turn out to be bad; indeed, it preserves the equivalence between Heisenberg and Schrödinger pictures for all the other 'usual' observables. In the derivation of expression (2.10), we found

$$\frac{d}{ds}\langle\mathcal{O}\rangle_s = Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}), \tag{5.13}$$

which is clearly a representation in the Heisenberg picture since we make the observable evolve over time. However, we could have remained in the Schrödinger picture by writing

$$\frac{d}{ds}\langle\mathcal{O}\rangle_s = Tr(\mathcal{O}\frac{\partial\rho_s}{\partial s}) \tag{5.14}$$

The two are equivalent thanks to proposition 5.2.1:

$$\Big(\frac{d}{ds}\langle\mathcal{O}\rangle_s\Big)^S = Tr(\mathcal{O}\frac{\partial\rho_s}{\partial s}) = Tr(\mathcal{O}\rho_s\Omega^s) = Tr(\mathcal{O}U(s)\rho_0U^\dagger(s)U(s)\Omega^0U^\dagger(s)) =$$
$$Tr(U^\dagger(s)\mathcal{O}U(s)\rho_0\Omega^0) = Tr(\mathcal{O}_s\rho_0\Omega^0) = Tr(\mathcal{O}_s\frac{\partial\rho_0}{\partial t}) = \Big(\frac{d}{ds}\langle\mathcal{O}\rangle_s\Big)^H.$$

If Ω^0 evolved as an observable we would lose this equivalence, which is fundamental in quantum mechanics, the only way to recover it would be to express $\frac{\partial\rho_t}{\partial t}$ in a completely different way from $\rho_t\Omega^t$. Moreover, proposition 5.2.1 guarantees an excellent result of consistency with proposition 2.2.1:

$$\langle\Omega^t\rangle_t = Tr\Big(U(t)\Omega^0U^\dagger(t)U(t)\rho_0U^\dagger(t)\Big) = \langle\Omega^0\rangle_0 = 0.$$

Every moment can be considered the initial one. If proposition 5.2.1 were not valid then this property of zero-mean would be lost, resulting in a serious contradiction.

Thanks to proposition 5.2.1, the solution can be expressed in the form (5.11). This solution was correct already previously but only formally because we did not know the dynamics of Ω^s and it may therefore have seemed of dubious validity, useless or excessively abstract. Now, instead, it is clear that the Liouville solution can be written as

$$\rho_t = \rho_0 e_R^{\Omega^0_{0,t}}, \quad \Omega^0_{0,t} = \int_0^t U(s)\Omega^0U^\dagger(s)ds. \tag{5.15}$$

To strengthen our argument and the validity of solution (5.15) we can show by substitution that $\rho_t = \rho_0 e_R^{\Omega^0_{0,t}}$ satisfies the Liouville equation. To do this, we first use proposition 5.2.1 to demonstrate that the Liouville equation written with the dissipation operator is truly equivalent to the usual Von Neumann form. Indeed, we have that

$$\begin{gathered}\frac{\partial\rho_t}{\partial t} = \rho_t\Omega^t = U(t)\rho_0U^\dagger(t)U(t)\Omega^0U^\dagger(t) = U(t)\rho_0\Omega^0U^\dagger(t) = \\ \frac{1}{i\hbar}U(t)[\mathcal{H},\rho_0]U^\dagger(t) = \frac{1}{i\hbar}\Big(HU(t)\rho_0U^\dagger(t) - U(t)\rho_0U^\dagger(t)\mathcal{H}\Big) = \frac{1}{i\hbar}[\mathcal{H},\rho_t].\end{gathered} \tag{5.16}$$

The equivalence between these two equations was actually already evident from the definition of Ω^t; with these steps we also showed it differently, finding further confirmation of the validity of proposition 5.2.1. Therefore, it is now clear that replacing the expression (5.15) in the Von Neumann problem is equivalent to replacing it in the equation (5.8). Let's proceed by substitution,

$$\frac{\partial \rho_t}{\partial t} = \frac{\partial}{\partial t}(\rho_0 e_R^{\Omega^0_{0,t}}) = \rho_0 \frac{\partial}{\partial t}(e_R^{\Omega^0_{0,t}}) = \rho_0 e_R^{\Omega^0_{0,t}} \frac{\partial}{\partial t}(\Omega^0_{0,t}).$$

Now we can use the first fundamental theorem of integral calculus,

$$\Omega^0_{0,t} = \int_0^t U(s)\Omega^0 U^\dagger(s) ds = \int_0^t \Omega^s ds \Rightarrow \frac{\partial}{\partial t}(\Omega^0_{0,t}) = \Omega^t.$$

Then we have

$$\frac{\partial \rho_t}{\partial t} = \rho_0 e_R^{\Omega^0_{0,t}} \Omega^t = \rho_t \Omega^t = \frac{1}{i\hbar}[\mathcal{H}, \rho_t],$$

where in the last equality we have used equation (5.16). Furthermore, the initial condition is satisfied,

$$\rho(0) = \rho_0 e_R^{\Omega^0_{0,0}} = \rho_0 e^0 = \rho_0$$

We may not have been formal enough, the property $\frac{\partial}{\partial t} e^{A(t)} = e^{A(t)} \frac{\partial}{\partial t} A(t)$ used previously has ambiguous validity due to the presence of time ordering T_R. However, even without showing it by substitution, it is proven that (5.15) is a solution of equation (5.8), which is perfectly equivalent to the Von Neumann equation.

In conclusion, expression (5.15) is a solution to the Von Neumann-Liouville problem. With this sentence we are not claiming that Liouville's problem always admits more than one valid solution. We have instead shown that the solution of the Von Neumann equation, ρ_t, can be expressed in different forms, not only through the well-known form $U(t)\rho_0 U^\dagger(t)$, but also in other ways, for example as in expression (5.15). The uniqueness of the Liouville problem's solution depends on the Hamiltonian operator $\mathcal{H}$. This uniqueness can therefore only be studied after having defined the Hamiltonian operator. If $\mathcal{H}$ is sufficiently regular then the solution is unique and consequently expression (5.15) is equivalent to the usual solution (5.4), they are just two different ways of writing the same thing; similarly, every different form that we will find below will in reality be perfectly equivalent to these two. If instead Liouville's problem could admit more than one solution then expression (5.4) and expression (5.15) could be a priori equivalent as well as different.

The same reasoning can be carried out for the adjoint of the non-Hermitian dissipation operator, $(\Omega^0)^\dagger$, the only difference is in the order in which the operators are multiplied. In this case we actually have

$$\frac{\partial \rho_t}{\partial t} = (\Omega^t)^\dagger \rho_t$$

This equation is of type (i) in (5.9). Therefore, the solution is

$$\rho_t = e_L^{\Omega^{0\dagger}_{0,t}} \rho_0, \quad \Omega^{0\dagger}_{0,t} = \int_0^t U(s)(\Omega^0)^\dagger U^\dagger(s) ds. \tag{5.17}$$

In the case of constant Hamiltonians, it is not convenient to express ρ in form (5.15) or (5.17). They involve time ordering operators, which are very complicated in practical uses. The usual form (5.4) is far more manageable. We thus highlight that time propagators $U(t)$ and $U^\dagger(t)$ are in no way replaced by the operators $e_R^{\Omega^0_{s,t}}$ and $e_L^{\Omega^{0\dagger}_{s,t}}$. $U(t)$ and $U^\dagger(t)$ remain essential for evolving the observables and density operators. Furthermore, they are used to evolve the dissipation operator Ω^0 over time, and so they are also fundamental to use this new formalism in Hamiltonian dynamics.

However, the 2 new forms (5.15) and (5.17) indicate that the dissipation operator has a precise role in the temporal evolution of ρ_t. From these results we begin to understand why it was not possible to insert only the Hermitian dissipation operator in the expression (4.6). The antihermitian part is as important as the Hermitian in the temporal evolution of a quantum system. Neither can be easily cut off. However, we do not completely exclude the possibility that, with more advanced mathematical techniques or by defining the dissipation operator differently, one can arrive at a formula similar to the classical (1.23), involving only a Hermitian dissipation operator.

In view of possible extensions of this new formalism, it could be very interesting to exploit the dissipation operators to construct some temporal propagation operator $\hat{\mathcal{U}}(t)$, which allows ρ to evolve in the usual form, $\rho_t = \hat{\mathcal{U}}(t)\rho_0\hat{\mathcal{U}}^\dagger(t)$. To get this form, we tried to somehow combine the two previous solutions (5.15) and (5.17), but without obtaining good results. A different kind of approach is developed in the next section.

5.3 Use of dissipation operators in time propagators

We wish to use dissipation operators to evolve ρ_t in a form more similar to that of time propagators (5.4). we would like to get something similar to

$$\rho_t = e_L^{-i\hat{\Omega}_{0,t}} \rho_0 e_R^{i\hat{\Omega}_{0,t}} = \hat{\mathcal{U}}(t)\rho_0\hat{\mathcal{U}}^\dagger(t). \tag{5.18}$$

This result would be good for the new formalism we are building, it would allow us to express the evolution of probability over time using a dissipation operator in a form completely similar to the one commonly used in quantum mechanics. There are problems where time propagators cannot be defined, for example for open, non-unitary dynamics. If it were possible to extend the dissipation operator to these dynamics, then, thanks to form (5.18), we could also directly obtain the corresponding extension of time propagator.

The dissipation operator formalism aims to describe more complex dynamics. However, if well derived, it must also be valid for constant Hamiltonian dynamics. It must therefore be unitary in the Hamiltonian case. We recall that if we want a unitary operator $\hat{\mathcal{U}}(t)$ in eq. (5.18), then $\hat{\Omega}$ must necessarily be Hermitian.

For our purpose, Stone's theorem [28] is of fundamental importance.

Theorem 5.3.1. *Consider a constant-Hamiltonian dynamics. Let $U(t)$ be a unitary group of the Hilbert space $\Big(V, \langle\ \cdot\ |\ \cdot\ \rangle\Big)$. Then, there exists a unique hermitian operator $\mathcal{H}$ such that:*

$$U(t) = e^{\frac{i}{\hbar}\mathcal{H}t}.$$

For constant Hamiltonians, therefore, $U(t)$ and $\hat{\mathcal{U}}(t)$ must necessarily coincide, due to consistency. For time-dependent Hamiltonians $\mathcal{H}(t)$ we have already shown that the time propagators are defined as

$$\begin{aligned} \mathcal{U}^\dagger(t) &= T_R\Bigg[exp\Bigg(+\frac{i}{\hbar}\int_0^t \mathcal{H}(s)ds\Bigg)\Bigg] \\ \mathcal{U}(t) &= T_L\Bigg[exp\Bigg(-\frac{i}{\hbar}\int_0^t \mathcal{H}(s)ds\Bigg)\Bigg] \\ \rho_t &= \mathcal{U}(t)\rho_0\mathcal{U}^\dagger(t). \end{aligned} \tag{5.19}$$

In the case in which the dynamics is described by a Hamiltonian constant over time these operators become the usual time propagators (1.14), in perfect agreement with Stones' Theorem. Expressing $\mathcal{H}(t)$ as a function of the dissipation operators defined so far is a good way to derive form (5.18) while remaining faithful to what is already known and to Stone's theorem. Following this procedure allows us to state the following proposition.

Proposition 5.3.2. *The density operator ρ_t at time $t \in \mathbb{R}$ can be expressed in the form*

$$\rho_t = e_L^{-i\hat{\Omega}_{0,t}}\rho_0 e_R^{+i\hat{\Omega}_{0,t}},$$

where $\hat{\Omega}_{0,t}$ is the integral between instants 0 and t of the new Hermitian operator $\hat{\Omega}^s$, which is defined as

$$\hat{\Omega}^s \equiv \frac{\tilde{\omega}^s}{\hbar} - i\overline{\Omega^s}. \tag{5.20}$$

Proof. Observing the compact forms (4.13), it is clear that we can express the Hamiltonian operator $\mathcal{H}(s)$ using the two Hermitian operators $\tilde{\omega}^s$ and $i\overline{\Omega^s}$,

$$\mathcal{H}(s) = \tilde{\omega}^s - \hbar i\overline{\Omega^s}.$$

Replacing the latter in (5.19) we find

$$\mathcal{U}(t) = T_L\left[exp\left(- i\int_0^t \frac{\tilde{\omega}^s}{\hbar} - i\overline{\Omega^s}ds\right)\right]$$

We therefore define the dissipative evolution operator as

$$\hat{\Omega}^s \equiv \frac{\tilde{\omega}^s}{\hbar} - i\overline{\Omega^s}.$$

It is consistently Hermitian since

$$\left(\hat{\Omega}^s\right)^\dagger = \frac{1}{\hbar}\left(\tilde{\omega}^s\right)^\dagger - \left(i\overline{\Omega^s}\right)^\dagger = \frac{1}{\hbar}\tilde{\omega}^s + i(\overline{\Omega^s})^\dagger = \frac{\tilde{\omega}^s}{\hbar} - i\overline{\Omega^s} = \hat{\Omega}^s.$$

Moreover, explicitly calculating the adjoint, we find

$$\left(\hat{\mathcal{U}}(t)\right)^\dagger = \left(e_L^{-i\hat{\Omega}_{0,t}}\right)^\dagger = e_R^{(-i\hat{\Omega}_{0,t})^\dagger} = e_R^{+i\hat{\Omega}_{0,t}}.$$

In conclusion, we can write

$$\rho_t = e_L^{-i\hat{\Omega}_{0,t}}\rho_0 e_R^{+i\hat{\Omega}_{0,t}}.$$

□

We can therefore define

$$\hat{\mathcal{U}}(t) \equiv e_L^{-i\hat{\Omega}_{0,t}};\;\; \hat{\mathcal{U}}^\dagger(t) = e_R^{+i\hat{\Omega}_{0,t}} = \hat{\mathcal{U}}^{-1}(t). \tag{5.21}$$

With this method the 'new' evolution operator $\hat{\mathcal{U}}(t)$ is actually exactly coincident, by construction, with the time propagator (5.5): $\hat{\mathcal{U}}(t) = \mathcal{U}(t)$. We simply rewrote $\mathcal{H}(s)$ as $\mathcal{H}(s) = \tilde{\omega}^s - i\hbar\overline{\Omega^s}$. In this way, we are already sure that $\hat{U}(t)$ forms a one-parameter unitary group. The unitary trace property is certainly preserved over time. The definition of $\hat{\mathcal{U}}(t)$ is consistent with Stone's theorem by construction. These are all necessary features for any new, well-defined time evolution operator

$\tilde{U}(t)$. However, it is clear that $\hat{\mathcal{U}}(t)$, defined as in (5.21), does not seem to really bring anything new. The advantage is that, if one could extend the definition of the dissipation operator Ω^0 to general dissipative (non-Hamiltonian) dynamics, then $\hat{\mathcal{U}}(t)$ could remain a time propagator.

It is interesting to understand if it is possible to find a valid evolution operator that is truly different from time propagator (5.5). However, this does not seem possible. We consider a time-dependent Hamiltonian dynamics $\mathcal{H}(s)$ and suppose there exists an evolution operator in the form

$$\tilde{\mathcal{U}}(t) = T_L\biggl[exp\biggl(\int_0^t A(s)ds\biggr)\biggr], \quad \text{with } A(s) \neq -\frac{i}{\hbar}\mathcal{H}(s). \tag{5.22}$$

We suppose further that also $\tilde{\mathcal{U}}(t)$ forms a one parameter unitary group.
Let's consider the particular case of constant Hamiltonian, $\mathcal{H}(t) = \mathcal{H}\ \forall t$, then, by Stone's theorem, one must necessarily have

$$T_L\biggl[exp\biggl(\int_0^t A(s)ds\biggr)\biggr] = T_L\biggl[exp\biggl(-\int_0^t \frac{i}{\hbar}\mathcal{H}ds\biggr)\biggr] = e^{-\frac{i}{\hbar}\mathcal{H}t}.$$

Furthermore, this must be valid for any instant in time, in conclusion we must have

$$T_L\biggl[exp\biggl(-\int_0^t \frac{i}{\hbar}\mathcal{H}(s)ds\biggr)\biggr] = T_L\biggl[exp\biggl(\int_0^t A(s)ds\biggr)\biggr], \quad \forall t \in \mathbb{R}$$

and then

$$\int_0^t -\frac{i}{\hbar}\mathcal{H}(s) - A(s)ds = 0 \quad \forall t \in \mathbb{R}.$$

But this is not possible having assumed $A(s) \neq -\frac{i}{\hbar}\mathcal{H}(s)$. We therefore conclude that the only way to construct a good time evolution operator is precisely the one used in proposition 5.3.2, i.e. to express $\mathcal{H}(s)$ as a function of some dissipation operators.

It is important to highlight why we chose the form (5.20) and not other different ones. Looking at (4.13), we could for example have chosen to express $\mathcal{H}$ as

$$\mathcal{H}(s) = \omega^s - i\hbar\Omega^s,$$

the corresponding operator inside the integral would have been $\hat{\Omega}_b^s = \frac{\omega^s}{\hbar} - i\Omega^s$. This last operator is certainly also Hermitian by construction, since the operator $\mathcal{H}(s)$ is Hermitian. However, if we calculate the adjoint of $\hat{\Omega}_b^s$, without exploiting the equivalence with the operator $\frac{i}{\hbar}\mathcal{H}(s)$, we obtain

$$\bigl(\hat{\Omega}_b^s\bigr)^\dagger = \Bigl(\frac{\omega^s}{\hbar} - i\Omega^s\Bigr)^\dagger = \frac{1}{\hbar}(\omega^s)^\dagger + i(\Omega^s)^\dagger.$$

Operators ω^s and Ω^s are neither Hermitian nor antihermitian. Therefore, $\hat{\Omega}^s_b$ is Hermitian for $\mathcal{H}(s)$-dynamics but may no longer be so for generalizations to non-Hamiltonian dynamics. Instead, operators $i\overline{\Omega}^s$ and $\frac{1}{\hbar}\tilde{\omega}^s$ are hermitians by definition. Therefore, with the choice (5.20), operator $\hat{\Omega}^s$ could remain Hermitian for some generalizations to non-Hamiltonian dynamics and so the time evolution operator $\hat{\mathcal{U}}(t)$ would remain unitary when possible.

The real advantage of being able to write the solution to the Liouville problem as $\rho_t = \hat{\mathcal{U}}(t)\rho_0\hat{\mathcal{U}}^\dagger(t)$ is that this form allows us to switch, also using this new formalism, from the Heisenberg representation to the Schrödinger representation and vice versa simply by using the cyclic property of the trace

$$\Big(\langle\mathcal{O}\rangle_t\Big)^S = Tr\Big(\mathcal{O}e_L^{-i\hat{\Omega}_{0,t}}\rho_0 e_R^{i\hat{\Omega}_{0,t}}\Big) = Tr\Big(e_R^{i\hat{\Omega}_{0,t}}\mathcal{O}e_L^{-i\hat{\Omega}_{0,t}}\rho_0\Big) = \Big(\langle\mathcal{O}\rangle_t\Big)^H$$

In other words, to calculate the expectation values $\langle\mathcal{O}\rangle_t$ it could be possible even in very complex dissipative dynamics to evolve the observables like

$$\mathcal{O}_t \equiv e_R^{i\hat{\Omega}_{0,t}}\mathcal{O}e_L^{-i\hat{\Omega}_{0,t}}, \tag{5.23}$$

and keep the probability density operator fixed at the initial instant $t = 0$. This may not be achievable in this form, but may only be possible by means of the new expression (2.10). In the next chapter we will see that keeping the probability fixed and evolving only the observables over time can also bring advantages in quantum mechanics, as regards dissipative dynamics. We will exploit idea (5.23) to extend our expression (2.10) to the Lindblad equations.

Chapter 6

Dissipation operator in dynamics of open quantum systems

Previously we studied some qubit systems, units of information at the basis of quantum computation. Quantum computing constitutes one of the greatest scientific revolutions of the XXI century. It uses hardware and algorithms that exploit quantum mechanics to solve complex problems that classical supercomputers cannot solve or cannot solve quickly enough. Today quantum computing already finds applications in the fields of information technology, financial services and cybersecurity. We are only at the beginning, the true potential of quantum computing has yet to be discovered. However, the road towards a real revolution is still very long. The promises of quantum computation have turned out to be hard to keep, since the fragile quantum coherence, necessary for quantum computation to work, usually rapidly decays. In presenting this process, called decoherence, and the related Lindblad equations that describe it, we will refer to the first chapter of the text [11].

Decoherence is induced by the presence of reservoirs that can significantly alter the true quantum dynamics. However, the coupling between a quantum system and a structured non-equilibrium environment may prove to be an opportunity: the smallest quantum systems can also be seen as nanomachines that exchange energy and matter with their surroundings. From a thermodynamic viewpoint, such nanomachines are coupled to an environment that is out of equilibrium and might thus be able to perform useful tasks such as generating electrical current from a heat gradient. Alternatively, they could function as heating or cooling devices. The effect of non-equilibrium environments on a quantum system is a topic that deserves to be thoroughly understood.

So far we have dealt exclusively with isolated quantum systems. However, we have now said that realistic quantum systems can usually not be regarded as closed. They are not perfectly isolated from their environment (composed of thermal reservoirs, detectors, and other things). The naive approach of simply simulating the evolution of both the system and its environment is complitely impossible: the number of degrees of freedom is of the order of 10^{23}. With our limited abilities we should therefore be content with a theory that describes only a small part of our universe, conventionally called system. When we treated cases of time-dependent Hamiltonians in the previous chapter we were already considering open systems: changing the parameters of the Hamiltonian normally requires an interaction with the outside world. However, in this restricted subspace called system, the dynamics may no longer be expected to be unitary. That is, a simple time dependence of external parameters in the Hamiltonian cannot account for the observed dynamics, which the Schrödinger equation will fail to predict.

It is therefore necessary to generalize the dynamics but also to maintain the probabilistic interpretation underlying quantum mechanics. For this purpose, the Kraus map was introduced. A Kraus map is the most general evolution preserving all the nice properties of a density matrix. This map is defined as

$$\begin{aligned} \rho(t+\Delta t) &= \sum_\alpha K_\alpha(t,\Delta t)\rho(t)K_\alpha^\dagger(t,\Delta t), \\ \text{with } K_\alpha(t,\Delta t) \text{ s.t. } &\sum_\alpha K_\alpha^\dagger(t,\Delta t)K_\alpha(t,\Delta t) = \mathbf{1}. \end{aligned}$$

If we constrain ourselves to master equations that are local in time and have constant coefficients, the most general evolution that preserves trace, self-adjointness, and positivity of the density matrix ρ is given by a Lindblad form

$$\dot{\rho} = \frac{1}{i\hbar}[\mathcal{H},\rho] + \sum_{\alpha,\beta=1}^{N^2-1} \gamma_{\alpha,\beta}\Big(A_\alpha \rho A_\beta^\dagger - \frac{1}{2}\{A_\beta^\dagger A_\alpha, \rho\}\Big).$$

The commutator term accounts for the unitary evolution, whereas the remaining terms describe the dissipative part of the evolution. $\gamma_{\alpha\beta}$ is the dampening matrix and it is hermitian and positive semidfenite. $\mathcal{H}$ is the effective Hamiltonian operator. It should be noted that when derived from a microscopic model, the effective Hamiltonian need not coincide with the system Hamiltonian. This demonstrates that the interaction with a reservoir may also change the unitary part of the evolution. It can be rewritten in a simpler form by diagonalizing γ and absorbing its eigenvalues into the Lindblad operators:

$$\dot{\rho} = \frac{1}{i\hbar}[\mathcal{H},\rho] + \sum_\alpha \left(L_\alpha \rho L_\alpha^\dagger - \frac{1}{2}\{L_\alpha^\dagger L_\alpha, \rho\}\right). \tag{6.1}$$

These equations are very useful and powerful for describing decoherence and dissipation phenomena in open quantum systems. However, they have some limitations. Their validity is restricted to thermally balanced environments, where interactions are linearly dissipative. In other environments, for example in non-Markovian cases (where the environment has a memory of the past), Lindblad equations may not correctly capture the system behavior. Moreover, when many energy states are involved, calculating the solution becomes very computationally intensive. Another problem concerns the positivity of $\rho(t)$.

The preservation of the positivity of ρ for the master Lindblad equation is demonstrated by discretizing the time derivative and transforming the differential equation into an iteration equation of the form $\rho(t + \Delta t) = \mathcal{L}(t)[\rho(t)]$. For details of this proof one can look, for example, at subsection 1.5.2 of text [11]. What we are interested in highlighting here is that the limit $\Delta t \to 0$ is taken in such a way that "the violation of positivity vanishes faster than the discretization width". This demonstration is affected, already at a theoretical level, by this question of the limit. This problem is further amplified when the solution is calculated with numerical methods: numerical solutions of the Lindblad master equation (6.1) using a forward-time discretization may yield negative probabilities if the time step Δt is chosen too large. This is a problem in many applications, we certainly want to avoid working with negative probabilities but this can often be computationally prohibitive. The formalism built in this thesis seems to be a good starting point for avoiding this problem. Using the quantum exact response formula (2.10) we could in fact keep the density operator fixed in time, precisely at the initial instant where it is certainly well defined, and calculate the expectation values of the observables by evolving the corresponding operators over time. This seems like a good idea but to put it into practice we must first extend the definition of the dissipation operator to dynamics (6.1) and then find a correct way to express $\mathcal{O}_t$ in the form (5.23). Finally, if it were possible to exploit this theory based on the dissipation operator to deal with Lindblad problems, we do not exclude that this could lead to improvements to other limits of the Lindblad equations.

6.1 Extension of the dissipation operator to Lindblad equations

There are several ways to extend the definition of the dissipation operator to include in it the dissipative part of dynamics (6.1). It can be very useful to rewrite the terms in the summation:

$$L_\alpha \rho L_\alpha^\dagger - \frac{1}{2}\{L_\alpha^\dagger L_\alpha, \rho\} = L_\alpha \rho L_\alpha^\dagger - \frac{1}{2} L_\alpha^\dagger L_\alpha \rho - \frac{1}{2} \rho L_\alpha^\dagger L_\alpha.$$

Operator $L_\alpha^\dagger L_\alpha$ multiply to the right of ρ in the last term and to the left in the second, a natural intuition is to include them respectively in Ω^0 and $(\Omega^0)^\dagger$. The first term, however, cannot be included naturally in either of the two, being ρ in the middle of L_α and $L_\alpha^\dagger$. We can try to use a trick similar to the one already used in the second chapter: multiply by ρ^{-1}. Motivated by these considerations we can define an operator that will be very useful for including this part in Ω^0:

$$D_\alpha \equiv \rho^{-1} L_\alpha \rho L_\alpha^\dagger - L_\alpha^\dagger L_\alpha.$$

Definition 6.1.1. *In the case of Lindblad equations the definition of the dissipation operator can be extended by including the Lindblad operators as follows*

$$\Omega_L^0 \equiv \Omega^0 + \sum_\alpha D_\alpha^0; \tag{6.2}$$

where the superscript 0 in D_α indicates that the density matrix within its definition is the initial one, ρ_0.

Proposition 6.1.2. *The Lindblad equations* (6.1) *can be expressed in the form*

$$\frac{\partial \rho}{\partial t} = \frac{1}{2}\Big(\rho \Omega_L^t + (\Omega_L^t)^\dagger \rho\Big). \tag{6.3}$$

Proof. First of all, we calculate the addition of D_α:

$$D_\alpha^\dagger = \Big(\rho^{-1} L_\alpha \rho L_\alpha^\dagger\Big)^\dagger - \Big(L_\alpha^\dagger L_\alpha\Big)^\dagger = \Big(\rho L_\alpha^\dagger\Big)^\dagger \Big(\rho^{-1} L_\alpha\Big)^\dagger - \Big(L_\alpha\Big)^\dagger \Big(L_\alpha^\dagger\Big)^\dagger =$$
$$\Big(L_\alpha^\dagger\Big)^\dagger \rho^\dagger L_\alpha^\dagger \Big(\rho^{-1}\Big)^\dagger - L_\alpha^\dagger L_\alpha = L_\alpha \rho L_\alpha^\dagger \rho^{-1} - L_\alpha^\dagger L_\alpha.$$

Thanks to the good linearity property we certainly also have:

$$\left(\sum_\alpha D_\alpha\right)^\dagger = \sum_\alpha D_\alpha^\dagger.$$

Now it is sufficient to show by explaining the calculations that the equation in form (6.3) is equivalent to the Lindblad ones.

$$\frac{\partial \rho}{\partial t} = \frac{1}{2}\Big(\rho \Omega_L^t + (\Omega_L^t)^\dagger \rho\Big) =$$
$$\frac{1}{2}\Big(\rho \Omega^t + (\Omega^t)^\dagger \rho\Big) + \frac{1}{2}\sum_\alpha \Big(L_\alpha \rho L_\alpha^\dagger - \rho L_\alpha^\dagger L_\alpha + L_\alpha \rho L_\alpha^\dagger - L_\alpha^\dagger L_\alpha \rho\Big) =$$
$$\frac{1}{i\hbar}[\mathcal{H}, \rho] + \sum_\alpha \left(L_\alpha \rho L_\alpha^\dagger - \frac{1}{2}\{L_\alpha^\dagger L_\alpha, \rho\}\right).$$

□

We emphasize that there are other ways to include Lindblad operators in Ω. We chose (6.2) because it seemed like the most natural way. However, we are building this new formalism now, we don't know what the truly best path is. For example, we could have included them simply by multiplying by ρ^{-1} first on one side and then on the other:

$$\Omega_L = \rho^{-1}\mathcal{L}[\rho]; \quad \Omega_L^\dagger = \mathcal{L}[\rho]\rho^{-1}; \tag{6.4}$$

where $\mathcal{L}[\cdot]$ denotes the Lindblad equations. However, this seems to be an unproductive path, in the sense that it is unlikely to lead to future simplifications. Anyway, more interesting choices than (6.2) could be found.

It is necessary to underline that previously, for Hamiltonian dynamics, we could express the Von Neumann equation as a linear combination of Ω and $\Omega^\dagger$,

$$\frac{\partial\rho}{\partial t} = a(\Omega)^\dagger\rho + b\rho\Omega \quad \text{with } a, b \in \mathbb{R}\ s.t.\ a + b = 1. \tag{6.5}$$

However, by extending this formalism to the Lindblad equations using (6.2), this last combination is no longer possible: constraint $a = b = 1/2$ is added and the only admissible form is eq. (6.3). This result is consistent, if the Lindblad operators were null then we would find the Von Neumann equation in the form (6.5) (with $a = b = 1/2$).

It is also interesting to understand if and how the time propagator can be extended to the Lindblad case. Previously we had

$$\rho_t = e_L^{-i\hat{\Omega}_{0,t}}\rho_0 e_R^{+i\hat{\Omega}_{0,t}}; \text{ with } \hat{\Omega}^s \equiv \frac{\tilde{\omega}^s}{\hbar} - i\overline{\Omega^s}.$$

The definition of $\overline{\Omega^s}_L$ follows in a constrained way from that of Ω_L, we necessarily have

$$\overline{\Omega}_L \equiv \frac{1}{2}(\Omega_L - \Omega_L^\dagger) = \overline{\Omega} + \frac{1}{2}\left(\sum_\alpha [\rho^{-1}, L_\alpha\rho L_\alpha^\dagger]\right) = \overline{\Omega}^t + K(t)$$

Instead, $\tilde{\omega}$ was specially defined to express $\mathcal{H}$ as $\mathcal{H} = \tilde{\omega} - \hbar i\overline{\Omega}$, we therefore have freedom on how to extend it, but the extension must necessarily be consistent. In general, we can write:

$$\tilde{\omega}_L^t = \tilde{\omega}^t + B_L(t).$$

We would like to use this freedom to build $\hat{\Omega}_L$ in such a way that

$$\rho_t = U_L(t)\rho_0 U_L^\dagger(t) \equiv e_L^{-i\hat{\Omega}_{0,t}}\rho_0 e_R^{+i\hat{\Omega}_{0,t}}; \quad \hat{\Omega}_{0,t} = \int_0^t ds\hat{\Omega}_L^s \tag{6.6}$$

is a solution of the Lindblad equations.

This is the idea from which we take inspiration. However, it is very difficult to put into practice. First of all, we don't know if, for Lindblad problems, such propagation operators $U_L(t)$ really exist. Secondly, assuming their existence, we do not know the form of B_L. Finally, even obtaining $\hat{\Omega}_L$, we would then have to know its time evolution to calculate the integral and express U_L. Knowing the temporal evolution of $\hat{\Omega}_L^t$ could be very complex, given that ρ_t is present inside it, which we are not aware of.

All these problems prevent us from an exact mathematical derivation. So we will move differently, we will combine the exact results obtained so far with hypotheses suggested by the previous considerations.

Given a Lindblad problem in form (6.1), we assume that we can still write:

$$\frac{d}{ds}\langle \mathcal{O}\rangle_s = Tr\left(\mathcal{O}_s^*\frac{\partial \rho_0}{\partial t}\right).$$

We emphasize that with this, we are assuming that the infinitesimal temporal variation of the expectation value of an observable $\mathcal{O}$ can be expressed relative to the initial density derivative, provided that the observable is made to evolve over time in an appropriate manner to make this possible, $\mathcal{O}_s^*$. For now, we are not assuming anything about the form of $\mathcal{O}_s^*$, it could be very complicated and not expressible via two time propagators.

This assumption allows us to exploit the dissipation operator (6.2). With steps similar to those already carried out for derivation of eq. (2.10), we obtain

$$\langle \mathcal{O}\rangle_t = \langle \mathcal{O}\rangle_0 + \frac{1}{2}\int_0^t \left(\langle \Omega_L^0 \mathcal{O}_s^*\rangle_0 + \langle \mathcal{O}_s^*(\Omega_L^0)^\dagger\rangle_0\right) ds. \tag{6.7}$$

Not knowing $\mathcal{O}_s^*$, to exploit this expression, we must make another hypothesis. To do this, we draw inspiration from the considerations of the previous chapter, in particular from eq. (5.23). We therefore hypothesize that, using this expression, the observables can evolve as

$$\mathcal{O}_t^* = U_L^\times(t)\mathcal{O}U_L(t) = e^{\frac{i}{\hbar}(\mathcal{H}+C^\times)t}\mathcal{O}e^{-\frac{i}{\hbar}(\mathcal{H}+C)t}. \tag{6.8}$$

In this case, we are not assuming that U_L is a "real" time propagator, in the sense that it would extend the Heisenberg representation, $\langle \mathcal{O}\rangle_t = Tr(U_L^\times(t)\mathcal{O}U_L(t)\rho_0)$. We are stating that such operators work like evolution operators when combined with expression (6.7). The symbol '×' indicates that the two evolution operators need not necessarily be adjoints of each other. It would be preferable, but for now we want to have as much freedom as possible to investigate the form of $\mathcal{O}_t^*$, therefore we take the liberty of using a $C^\times$ similar but possibly a little different from $C^\dagger$.

Assumption (6.8) is reasonable, we have in fact

$$\hat{\Omega}_L^t = \frac{\tilde{\omega}^t}{\hbar} + B_L(t) - i(\overline{\Omega^t} + K(t)) = \frac{\mathcal{H}}{\hbar} + B_L(t) - iK(t).$$

The freedom we have on $B_L(t)$ allows us to express the entire second part with a single arbitrary operator $C(t) = \hbar(B_L(t) - iK(t))$. It is also reasonable to hypothesize the temporal independence of C. Just as the two time-dependent operators $\overline{\Omega^t}$ and $\tilde{\omega}^t$ reduce to the constant Hamiltonian $\mathcal{H}$, the same could happen for $B_L(t)$ and $K(t)$, also because all the Lindblad operators are time-independent in equation (6.1). We would therefore have $\hat{\Omega}^t_L = \hbar^{-1}(\mathcal{H} + C)$, from which, remembering eq. (6.6), hypothesis (6.8) follows.

We don't know C (and $C^\times$), the idea is to apply the expression (6.7) to a particular case of Lindblad equations, whose analytical solution is known. We will try to construct C by inspection for the given Lindblad problem. Once found, the process can be repeated for various particular Lindblad equations. If the procedure works for several particular cases then one can try to extrapolate a general form for C and $C^\times$ (and thus for $U_L(t)$ and $U^\times_L(t)$). After having defined a good general expression, assumption (6.8) can be justified by reasoning a posteriori.

6.2 Application to a Lindblad equation

Now we begin the study of expression (6.7) by choosing a particular Lindblad equation in simple form. We consider the following particular case,

$$\frac{\partial \rho}{\partial t} = -i[\omega\sigma_z, \rho] + \gamma\bigg(\sigma^-\rho\sigma^+ - \frac{1}{2}\{\sigma^+\sigma^-, \rho\}\bigg); \quad \sigma^\pm \equiv \frac{1}{2}(\sigma_x \pm i\sigma_y). \tag{6.9}$$

This equation dictates the evolution of a $(|0\rangle, |1\rangle)$ qubit open system. It is already in form (6.1), we just need to highlight the correspondence with the general notation,

$$\alpha = 1; \ \mathcal{H} = \omega\sigma_z; \quad L = \sqrt{\gamma}\sigma^-; \quad L^\dagger = \sqrt{\gamma}\sigma^+.$$

Expressing eq. (6.9) in single components one finds

$$\dot\rho_{00} = -\gamma\rho_{00}; \ \dot\rho_{01} = \Big(-\frac{\gamma}{2} - 2i\omega\Big)\rho_{01}; \ \dot\rho_{10} = \Big(-\frac{\gamma}{2} + 2i\omega\Big)\rho_{10}; \ \dot\rho_{11} = +\gamma\rho_{00}; \ \rho(0) = \rho^0.$$

The analytical solution is easily calculable:

$$\rho(t) = \begin{bmatrix} \rho^0_{00}e^{-\gamma t} & \rho^0_{01}e^{-(0.5\gamma + 2i\omega)t} \\ \rho^0_{10}e^{-(0.5\gamma - 2i\omega)t} & \rho^0_{11} + \rho^0_{00}(1 - e^{-\gamma t}) \end{bmatrix}.$$

Therefore, the expectation value of the observables can be obtained as

$$\langle\mathcal{O}\rangle_t = Tr(\rho(t)\mathcal{O}). \tag{6.10}$$

We want to use expression (6.7) to calculate $\langle\mathcal{O}\rangle_t$. By comparing the results obtained with the analytical solution, we may be able to define operators C and $C^\times$ for this particular case. To do this, we used the matlab code in Appendix C.

We were unable to achieve this goal, however we found an interesting result in this regard. If we restrict the field of observables to diagonal operators,

$$\mathcal{O} = \begin{bmatrix} a & 0 \\ 0 & b \end{bmatrix}, \quad a, b \in \mathbb{R}, \tag{6.11}$$

then the expression (6.7) offers exact results for a suitable $\mathcal{O}_s^*$.
In particular, defining

$$C \equiv -i\gamma\sigma^+\sigma^-, \; C^\times \equiv +i\gamma\sigma^-\sigma^+, \tag{6.12}$$

formula (6.7) offers results coinciding with the known ones (6.10), for any initial condition $\rho(0)$ and for all real frequencies ω, γ. In particular, in figure 6.1, we show the numerical results obtained for the two projectors π_0 ($a = 1, \; b = 0$) and π_1 ($a = 0, \; b = 1$); all the diagonal observables can be obtained as their linear combination.

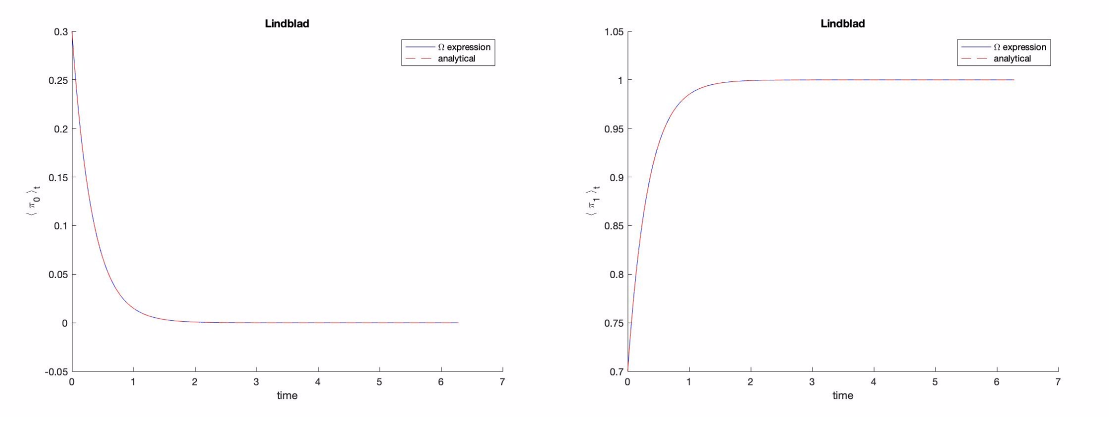

Figure 6.1: Comparison of the results offered by expression (6.7) (solid blue line) with those known theoretically (dashed red line) for the problem (6.9). On the left $\langle \pi_0 \rangle_t$, on the right $\langle \pi_1 \rangle_t$. In both panels: $\omega = 0.5, \; \gamma = 3$, initial condition ρ_0 identified by the Bloch vector $\vec{a} = (0.2; \; 0.3; -0.4)$. The curves overlap: the results offered by (6.7) are correct.

We underline that $C^\times$ is slightly different from the adjoint of C, $C^\dagger = i\gamma\sigma^+\sigma^-$, the two operators used, U_L and $U_L^\times$, do not form a unitary group; this question should be further investigated but for the moment we don't deal with it. Of course we tried using $C^\dagger$ instead of $C^\times$, but the results weren't great. Anyway, this result is not strange, dissipative dynamics are non-unitary, it is reasonable to use propagation operators which themselves are not unitary and without the constraint of necessarily having to be one the adjoint of the other.

The class of diagonal operators already represents an important category of observables, however, we would like to be able to calculate the expectation value of any Hermitian operator with expression (6.7). What we found suggests investigating expression (6.7) for the complementary class of operators,

$$\mathcal{O} = \begin{bmatrix} 0 & c+id \\ c-id & 0 \end{bmatrix}; \; c, d \in \mathbb{R}. \tag{6.13}$$

If we could find a correct form for $\mathcal{O}_t^*$ also in this case, we could then combine the results obtained and find a valid expression for any Hermitian operator, combination of these two classes of operators. By inspection, with numerical attempts on matlab, we have found the form for $\mathcal{O}_t^*$ that offers exact results for this second case. We can define the evolution of the observables for this second case as

$$\mathcal{O}_t^* = e^{\frac{i}{\hbar}(\mathcal{H}+M^\times)t}\mathcal{O}e^{-\frac{i}{\hbar}(\mathcal{H}+M)t}; \quad M = -\frac{i}{4}\gamma Id = -M^\times. \tag{6.14}$$

This form, combined with the usual expression (6.7), offers exact results for all observables belonging to this second class, which we will call second diagonal-class. In figure 6.2, we show the numerical results obtained for two arbitrary cases.

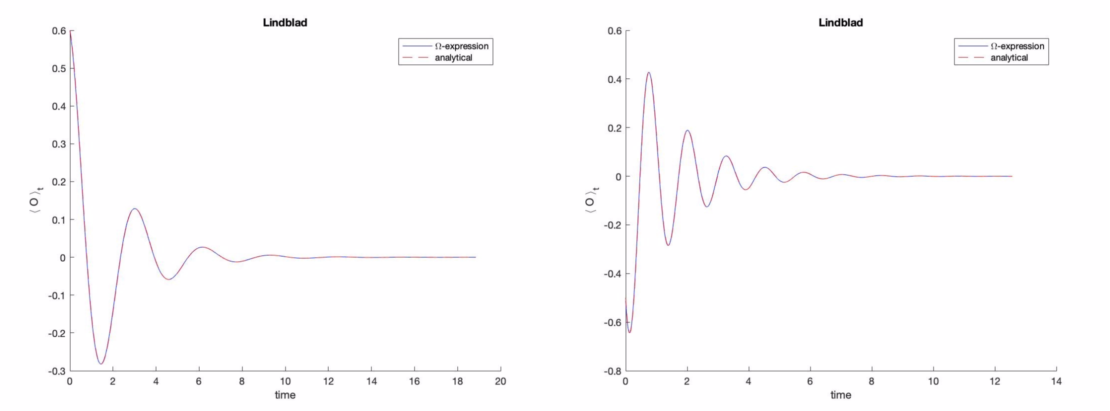

Figure 6.2: Comparison of the results offered by expression (6.7) (solid blue line) with those known theoretically (dashed red line) for the problem (6.9), second-diagonal class $\mathcal{O}^2$. On the left, $c = 1, \; d = 1, \; \omega = 1, \; \gamma = 1, \; \rho_0$-Bloch vector $\vec{a} = (0.3, \; 0.3, \; -0.4)$. On the right, $c = -3, \; d = -1, \; \omega = 2.5, \; \gamma = 1.3$. ρ_0-Bloch vector $\vec{a} = (0.2, \; -0.1, \; 0.6)$. The curves always overlap: the results offered by (6.7) are correct.

In summary, the new expression (6.7) offers exact results for the expectation value of any Hermitian operator $\mathcal{O}$. However, we must pay attention to how to make this observable evolve over time. An Hermitian observable $\mathcal{O}$ in dimension 2 can always be expressed as a linear combination of the two classes (6.11), which we denote by $\mathcal{O}^1$, and (6.13), by $\mathcal{O}^2$:

$$\mathcal{O} = \mathcal{O}^1 + \mathcal{O}^2.$$

To use expression (6.7), the observable must evolve as

$$\mathcal{O}_t^* = e^{\frac{i}{\hbar}(\mathcal{H}+C^\times)t}\mathcal{O}^1 e^{-\frac{i}{\hbar}(\mathcal{H}+C)t} + e^{\frac{i}{\hbar}(\mathcal{H}+M^\times)t}\mathcal{O}^2 e^{-\frac{i}{\hbar}(\mathcal{H}+M)t};$$
$$C = -i\gamma\sigma^+\sigma^-, \ C^\times = i\gamma\sigma^-\sigma^+; \quad M = -\frac{i}{4}\gamma Id = -M^\times.$$

With a view to extrapolating a form for generic Lindblad equations, it is appropriate to point out some properties of this particular case. C, $C^\times$, M, $M^\times$ all commute with the Hamiltonian operator $\mathcal{H}$. Therefore the usual exponential property holds and we can equivalently write:

$$\mathcal{O}_t^* = e^{\frac{i}{\hbar}C^\times t}\mathcal{O}_H^1(t)e^{-\frac{i}{\hbar}Ct} + e^{\frac{i}{\hbar}M^\times t}\mathcal{O}_H^2(t)e^{-\frac{i}{\hbar}Mt} \tag{6.15}$$

(where the subscript 'H' indicates evolution in simple Heisenberg picture).
We also note that $M^\times$ is the adjoint of M, $M^\dagger = M^\times$. Furthermore, for class (6.11), $[O^1, \mathcal{H}] = 0$, so writing $\mathcal{O}_t^1 = e^{\frac{i}{\hbar}C^\times t}\mathcal{O}^1 e^{-\frac{i}{\hbar}Ct}$ is also valid, without using Heisenberg time propagators. It may also seem strange to use the identity at the exponential in a general form. In this particular case, we have

$$Id = \{\sigma^-, \sigma^+\} = \sigma^-\sigma^+ + \sigma^+\sigma^-.$$

Therefore it is possible that in other cases the M operator is defined via the anticommutator of Lindblad operators.

In conclusion, we realize a posteriori that we can also simply write,

$$\text{Diag 1: } \langle\mathcal{O}^1\rangle_t = \langle\mathcal{O}^1\rangle_0 + \frac{1}{2}\int_0^t e^{-\gamma s}\Bigg(\langle\Omega_L^0\mathcal{O}_H^1(s)\rangle_0 + \langle\mathcal{O}_H^1(s)(\Omega_L^0)^\dagger\rangle_0\Bigg)ds.$$
$$\text{Diag 2: } \langle\mathcal{O}^2\rangle_t = \langle\mathcal{O}^2\rangle_0 + \frac{1}{2}\int_0^t e^{-\frac{1}{2}\gamma s}\Bigg(\langle\Omega_L^0\mathcal{O}_H^2(s)\rangle_0 + \langle\mathcal{O}_H^2(s)(\Omega_L^0)^\dagger\rangle_0\Bigg)ds.$$
$$\langle\mathcal{O}\rangle_t = \langle\mathcal{O}^1\rangle_t + \langle\mathcal{O}^2\rangle_t.$$

In this case the exponentials $e^{-\gamma s}$ and $e^{-\frac{1}{2}\gamma s}$ are simple scalar functions. Previously, this temporal dependence was expressed by incorporating it into the evolution of the observables taking the exponential of the M and C operators, as shown in (6.15). However, it could be justified in other ways, for example by taking it as a temporal dependence of Ω_L^0,

$$HP: \ (\text{diag 1}) \ \Omega_L^0(t) = e^{-\gamma t}\Omega_L^0; \qquad (\text{diag 2}) \ \Omega_L^0(t) = e^{-\frac{1}{2}\gamma t}\Omega_L^0. \tag{6.16}$$

We are at the beginning, we cannot know which is the best approach. Anyway, for now, we think it is better to keep the dissipation operator fixed at the initial instant. Ω_L^0 allows us to use only the equilibrium density operator ρ_0, which has many advantages, imposing a time dependence might not be convenient.
We therefore prefer the way (6.15), which includes this temporal dependence in the evolution of the observables via specific time propagators. Furthermore, we do not exclude that it is possible to express it by defining C and M in different ways. In general, we must not exclude any path a priori, only future studies will be able to reveal the best choice.

We have shown that the expression (6.7) based on the dissipation operator works perfectly for this particular Lindblad equation (6.9). The goal is to find a generally valid expression for any Lindblad equation. To achieve this, it is necessary to apply this formalism to many different Lindblad equations, in order to reach an always valid formula. This first application seems to suggest using the expression (6.7), evolving the observables as in (6.15), defining

$$M = -\frac{i}{4}\{L_\alpha, L_\alpha^\dagger\} = -M^\times; \quad C = -iL_\alpha^\dagger L_\alpha; \quad C^\times = iL_\alpha L_\alpha^\dagger.$$

However, we have seen that this simple case has several properties. It may be possible to find other, even very different, ways of defining these operators and obtaining equivalent exact results. Furthermore, other ways can be explored, studying the temporal dependence of Ω_L could be a valid alternative, as shown in (6.16). It is also interesting to understand what happens in dimension 3 or higher, where the decomposition into the two diagonals no longer covers all possible Hermitian observables. In general, one could also try to arrive at a single expression, which does not require such a decomposition. It is certainly worth carrying out studies of other Lindblad applications in future developments of this work to clarify all these questions.

If it were possible to define a general expression based on the dissipation operator then this could resolve some defects and suggest numerous interesting lines of research. First of all, it would be a good starting point to avoid the grain of negative probabilities. Secondly, one could try, with the necessary mathematical care, to define Ω^0, not through the initial condition ρ_0, but with more clever choices. This could for example significantly improve the computational problems related to these equations, or provide new physical interpretations.
Determining exactly which operators are appropriate for a given system is not always clear and requires complex theoretical work. In many cases, choosing L_k operators can be an ambiguous or approximate process. If expression (6.7) turns out to be excellent in the future, it is not a bad idea to try to mathematically

describe the dissipation and decoherence with the opposite approach: not through L_k operators but directly by studying Ω operator.

The Lindblad equations are intimately linked to the concept of quantum entropy [29], [30]. This is an advanced question, for now certainly very far from being investigated using the dissipation operator method. However, since this response theory is in an initial state, we do not exclude that future extensions of this work may be relevant in studies on these directions. We need to proceed step by step, the first thing is to understand if there is a general expression valid for solving any Lindblad equation, not just a particular case. If it were possible, even only partially, then one could really think about studying quantum entropy and other questions, linked to Lindblad equations, using this approach. The theory is in an embryonic state, so there are still many things to discover, as well as potential.

Chapter 7

Conclusion and future developments

The linear quantum response theory is the most used today to deal with equilibrium-perturbed quantum systems. The response to a small perturbation is determined by the equilibrium dynamics and by the time correlation function of the perturbation and the observable of interest, computed with respect to the known equilibrium density operator. This approximate approach has reached an excellent degree of completeness. It is applicable not only to closed systems but also to open dissipative systems, the equilibrium of which is a stationary state of the Lindblad equations. Non-Markov effects can also be taken into account. This method has allowed the study of non-equilibrium quantum systems, offering important results and bringing progress in various scientific sectors. It will continue to be important in the future, as it is easily applicable whenever other more precise approaches cannot be exploited. However, linear response theory has limitations. Firstly, it requires that the perturbation can be assumed to be small, obviously in many cases this is not possible. Secondly, in the presence of non-linearity or anomalies, even a small initial perturbation can generate drastic changes, for example it can lead to a phase transition. The linear response may fail to capture these behaviours. Linear response theories can be extended taking higher-order terms in the expansion of the perturbation. This approach offers greater precision, but it is very cumbersome. Above all, it remains an approximate method, presenting the same problems as the linear approach.

There is therefore a strong need to develop a quantum exact response theory. This would lead to important new discoveries. Research has recently begun to be carried out in this direction and some promising approaches have been developed. However, we are at the beginning: an exact, valid and general method does not yet exist in quantum mechanics. In this thesis, we attempted to lay the foundations for an exact method inspired by the Dissipation Function.

The Dissipation Function arises in the field of Fluctuation Theorems of "classical" (non-quantum) nature. It was initially developed as the energy dissipation rate in these Fluctuation Relations. A dynamical-systems interpretation has been provided for the Dissipation Function. In this context, it is defined as

$$\Omega^{f_t}(\Gamma) \equiv -[\Lambda(\Gamma) + G(\Gamma) \cdot \nabla_\Gamma ln f_t(\Gamma)].$$

This is the basis for a general exact response theory. It can be used to describe the exact evolution of the ensemble average as

$$\langle \mathcal{O} \rangle_{f_t} = \langle \mathcal{O} \rangle_{f_0} + \int_0^t \langle (\mathcal{O} \circ S^s)\Omega^{f_0} \rangle_{f_0} ds.$$

This exact response formula has several advantages. It keeps the probability fixed: evolving observables over time is easier than evolving the density, which requires reversed dynamics. The response is calculated as a correlation function with an important physical observable, Ω, and this has enabled new physical interpretations. It offered new perspectives into second-law inequality, but interpreted in terms of relative entropies, independent of any putative thermodynamic context; it can also provide necessary and sufficient conditions for relaxation towards equilibrium, in terms of observable behaviour, through the notion of ΩT-mixing. Moreover, this form has the advantage of smoothing the $\langle \mathcal{O} \rangle_t$ signal and cleaning it from noise.

To build a quantum exact response theory, the idea exploited for this thesis is to develop the quantum translation of this classical theory based on the Dissipation Function. Working in finite dimensional Hilbert spaces, we initially assumed a Hamiltonian dynamics of the type $\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_{ext}$. $\mathcal{H}_0$ is considered the equilibrium dynamics, the corresponding invariant density operator ρ_0 represents the quantum system at the initial stationary equilibrium. The perturbation is of the type $\lambda \mathcal{H}_{ext}$, with lambda (and so the perturbation) arbitrarily large. It is turned on at the initial instant and then kept constant over time. Under these assumptions, we defined the dissipation operator as

$$\Omega^0 \equiv \frac{1}{i\hbar} \rho_0^{-1} [\mathcal{H}, \rho_0].$$

Exploiting the latter, we derived an exact response expression,

$$\langle \mathcal{O} \rangle_t = \langle \mathcal{O} \rangle_0 + \int_0^t \langle \Omega^0 \mathcal{O}_s \rangle_0 ds,$$

where $\mathcal{O}_s$ is the evolved observable in Heisenberg picture according to the total (exact) dynamics $\mathcal{H}$. This method has more general validity, it is applicable to any constant Hamiltonian $\mathcal{H}$ and any initial density operator ρ_0.

By applying this expression to qubit systems, we numerically tested its validity. We also compared the results with those offered by the linear response theory: for small perturbations they coincide, while for large perturbations the linear theory fails while the new formula (2.10) continues to be correct.
However, we underline that for the analysed problems the results can be calculated exactly as $\langle\mathcal{O}\rangle_t = Tr(U(t)\rho_0 U^\dagger(t)\mathcal{O})$, the linear response is not used for these simple cases. In this sense, we can say that the new expression (2.10) is, for now, just a different formalism for calculating $\langle\mathcal{O}\rangle_t$, equivalent to the Heisenberg and Schrödinger pictures. Anyway, finding different formalisms to rewrite the same result is often a great way to discover different points of view on a theory, and to move an important first step towards new discoveries. Expression (2.10) is already an exact response formula for arbitrarily large constant perturbations. In future developments one can try to extend it to time-dependent perturbations, or dissipative, non-Hamiltonian perturbations. This would offer an exact response theory in fields where an approximate approach is the only one that can be used today: it would constitute an extraordinary result. Succeeding in this goal is not easy, it certainly requires hard work. We don't know if this is possible, but the analogous classical theory works well for this type of perturbations, so we think it is worth investigating the question also in the quantum world, through the new expression.

Moreover, thanks to its analogy to classical theory, also other advantages offered by the classical expression (1.23) could be transferred to the quantum field. In this regard, we have demonstrated two properties of the dissipation operator,

$$\langle\Omega^0\rangle_0 = 0 \quad\text{and}\quad \frac{d}{ds}\langle\Omega^0\rangle_s|_{s=0} \geq 0.$$

By combining them, it seems possible to maintain the association of $\langle\Omega_{0,s}\rangle_0 \geq 0$ with the relative entropy measure $D(f_0\|f_{-s})$, finding a sort of second law inequality, independent of any thermodynamic context, as already done for dynamical systems. Furthermore, classical theory suggests the possibility of associating to operator Ω, even in quantum mechanics, the physical observable of dissipation (more precisely, of generalised entropy production). The latter is a quantity that can be measured in the laboratory, and it may be interesting to understand if a quantum equivalent exists. These last two considerations are interesting to explore further, but they are also delicate because operator Ω is not Hermitian, and this can cause problems in the attempt to associate it with real physical observables.

We have defined a Hermitian dissipation operator $\tilde{\Omega}$. By exploiting it to derive the exact response expression, however, an antihermitian operator also appears,

$$\langle\mathcal{O}\rangle_t = \langle\mathcal{O}\rangle_0 + \int_0^t \left(\langle\tilde{\Omega}^0;\mathcal{O}_s\rangle_0 + \frac{1}{2}\langle[\overline{\Omega^0},\mathcal{O}_s]\rangle_0\right)ds.$$

$\tilde{\Omega}$ and $\overline{\Omega}$ are nothing other than the Hermitian and antihermitian parts of Ω, and this expression deviates from the analogy with the classical one. Today, we consider the previous form (eq. (2.10)) better, as it is simpler. However, they offer equivalent and exact results, we also present this second one, as it may prove more useful in future studies on this topic and in possible extensions.

We reiterate that we have built this formalism from scratch, the choice of new operators and expressions is free, as long as it offers exact results. We don't even know what is the best way to define the dissipation operator and build the theory. We have presented the best results found by us. However, there is no definitive rule, there may be better ways to define the dissipation operator on which to base the theory; further research into different ways of doing this may be very productive.

We analysed the Von Neumann equation in more detail, focusing on the role that the dissipation operators defined so far assume in expressing its solution. These results may seem impractical, but they help to understand possible ways for extending the theory to more complicated dynamics. We found that, for constant Hamiltonian dynamics, the dissipation operator evolves in 'reversed time' with respect to the observables, like a probability, $\Omega^t = U(t)\Omega^0 U^\dagger(t)$. This seems initially inconvenient, but in reality it guarantees excellent consistency results for this theory. Still considering Hamiltonian $\mathcal{H}(t)$ dynamics, time propagators can be written as

$$\hat{\mathcal{U}}(t) = e_L^{-i\hat{\Omega}_{0,t}};\;\; \hat{\mathcal{U}}^\dagger(t) = e_R^{+i\hat{\Omega}_{0,t}}.$$

According to Stones' theorem, these coincide exactly with the usual ones, eq.(5.5). This is not a new result, but it suggests an interesting fact: exploiting the new formalism for dissipative (non-Hamiltonian) dynamics, it may be possible to continue evolving the observables as

$$\mathcal{O}_t = e_R^{i\hat{\Omega}_{0,t}}\mathcal{O}e_L^{-i\hat{\Omega}_{0,t}}.$$

This conjecture can prove very interesting in extending the new formalism to these open quantum dynamics.

Quantum dissipative dynamics are described by the Lindblad equations, only the probability evolves over time, the observables are kept fixed. This approach has some problems, for example, the solution can result in negative probabilities. Extending the quantum response theory based on the Dissipation Function to this type of problems could therefore bring important advantages. We therefore investigated this approach. We have extended the definition of the dissipation operator to this case: $\Omega^0_L = \Omega^0 + \sum_\alpha D^0_\alpha$. Making some hypotheses suggested by the previous results, we constructed the expression

$$\langle \mathcal{O} \rangle_t = \langle \mathcal{O} \rangle_0 + \frac{1}{2}\int_0^t \bigg(\langle \Omega^0_L \mathcal{O}^*_s \rangle_0 + \langle \mathcal{O}^*_s (\Omega^0_L)^\dagger \rangle_0 \bigg) ds.$$

The general form of O^*_t is not known. By applying this expression to many particular cases it could be possible to arrive at a general definition for O^*_t. We therefore studied a particular case, eq. (6.9). By applying a decomposition to $\mathcal{O}$ in the two diagonals, exact results are obtained with the choice

$$\mathcal{O}^*_t = e^{\frac{i}{\hbar}C^\times t}\mathcal{O}^1_H(t)e^{-\frac{i}{\hbar}Ct} + e^{\frac{i}{\hbar}M^\times t}\mathcal{O}^2_H(t)e^{-\frac{i}{\hbar}Mt}.$$

$$M = -\frac{i}{4}\{L_\alpha, L^\dagger_\alpha\} = -M^\times;\quad C = -iL^\dagger_\alpha L_\alpha;\quad C^\times = iL_\alpha L^\dagger_\alpha.$$

We have also seen that these exact results can also be justified in different ways, for example, by defining M and C in other ways, hypothesizing a temporal dependence of Ω^0_L or in even different ways. We are building this theory from scratch, so there is a lot of freedom and this can be considered an advantage, imagination and intuition can be fully exploited.

Future developments certainly concern the application to other different Lindblad equations. Through these we could obtain a generally valid expression. It is then interesting to study whether it is possible to avoid the decomposition into the two diagonals and investigate the cases of dimension 3 and higher, where this decomposition does not cover all the Hermitian observables. Even in this case, it may be profitable to investigate other ways to define Ω^0_L. One can also try to obtain a more compact form for the expression (6.7).

Furthermore, to define Ω^0_L, we have always used ρ_0 considered as initial conditions for the Lindblad equations. Through some adjustments and care, one could think of defining Ω_L by choosing more convenient density operators. Understanding what is meant by 'convenient' from this perspective can again be the subject of future studies. We suggest experimenting with choices that can speed up the computational calculation or lead to physical interpretations.

If this method proves to work well, then one can think of using this basis to solve problems related to Lindblad eq., not only that of negative probability but, for example, also the description of dissipation, often complicated and approximate via operators L_k. One could also use this method to study other questions related to open quantum systems, such as quantum entropy. These are just some of the future perspectives that come to mind. In general, since the theory is in an initial state, several original research can be undertaken on this basis, many of which we still cannot predict.

All the results of this thesis are valid in finite-dimensional Hilbert spaces. This is a limitation, but we remember that one of the most promising areas of quantum physics, quantum computing, is based entirely on qubits, systems described precisely in finite-dimensional Hilbert spaces. Future research can extend the validity of this theory to infinite dimensional Hilbert spaces through the appropriate techniques and hard work. In our opinion, this extension should be feasible for infinite dimensional operators with a discrete spectrum. Conceptually it is possible to think of these operators as an infinite concatenation of finite matrices, certainly realizing this idea is a very difficult task, but with the right advanced techniques of functional analysis it should be possible. The case of continuous spectrum operators should be more delicate. This second question should however be analyzed only after having found the extension to compact operators.

This thesis is to be considered a first approach to the construction of an exact quantum response theory, based on the Dissipation Function. We are at the beginning, we have found some interesting results, however we cannot know how profitable this type of approach may be in the future. We believe it is a new and original method that can offer a different point of view on quantum response theory. It is an approach still in its embryonic state. However, it seems promising given the first results found, and given the similarity to the classical exact response theory, which is robust and general. We think it is worth carrying out further mathematical and physical research in this direction to obtain new discoveries.

Appendix A

Matlab code for numerical tests

```
%Pauli matrices
s1=[0 1
    1 0];
s2=[0 -1i
    1i 0];
s3=[1 0
    0 -1];

%density operator
%CONSTRAINT: a1^2+a2^2+a3^2<1
a1=0; %real non-diagonal elements
a2=0.1; %imaginary non-diagonal elements
a3=-0.5; %diagonal elements (<0 weight on e1, >0 on e0)
rz=0.5*(eye(2)+a1*s1+a2*s2+a3*s3)


%Hamiltonian (real coeefficients c_i)
c0=0.1;
c1=0.1;
c2=0.2;
c3=3;
H=c0*eye(2)+c1*s1+c2*s2+c3*s3

%Observable (real coefficients o_i)
```

```
o0=-0.1;
o1=-0.2;
o2=0;
o3=-0.5;
oss=o0*eye(2)+ o1*s1+o2*s2+o3*s3
%-----------------------------------------

%dissipation operator
comm=H*rz-rz*H;
omz=(-1i*inv(rz)*comm);

%hermitian and antihermitian
omzc=(-1i*comm*inv(rz));
omzS=0.5*(omz+omzc);
omzA=0.5*(omz-omzc);

%oss=omz %(to choose particular observables)

% time propagators
[C,D]=eig(H);
expp=@(t) C*diag(exp(diag(1i*t*D)))*inv(C); %U^+(t)
expm=@(t) C*diag(exp(diag(-1i*t*D)))*inv(C); %U(t)

%time interval: [shift,t+shift+long]
t=2*pi;
shift=0; %for convenience
long=0; %for convenience
dim=10000; %number of points in time interval
   discretization
time=linspace(shift, shift + t +long, dim);

% calculation of the response:
%Heisenberg formalism
Heisenberg=zeros(dim,1);

%Dissipation operator formalism
dissipationOp=zeros(dim,1);
dissipationResponse=zeros(dim,1);

%Hermitian dissipation operator formalism
HermitianDissip=zeros(dim,1);
```

```
HDissResponse=zeros(dim,1);

for k=1:dim
    %calculation of the dissipation opeator formula
    r1t=omz*expp(time(k))*oss*expm(time(k)); %Omega*Oss
    dissipationOp(k)=sum(diag(rz*r1t)); %<Omega*Oss>_0
    dissipationResponse(k)=trapz(time,dissipationOp);
    %integral over time

    %calculation of the Heisenberg formula
    heis=expp(time(k))*oss*expm(time(k));
    Heisenberg(k)=sum(diag(rz*heis));

    %calculation of the hermitian dissipation formula
    osstempo=expp(time(k))*oss *expm(time(k));
    corrS=0.5*(omzS*osstempo+osstempo*omzS); %Herm part
    commA=omzA*osstempo-osstempo*omzA; %antiH part
    HermitianDissip(k)=sum(diag(rz*corrS))+0.5*sum(diag(rz*commA));
    HDissResponse(k)=trapz(time,HermitianDissip);
    %integral over time

end
%<O>_t=<O>_0+ Response
osszero=sum(diag(rz*oss)); %<O>_0
HDissResponse=osszero+HDissResponse;
dissipationResponse=osszero+dissipationResponse;
%-----------------------------------------------
%graphic plot
hold on;
plot(time,HDissResponse,'-g')
plot(time,Heisenberg,'-r')
plot(time,dissipationResponse,'-b')
xlabel('time')
ylabel('\langle O \rangle_t')
title('comparison of the three expressions for \langle O \rangle_t')
legend('Hermitian \Omega^0 ','Heisenberg','n-h\Omega^0')
```

Appendix B

Matlab code: comparison with linear response

```
s1=[0 1
    1 0];
s2=[0 -1i
    1i 0];
s3=[1 0
    0 -1];
% a1^2+a2^2+a3^2<1
a1=0;
a2=0;
a3=0.5;
rz=0.5*(eye(2)+a1*s1+a2*s2+a3*s3)

frZero=1;
frX=1;
Hzero=0.5*frZero*s3;
Hex=0.5*frX*s1-0.5*frZero*s3;
lambda=5;

H=Hzero+lambda*Hex;

or=0; %real number
oi=1; %real number
oss=diag([0 0])+ or*s1+oi*s2;
```

```

%exactResponse with Omega
comm=H*rz-rz*H;
omz=-1i*inv(rz)*comm;

osszero=sum(diag(rz*oss)); %<O>_0

% Omega/Heisenberg time propagator: exact dynamics H
[C,D]=eig(H);
expp=@(t) C*diag(exp(diag(1i*t*D)))*inv(C);
expm=@(t) C*diag(exp(diag(-1i*t*D)))*inv(C);

%Linear Resp. time propagator: equilibrium dynamics H0
[Cl,Dl]=eig(Hzero);
exppl=@(t) Cl*diag(exp(diag(1i*t*Dl)))*inv(Cl);
expml=@(t) Cl*diag(exp(diag(-1i*t*Dl)))*inv(Cl);

%time domain [0,t]
t=2*pi;
dim=1000;
time=linspace(0, t, dim);

%Response calculation
responseHeisnberg=zeros(dim,1);
responseLinear=zeros(dim,1);
graphicResponseLinear=zeros(dim,1);
responseOmega=zeros(dim,1);
graphicResponseOmega=zeros(dim,1);

for k=1:dim
    %Linear response:
    osstl=exppl(time(k))*oss *expml(time(k));
    responseLinear(k)=1i*sum(diag(rz*(osstl*Hex-Hex*
   osstl)));
    graphicResponseLinear(k)=trapz(time,responseLinear);

    %Heisenberg picture, exact response:
    heisenberg=expp(time(k))*oss*expm(time(k));
    responseHeisnberg(k)=sum(diag(rz*heisenberg));

    %Dissipation operator quantum exact response:
```

```
    r1t=omz*expp(time(k))*oss*expm(time(k));
    responseOmega(k)=sum(diag(rz*r1t));
    graphicResponseOmega(k)=trapz(time,responseOmega);
end

graphicResponseLinear=osszero-lambda*(graphicResponseLinear);
graphicResponseOmega=osszero+graphicResponseOmega;
hold on;
plot(time,graphicResponseOmega,'-k')
plot(time,responseHeisnberg,'--r')
plot(time,graphicResponseLinear,'-b')
xlabel('time')
ylabel('\langle\sigma_y\rangle_t')
title('\lambda=0.001, comparison for \langle \sigma_y \rangle_t')
legend('\Omega^0 ', 'Heisenberg','Linear')
```

Appendix C

Matlab code: application to the Lindblad equation

```
s1=[0 1
    1 0];
s2=[0 -1i
    1i 0];
s3=[1 0
    0 -1];

%CONSTRAINT: a1^2+a2^2+a3^2<1
a1=0.2;
a2=0.6;
a3=-0.1;
rz=0.5*(eye(2)+a1*s1+a2*s2+a3*s3)

%Observable
a=1; %real numbers
b=0;
ossd1=[a 0
    0 b];
c=1; %real numbers
d=1;
ossd2=[0 +c-d*1i
    +c+d*1i 0]; %diag2
%---------------------------------------------
```

```
%Lindblad equations
sp=0.5*(s1+1i*s2); %Lindblad operator dagger L^+
sm=0.5*(s1-1i*s2); %Lindblad operator L
frGamma=1;
frOmega=1;
H=frOmega*s3;
%analytical solution (e=|0>; g=|1>)
rhoee=@(t) rz(1,1)* exp(-frGamma*t);
rhogg=@(t) rz(2,2)+rz(1,1)*(1- exp(-frGamma*t));
rhoeg= @(t) rz(1,2)*exp(-(0.5*frGamma+2*1i*frOmega)*t);
rhoge= @(t) rz(2,1)*exp(-(0.5*frGamma-2*1i*frOmega)*t);
rhoesatta=@(t) [rhoee(t) rhoeg(t)
                 rhoge(t)  rhogg(t)];

%time interval:
t=6*pi;
dim=1000; %number of points in the discretization
time=linspace(0,t, dim);

%Dissipation operator expression
rzm=inv(rz);
omz=-1i*rzm*comm(H,rz);
omzc=-1i*comm(H,rz)*rzm;
omLz=omz+frGamma*(rzm*sm*rz*sp-sp*sm); %Omega_L
omLzc=omzc+frGamma*(sm*rz*sp*rzm-sp*sm); %Omega_L^+

%------------------------------------------

%time propagator in Lindblad case
P=-frGamma*1i*sp*sm;
Pc=frGamma*1i*sm*sp;
evol=P+H; %diag 1
evolC=+Pc+H;

M=H-0.25*1i*frGamma*eye(2); % H+M %diag 2
MC=H+0.25*1i*frGamma*eye(2); % H+M

%eigenvalues eigenvectors to build up the exponential

[C1,D1]=eig(evol);
[C1c,D1c]=eig(evolC);
```

```

[C2,D2]=eig(M);
[C2c,D2c]=eig(MC);

%diag 1
p1expm=@(t) C1*diag(exp(diag(-1i*t*D1)))*inv(C1); %U(t)
p1expp=@(t) C1c*diag(exp(diag(1i*t*D1c)))*inv(C1c);

%diag 2
p3expm=@(t) C2*diag(exp(diag(-1i*t*D2)))*inv(C2);%U_L(t)
p3expp=@(t) C2c*diag(exp(diag(1i*t*D2c)))*inv(C2c);

%Response calculation
exactResponseD2=zeros(dim,1); %analytical
exactResponseD1=zeros(dim,1);

OmegaDissDiag=zeros(dim,1);  %Dissip. op, diag 1
OmegaDResponse=zeros(dim,1);

OmegaDissDiag2=zeros(dim,1); %Dissip op, diag 2
OmegaD2Response=zeros(dim,1);

for k=1:dim
    %diag 1 dissipation operator
   rpt=0.5*(omLz*p1expp(time(k))*ossd1*p1expm(time(k))+p1expp(time(k))*...
       ossd1*p1expm(time(k))*omLzc);
    OmegaDissDiag(k)=sum(diag(rz*rpt));
    OmegaDResponse(k)=trapz(time,OmegaDissDiag);

    %diag 2 dissipation operator
    r2t=0.5*(omLz*p3expp(time(k))*ossd2*p3expm(time(k))+p3expp(time(k))*...
        ossd2*p3expm(time(k))*omLzc);
    OmegaDissDiag2(k)=sum(diag(rz*r2t));
    OmegaD2Response(k)=trapz(time,OmegaDissDiag2); %diag 2

    %analytical results
    exactResponseD1(k)=sum(diag(rhoesatta(time(k))*ossd1)); %diag 1
```

```
    exactResponseD2(k)=sum(diag(rhoesatta(time(k))*ossd2
   )); %diag 2
end
%<O>_t=<O>_0+ Response
osszero2=sum(diag(rz*ossd2)); %<O>_0
osszero1=sum(diag(rz*ossd1));
OmegaD2Response=osszero2+OmegaD2Response;
OmegaDResponse=osszero1+OmegaDResponse;

%plot diag 1
hold on
plot(time, OmegaDResponse, 'b')
hold on
plot(time, exactResponseD1, 'r--')
xlabel('time')
ylabel('\langle \pi_1 \rangle_t')
title('Lindblad')
legend( '\Omega expression','analytical')

%plot diag 2
figure;
hold on
plot(time, OmegaD2Response, 'b')
hold on
plot(time, exactResponseD2, 'r--')
xlabel('time')
ylabel('\langle O \rangle_t')
title('Lindblad')
legend('\Omega-expression','analytical')
```

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