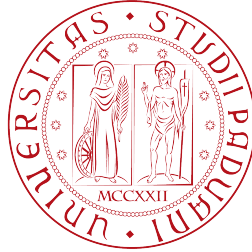


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Quantum Pure States Statistics
towards
Quantum Dynamics Simulations

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Abstract

Despite early developments on the foundations of quantum mechanics concern the wave function, quantum statistics has been developed with the density matrix formalism, leading to very important results in explaining molecular observations. Only recently, several authors argued a new interpretation by focusing on the wave function representing the quantum state of an isolated system, showing how a single wave function can exhibit statistical properties and generate the same results expected in the standard quantum statistical framework.

Starting from these results, investigation on the foundations of quantum statistical mechanics has gained recently a renewed interest. As a matter of fact, the possibility of studying single molecule properties as well as the need of a better understanding of the effect of quantum dynamics, in order to develop new nanoscaled materials suitable to quantum computing tasks, have opened new intriguing questions leading to quantum statistical approaches far from being well understood and accepted. In this framework the behaviour of a single realization of quantum systems has gained a central role in the description of molecular systems.

Furthermore, in recent years, an increasing number of studies has been presented on quantum dynamics through the numerical solution of the Schrödinger equation for systems of interacting components. These studies demonstrates that Quantum Dynamics Simulations could be a practicable route. In order to study phenomena such as dissipation, relaxation and thermalization, the focus has to be moved from isolated molecules to modular systems made of mutual interacting components, with model Hamiltonians possessing a sufficiently low

dimensional representation.

An important issue concerns the rules to be employed for the choice of the initial quantum state $|\Psi(0)\rangle$ for the simulation of isolated systems. As long as one considers molecular degrees of freedom interacting with a (model) environment, there are no reasons to select a particular quantum state for the overall system and, therefore, a random choice has to be performed amongst a well defined statistical ensemble of pure states. Furthermore, one would like to operate a choice assuring that the simulation of the system is in a well defined thermal state with given temperature. This necessarily calls for a statistical description like for classical systems.

A useful parametrization of the wave function will be presented in order to highlight the most appropriate variable for the statistical analysis. In particular some of them, called *phases*, retain all the dynamical information whereas the others, called *populations*, are the constants of motion. The latter, in particular are very important because they describe the equilibrium properties strictly related to the thermodynamic description.

Since the dynamics of wave function does not supply any information about populations, the definition of a probability distribution on these variables is required. Different probability distributions on populations have been proposed, only on the bases of reasonable assumptions and they validation has been performed only with *a posteriori* considerations. In particular Fresch and Moro have demonstrated how the agreement with thermodynamics can be employed to discriminate different probability distributions on pure states. This had led the uniform ensembles to be, up to now, the most self-consistent models for quantum pure states.

However, in this thesis I will highlight a drawback of the uniform distribution ensemble that can be described as follow: if we bring into contact two systems, even through a perturbative interaction, we are not able to describe the equilibrium properties after the interaction within the uniform distribution statistics, since the uniform character is lost. It represents a severe shortcoming of the statistical ensemble from a methodological point of view, since closed systems can be always considered as the result of interaction among previously isolated systems.

On the other hand this drawback introduces a further requirement of a different nature that can be used for the definition of a new statistical ensemble.

ble. In this work I intend to find and characterize a statistical ensemble for populations that overcomes the drawbacks of the uniform distribution of pure states. The invariance of the thermal state in the coupling of identical systems will be used as a guideline in the definition of a new probability distribution on populations.

Such an ensemble for pure states, called Thermalization Resilient Ensemble, provides a convenient framework for treating the interactions between quantum systems, as long as the structure of the statistical distribution is preserved and the identification of thermodynamic properties is assured. In perspective it should be the privileged statistical ensemble to implement Quantum Dynamics Simulations.

Once the average properties of the Thermalization Resilient Ensemble have been introduced, I will obtain a probability distribution on pure states with the use of a geometrical analysis on the Hilbert space. The surface elements of an ellipsoidal manifold will be related to the probability density on populations. As a matter of fact the explicit form of the probability distribution is a prerequisite in order to perform Quantum Dynamical Simulations. However the results obtained through the geometrical analysis cannot be easily extended to systems with unbounded energy spectrum and an alternative strategy has been developed.

A scaling algorithm on the basis of the uniform statistical ensemble will be described and this allows a well defined sampling of a probability distribution with desired averages. In this framework I demonstrate the emergence of thermodynamic behavior in the limit of macroscopic systems.

In the last part of the thesis I consider the dynamical features of the thermalization experiment. Two identical systems, initially at different temperature, will be brought in interaction and the analysis of the final equilibrium state will be performed for two different generic forms of the interaction Hamiltonian, highlighting how the statistical approach can be very useful in the definition of the equilibrium in complex quantum systems.

Sommario

Nonostante i primissimi sviluppi dei fondamenti della meccanica quantistica riguardassero la funzione d'onda, la statistica quantistica si è sviluppata attraverso il formalismo della matrice densità, portando a risultati considerevoli nella descrizione di fenomeni molecolari. Solo recentemente diversi autori hanno suggerito una nuova interpretazione della statistica quantistica, focalizzandosi sulla funzione d'onda che rappresenta lo stato di un sistema quantistico isolato. Essi hanno mostrando come una singola funzione d'onda possa presentare proprietà statistiche e ricondurre agli stessi risultati attesi dalla statistica quantistica tradizionale.

Grazie a questi contributi, lo studio dei fondamenti della meccanica statistica quantistica ha suscitato un rinnovato interesse. Infatti, la possibilità di studiare proprietà di singola molecola, unita alla necessità di una migliore comprensione degli effetti della dinamica quantistica per lo sviluppo di nuovi materiali nanostrutturati adatti al *quantum computing*, ha sollevato nuove stimolanti domande che rendono la statistica quantistica lontana dall'essere pienamente compresa e accettata. In questo contesto, il comportamento di una singola realizzazione di un sistema quantistico detiene un ruolo centrale nella descrizione di sistemi molecolari.

Recentemente è stato presentato un crescente numero di studi di dinamica quantistica che prevede la soluzione numerica dell'equazione di Schrödinger per sistemi a componenti interagenti. Questi lavori dimostrano come le Simulazioni di Dinamica Quantistica possano essere una via percorribile allo scopo di studiare fenomeni quali la dissipazione, il rilassamento e la termalizzazione. L'attenzione si è quindi spostata dalle molecole isolate a sistemi costituiti da

componenti mutualmente interagenti attraverso Hamiltoniani modello caratterizzati da una bassa dimensionalità.

È importante a questo proposito l'individuazione di regole che possano essere utilizzate nella scelta dello stato iniziale delle simulazioni per ogni sistema isolato. Infatti, ogniqualvolta vengano considerati gradi di libertà molecolari interagenti con un ambiente modello, non esistono ragioni per selezionare uno stato particolare per il sistema rispetto ad altri, e quindi una scelta casuale all'interno di un insieme statistico ben definito deve essere effettuata. Inoltre si preferisce effettuare tale scelta in modo da assicurare al sistema un ben definito stato termico ed una data temperatura. Tutto ciò richiede una descrizione di tipo statistico analoga a quella condotta per i sistemi classici.

Sarà presentata un'utile parametrizzazione della funzione d'onda allo scopo di evidenziare le variabili più adatte all'analisi statistica. Alcune di esse, dette *fasi*, contengono le informazioni dinamiche, mentre le altre, dette *popolazioni*, rappresentano le costanti del moto. Queste ultime, in particolare, sono molto importanti poiché descrivono le proprietà di equilibrio strettamente legate ad una descrizione termodinamica.

L'individuazione di una distribuzione di probabilità sulle popolazioni è necessaria dato che la dinamica della funzione d'onda non fornisce nessuna informazione riguardo ad esse. Sulla base di assunzioni ragionevoli, sono state proposte diverse distribuzioni sulle popolazioni la cui validazione può essere effettuata solo attraverso considerazioni *a posteriori*. In particolare Fresch e Moro hanno dimostrato come l'accordo con la termodinamica possa essere utilizzato per discriminare diverse distribuzioni di probabilità sugli stati puri. Questo ha portato gli *ensemble* uniformi ad essere i modelli fino ad ora formulati più autoconsistenti nella descrizione di sistemi isolati.

Tuttavia, in questa tesi evidenzierò un inconveniente delle distribuzioni uniformi che può essere riassunto come segue: quando vengono posti in contatto due sistemi, anche solo attraverso un'interazione perturbativa, non è più possibile descrivere le proprietà di equilibrio dopo l'interazione attraverso una distribuzione statistica di tipo uniforme, poiché perde tale carattere di uniformità. Ciò rappresenta un grave limite del modello da un punto di vista metodologico poiché sistemi chiusi possono sempre essere considerati come derivanti dall'interazione tra sistemi precedentemente isolati.

D'altra parte quest'inconveniente introduce un'ulteriore proprietà di di-

versa natura che può essere utilizzata nella definizione di un nuovo insieme statistico. In quest'elaborato intendo trovare e caratterizzare un insieme statistico per le popolazioni che superi l'inconveniente delle distribuzioni uniformi. L'invarianza dello stato termico nell'accoppiamento di sistemi identici verrà considerato come guida nella definizione di una nuova distribuzione di probabilità sulle popolazioni.

Tale *ensemble*, detto *Thermalization Resilient Ensemble*, fornisce un contesto adatto al trattamento delle interazioni tra sistemi quantistici, fintanto che la struttura della distribuzione statistica è preservata e l'identificazione delle proprietà termodinamiche assicurata. Questo potrebbe diventare l'*ensemble* statistico privilegiato per l'implementazione di Simulazioni di Dinamica Quantistica.

Dopo aver introdotto le proprietà medie del *Thermalization Resilient Ensemble*, ricaverò una distribuzione di probabilità sugli stati puri, mediante un'analisi geometrica sullo spazio di Hilbert. Gli elementi di superficie di un ellissoide verranno messi in relazione alla densità di probabilità sulle popolazioni. La forma esplicita della distribuzione di probabilità, infatti, è un prerequisito indispensabile per eseguire simulazioni di Dinamica Quantistica. Tuttavia, i risultati ottenuti mediante l'analisi geometrica non possono essere facilmente estesi a sistemi con spettro delle energie non limitato e si è reso necessario lo sviluppo di una strategia alternativa.

Verrà quindi descritto un algoritmo di riscaldo di un *ensemble* statistico uniforme che permette un campionamento ben definito di una distribuzione di probabilità con i valori medi desiderati. In questo contesto dimostrerò come il comportamento termodinamico emerga nel limite di sistemi macroscopici.

Nell'ultima parte di questo elaborato di tesi considererò gli aspetti dinamici dell'esperimento di termalizzazione. Due sistemi identici, inizialmente a diverse temperature, verranno messi a contatto attraverso due generiche forme dell'Hamiltoniano di interazione. Verrà poi effettuata l'analisi dello stato di equilibrio finale, evidenziando come l'approccio statistico possa essere molto utile nella definizione dell'equilibrio in sistemi quantistici complessi.

CHAPTER 1

Introduction

There is no line of argument proceeding from the laws of microscopic mechanics to macroscopic phenomena that is generally regarded by physicist as convincing in all respect.

— E. T. Jaynes [1]

1.1 Foundation of Statistical Mechanics

A cup of coffee naturally cools and an ice-cream melts when we walk in the park. Our every day experience is about phenomena that occurs in the macroscopic systems and that phenomena universally follow the laws of thermodynamics: the heat flows from a warmer to a colder body, a gas occupies all the available volume etc. The thermodynamic theory explains and describes the properties of the macroscopic world and it was developed long before the proof of the atomic structure of the matter. It was the 1842 when J. R. Mayer wrote the first fundamental law of thermodynamic by stating the conservation energy principle [2] and hypothesizing that mechanical work could be transformed into dissipated heat, but only some years later Joule was been able to experimentally verify the equivalence between work and heat in energetic term, by his famous experiment. At the same time the reversibility of a process

was investigated in terms of entropy that takes into account different ways in which the energy can be divided in terms of work and heat. Its large applicability and its mathematical simplicity have lead thermodynamics to become a so powerful theory that has led Einstein to state

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts" [3].

At the beginning of the 20th century, the thermodynamics was not the only theory available to explain our sensible world, in fact the mechanical laws had represented a different perspective on the behaviour of natural phenomena and the mechanics of moving bodies was well formalised only some decades before. Lagrange work on the late seventeenth, and the Hamilton's one in 1833, provided the general formulation we use nowadays, where the dynamical laws are described by differential equations with respect to generalized coordinates and momenta.

In a cultural framework where the mechanical laws were well established and the thermodynamics was demonstrating is wide applicability, the scientists of the 20th century tried to unify this two theories. They hypothesised that thermodynamics should be a manifestation of the interaction between the matter constituents, which can be described by mechanical laws. The atomistic basis of thermodynamics was firstly explored by Maxwell with the pressure described as an effect of collisions of the molecules with the container walls [4].

The most intensive work on the unification of mechanics and thermodynamics was made between the nineteenth and twentieth century with the development of the *statistical mechanics*, with a twofold scope. On the one hand it should explain thermodynamic observations from a purely mechanical sight and, on the other hand, it represent an important tool for the validation of our description of the matter at the atomistic/molecular level. If, by starting from a microscopic model for the dynamics of a system, one is able to reproduce macroscopic observables, then a valid test for the microscopic de-

scription results. Statistical mechanics has so assumed an important role in investigating natural phenomena. Later on with the development of the quantum mechanics and its prediction capability about fundamental constituent of matter, a quantum analogue of statistical mechanics, called *quantum statistical mechanics*, was developed. It has allowed the understanding of important phenomena like, for example, magnetism, electronic properties of solids and superconductivity.

The first major challenging problem faced with the foundation of statistical mechanics was represented by the difference in the number of parameters that mechanics and thermodynamics use to describe the same system. For definition, a macroscopic system, like a glass of water, a crystal or a cubic meter of gas, is made by a huge number N of components, where N is of the order of the Avogadro's number. The thermodynamic theory describes it with few state functions that account for the macroscopic properties of the system at equilibrium, while a mechanical description needs the positions and the momenta for each component of the system. In principle the mechanical description gather much information as long as the general solution is known but it would require the knowledge of all the initial conditions, which is practically impossible. On the other hand, although the motion of a macroscopic system obeys to the same mechanical laws as the system with a small number of particles, the presence of a large number of degrees of freedom gives rise to a qualitative new regularities, that determine the thermodynamics laws. It seems that the detailed time evolution plays no role for the macroscopic properties.

By starting from the lack of knowledge about the *microscopic state* or *microstate*, that is the set of positions and momenta for the components of the system, and from the well defined macroscopic observations, the statistical mechanics was developed. Gibbs, often considered as the pioneer of statistical mechanics, together with Boltzmann, suggested to consider all the possible mechanical states of the system, compatible with the macroscopic information, instead of selecting a specific microscopic state and observe its time evolution. It corresponds to observe an *ensemble* of systems, distributed on an suitable set of possible states [5]. More formally, the microscopic state of a system composed by N particles is described as a point $(q, p) = (q_1, \dots, q_{3N}, p_1, \dots, p_{3N})$, in the *phase space* Γ , where q_i and p_i represent the generalized coordinates and momenta, respectively. A change in the system state is described by a displace-

ment of the representative points in the phase space. The *ensemble* of systems then evolves as a cloud of representative points, each of them completely independent from the others. The statistical weight for the system when it is in the neighbourhood of a microstate (q, p) at time t is given by the probability density $\rho(q, p, t)$. In this condition, the probability distribution appears the appropriate tool for taking into account all the possible states for the system, and it can be interpreted as a manifestation of our lack of knowledge about the initial condition.

From the probability distribution on the phase space it is possible to calculate all kinds of average properties for the systems. For example, given an observable specified as a function $A(q, p)$ of phase space points, its ensemble average is defined as

$$\langle A \rangle := \int dp dq \rho(q, p, t) A(q, p) \quad (1.1)$$

and represents the average value with respect to all the states described within the ensemble. The most important success of the statistical mechanics derives from the capability of ensemble average to reproduce the values of thermodynamic observables as well as the amplitude of their fluctuations.

As just recalled, statistical mechanics start from the assumption of having some knowledge about the system, but not enough for a complete specification of its microscopic state, and it leads to an ensemble of systems of the same structure, distributed on all the accessible states of phase space with equation (1.1) providing the tools of making predictions on the average. If the probability distribution does not have an explicit time-dependence, it describes a system in the *statistical equilibrium*.

Let's consider now an isolated system, we suppose to have only partial information about the system, for example: its volume, its number of particles and its total energy lying within the energy shell $[E, E + \delta E]$. Without any further information we can only assume that, in equilibrium conditions, no particular region of the energy shell in the phase space plays a special role, provided that the previously mentioned constraints are satisfied. It corresponds to state that they should have the same statistical weight. As a consequence, all the points in the phase-space with the system energy $H(q, p)$ in the domain $E \leq H(q, p) \leq E + \delta E$ are equally probables. The ensemble with this prop-

erties is called *microcanonical*. Then, if the energy width δE is small enough, the associated distribution function ρ_{MC} is assumed to have the form

$$\rho_{MC} = \begin{cases} \frac{1}{\Omega(E)\delta E} & \text{if } E \leq H(q, p) \leq E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad (1.2)$$

where the normalization constant $\Omega(E)$ depends only on the energy. The microcanonical distribution is usually employed to predict properties of isolated systems with an energy defined within the range $[E, E + \delta E]$. Although we can understand the reason for attributing the same probability to regions of the phase space having the same volume, it is important to stress out that such *a priori* equ-probability plays the role of a fundamental postulate, and it is often invoked in the justification of of statistical methods for practical purposes.

Despite its success on the predictability on macroscopic systems, the conceptual bases of the statistical mechanics are still controversial. The most accepted justification is related to the ergodic theory, formulated by G. D. Birkhoff [6] and well summarized in the Khinchin's book [7]. It connects the single trajectory of a dynamical system with the averages on the phase space proposed by Gibbs. In particular the subspace covered by a trajectory should have specific properties in order to ensure that the infinite limits of the time average of an observable can be replaced by phase-space average of the same observable. A system is called *ergodic* if it nearly cover the subspace of the phase space with constant energy during its evolution. However it is not possible to demonstrate that a generic system, whose time evolution is described by classical mechanics, is ergodic. The statistical mechanics foundations are still an open issue despite the important role of its applications in investigating molecular phenomena.

When material systems are analysed at the molecular level, the classical mechanics should be replaced by quantum mechanics that supplies a more accurate and fundamental description of dynamical phenomena at this scale. Correspondly the classical statistical mechanics should be generalized in the form of a quantum statistical mechanics. Despite the revolutionary character of quantum mechanics and its deep differences with respect to classical mechanics, the development of quantum statistical methods has a strong analogue

with the classical counterparts and it is still structured like in the formulation given by Gibbs. The probability distribution is replaced by the so called *density matrix* that takes into account both the lack of information about the state of a system (as the classical probability distribution) and the lack of information about the outcomes of a measure, that is purely a quantum effect. The equilibrium situation for an isolated quantum system is described by the correspondent microcanonical ensemble in correspondence of a collection of systems with energy in the interval $[E, E + \delta E]$ and with an equal *a priori* probability. For several decades this formulation has been employed and has produced remarkable results in many fields of molecular problems, like magnetism, electric properties of solids etc. Despite, or perhaps thanks to, this success the foundation of quantum statistical mechanics has not been the topic of a scientific debate as its classical analogue [8, 9].

Only recently several authors are arguing about new interpretations of statistical mechanics relying the basic quantum mechanical tools. Here we want only to cite the huge effort from Gemmer, Michel and Mahler in their book [10] where they report and develop the thermodynamics description as emerging from a quantum mechanical perspective. Even if our approach is slightly different we share the importance of the typicality in the emergence of thermodynamics from a purely mechanical behaviour.

Both equilibrium and non-equilibrium quantum statistical mechanics have attracted a significant amount of attention due to the important improvements on the technological side that has allowed the possibility to investigate single molecule properties as well as quantum effect, like coherences in molecular systems.

In my opinion, the most important progress in the last years resides in the change of perspective which attributes to the wave function a central role in the quantum statistical mechanics because it fully represents the physical behaviour of an isolated systems.

1.2 Pure State Quantum Statistical Mechanics

Despite early developments on the foundations of quantum mechanics concern the wave function, quantum statistics was developed within the density matrix formalism, leading to very important results in explaining molecular observations. Unlike its classical analogue, whose foundations have been debated for decades, the quantum statistical mechanical formalism has been largely accepted quite early. Only recently several authors argued a new interpretation on this topic based on the wave function and, following Lloyd [11, 12] and Gogolin [13], we refer to it as *pure state quantum statistical mechanics*. The main goal is to connect the thermodynamic behavior with the quantum world within a more self-consistent framework. The field has attracted much attention and very different contributions are present in literature nowadays.

One of the first interesting understanding is by Lloyd that has compared the results of a measurement on many copies of the same system, all prepared in the same state (wave function), with the results predicted by microcanonical formulation. He discovered that most pure states for the system produce the statistical distribution of results that differs from the ensemble averages by only a small amount. It is a very interesting result demonstrating that, thanks to the intrinsic statistical behavior of quantum states, a single wave function can reproduce the same results of standard equilibrium quantum statistics. Although his scopes were very far from ours, he gave an hint to the connection between single wave function representation of a quantum system and the statistical mixture of the standard statistical formulation.

Some years later, both Deutsch [14] and Srednicki [15] independently extended this result by identifying properties for the wave function that allow a system to thermalize, in the sense that the wave function reproduce the microcanonical results, considered as equilibrium properties. In particular Srednicki elaborated the so called *eigenstate thermalization hypothesis* (ETH) where he suggested that a system thermalizes, for physical interesting observables, when it has eigenstates that reproduce the behaviour described by the microcanonical ensemble. This hypothesis has been largely investigated in the last years from both points of view of supporting evidences (see ref. [16, 17, 18] and related references) and of his breakdown conditions [19, 20]. Even though the

large number of papers on this topic, there are no general theoretical explanation supporting this hypothesis.

The work of Lloyd with the works related to ETH just mentioned can be considered as examples of how a single wave function can exhibit statistical properties and generate the same results expected in the standard quantum statistical framework. In the same direction an important contribution is the one by Goldstein and al. in ref. [21]. They have considered a system weakly coupled with a thermal bath, demonstrating that the reduced density matrices for the overwhelming majority of the wave functions, describing the composite system (system + bath), are canonical. It means that it is possible to reproduce the results of standard quantum statistical mechanics without considering a statistical mixture of wave functions. The canonical ensemble seems to be inevitable in quantum mechanics, leading to the conclusion that the microcanonical ensemble is unnecessary. This represents a very important result because it promotes the substitution of an unprovable assumption (the equal *a priori* probability) with a demonstrable principle, called *canonical typicality*.

Popescu et al. have pushed further the reasoning by generalizing the canonical typicality in a *general canonical principle* [22]. The generalization resides in the general constraints considered for the overall system state that do not consist only in the standard energy constraint. Since the canonical state represents the state of a sufficiently small subsystem when the overall system is in the equiprobable state, the general canonical principle, using the words of the authors, can be interpreted as "a principle of apparently equal *a priori* probability so, the overwhelming majority of pure state are not distinguishable from the microcanonical ensemble from the subsystem point of view. As Popescu et al. have recognized, all these results are kinematic without invoking the quantum dynamics.

An interesting intuition about that topic came from the work of Zurek in his *decoherence program* [23, 24] where he puts the attention on the unitary evolution of the wave function. In his opinion the classical experience can be explained with a *environment-induced superselection* of the quantum state caused by the interaction with the environment. Although the topic is still under debate, in our opinion it has touched the point: the wave function fully characterize the state of a quantum system and the interaction between system and environment has to be taken into account to understand both quantum

dynamics and the emergence of the classical world.

In our opinion a deeper knowledge about thermalization processes could give important insight on the relaxation that are largely widespread in several fields of chemical interest.

The brief report just presented, far from being exhaustive, was intended to introduce the new the perspective of quantum statistical mechanics. Away from the ensemble sight, several authors have started to consider the wave function as central object of investigation, leading interesting progresses in the interpretation of thermodynamics as emerging from first principle as well as relaxation to equilibrium situation from a purely quantum dynamics.

1.3 Our approach: overview of the thesis

Investigation on the foundation of quantum statistical mechanics has recently gained a renewed interest. As a matter of fact, the possibility of studying single molecule properties as well as the necessity of a better understanding on quantum dynamics, in order to develop new nanoscaled materials suitable to quantum computing tasks, have opened new intriguing questions leading the quantum statistical mechanics far from being well understood and accepted.

The most relevant change of perspective of the last years is about the object of interest: from the statistical density matrix describing the average over many realizations of the same quantum system to the wave function describing the single realization. Several authors have shown [11, 21, 22, 25] that the statistical analysis on the wave function can provide an equivalent description of that deriving from statistical density matrix and the equal *a priori* probability postulate of the standard quantum statistical mechanics can be overcome. The main advantage of the analysis on the wave function is the possibility to describe its quantum dynamics directly from the solution of Schrödinger equation.

With this thesis I want to give a little contribution on the statistical description of quantum pure states and to show how the statistical tools can provide new insights on the study of dynamical processes fully from a quantum perspective. With some effort it might produce new and interesting understanding on relaxation at molecular level described within a self consistent theoretical framework.

In the following chapter I will introduce a useful parametrization of the wave function that allows to identify the dynamical variables and the constants of motion. In particular those constants are the only variables that describe the equilibrium of any generic property of the quantum system and also the most difficult to analyse, due to the absence of any *a priori* information about them. Then I will briefly introduce the statistical description on the wave function by describing the mostly accepted probability distribution on the constants of motion, characterized by its uniformity in the Hilbert space. It will be explained that thermodynamic description naturally emerge from that ensemble since different realizations of a quantum system behave essentially in the same way, once the large size limit is considered. This will conclude the introductory part of my thesis.

In the third chapter I will highlight the major drawback of the uniform ensemble that emerges from the realization of the thermalization experiment. Once two systems with different temperatures are brought in contact, the final equilibrium state cannot be anymore described by the uniform ensemble, since an anisotropy on the Hilbert space naturally arises. Precisely from the failure of uniform ensembles a new guideline has been identified in order to develop a statistical ensemble able to describe the equilibrium after the thermalization. The invariance with respect to the thermalization shows to be a valid criterion that leads to the Thermalization Resilient Ensemble whose properties are in agreement with thermodynamics. One of the main features of the new ensemble is that clear thermal states can be easily defined even at microscopic level.

The fourth chapter is devoted to the development and characterization of the probability distribution of the Thermalization Resilient Ensemble through a geometrical analysis of a surface embedded in the Hilbert space. In particular a surface element of an ellipsoid will be related to the probability density on the constants of motion which, in turn, accounts for the anisotropy of the Hilbert space. However the model parameters are hardly manageable and the connection between them and the thermalization resilient ensemble is not easy to rationalise.

An alternative sampling algorithm of the Thermalization Resilient ensemble will be developed in the fifth chapter, starting from the well known behaviour of uniform sampling through a scaling procedure. This allows for the

single realizations of quantum systems with a well defined thermal state as well as the explicit emergence of the thermodynamics in increasing the number of components for the quantum system.

In the last chapter the thermalization experiment will be completely described at quantum level with the tools developed in the previous chapters. Two identical system will be brought into interaction by the use of two different Hamiltonians. The subsystem energies will be presented in order to characterize the equilibrium properties. It will be accompanied by an analytical description.

CHAPTER 2

Statistics of Isolated quantum systems

In this chapter a brief introduction about the standard quantum mechanical formalism is provided in order to recall the basic principles and to introduce the notation that will be used in the rest of the thesis. We then explore the meaning of equilibrium in quantum systems from a statistical point of view. The importance of the equilibrium resides in its connection with thermodynamics and its emergence from the quantum description, based on the dynamics of the wave function.

A useful parametrization of the wave function will be presented in order to highlight which information can be deduced from its dynamics and, at the same time, it will be clear that the constants of motion, called *populations*, retain all the equilibrium information strictly related to the thermodynamic description.

The properties of the wave function parameters will be presented providing the needed tools to describe ensembles of wave functions. By following the ergodic theorem, it is possible to obtain a uniform statistical distribution on the dynamical variables from the dynamics. On the other hand, the absence of any *a priori* information about populations complicates their analysis. As a matter of fact only reasonable hypothesis can be taken into account that lead to different possible probability distributions. The most self-consistent one and well analysed, available in literature, is called *Random Pure State Ensemble*

(RPSE). Its main features will be presented as well as its major drawbacks.

2.1 Quantum dynamics of isolated systems

The state of an isolated quantum systems is fully described by the *wave function* $|\Psi(t)\rangle$ and, whatever the wave function is, the system is said to be in a *pure state*. A wave function can be defined only for completely isolated systems and formally it can be represented as a ray vector in a Hilbert vectorial space \mathcal{H} . All vectors that differs only by their modulus represent the same quantum state. A unitary modulus is often chosen as representative and the wave function is then normalized as

$$\langle\Psi(t)|\Psi(t)\rangle = 1 \quad (2.1)$$

where the $\langle\cdot|\cdot\rangle$ represents the scalar product in the bra-ket notation. Where not otherwise specified, the wave function will be considered normalized. For the properties of Hilbert space, it is possible to choose a orthonormal basis set (u_1, \dots, u_i, \dots) and express each vector of the space as a linear combination.

$$|\Psi(t)\rangle = \sum_i c_i(t) |u_i\rangle \quad (2.2)$$

where the coefficients of the expansion $c_i(t) = \langle u_i | \Psi(t) \rangle$ represent the projection of the wave function on the selected basis vectors or, in other words, they are the coordinates with respect each basis vector. The set of coefficients completely describes the dynamics of the wave function and retains all the information about its behaviour, it can be interpreted as the analogue of the set of coordinates and momenta in the classical phase space. In principle, the Hilbert space has infinite dimension but, for practical purpose, the wave function is commonly considered to belong to a finite dimensional subspace of the total Hilbert Space $\mathcal{H}_N \subseteq \mathcal{H}$, where N is its dimension.

The wave function is time dependent and evolves according to the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (2.3)$$

where i is the imaginary unit, \hbar the reduced Plank constant and \hat{H} is the time-independent Hamiltonian operator that represents the energy of the sys-

tem. Equation (2.3) implies that the eigenvectors of the Hamiltonian $|E_k\rangle$ are a privileged basis in the description of the time evolution of the wave function since they allow to obtain a direct solution of equation (2.3). Given the eigenvalue problem of the Hamiltonian as

$$\hat{H} |E_k\rangle = E_k |E_k\rangle \quad (2.4)$$

where E_k is the eigenvalue associated to the eigenvector $|E_k\rangle$, and where the eigenvectors are orthonormal, i.e.

$$\langle E_k | E_{k'} \rangle = \delta_{k,k'} \quad (2.5)$$

the solution of Schrödinger equation leads to

$$c_k(t) = c_k(0) e^{-\frac{i}{\hbar} E_k t} \quad (2.6)$$

where $c_k(0) = \langle E_k | \Psi(0) \rangle$ represents the initial condition in the energy representation. The wave function can be then expressed as

$$|\Psi(t)\rangle = \sum_k c_k(0) e^{-\frac{i}{\hbar} E_k t} |E_k\rangle \quad (2.7)$$

in order to highlight the oscillating behavior of the time dependence with respect each Hamiltonian eigenvectors.

An equivalent description of a pure state can be performed with the use of the density matrix operator $\hat{\rho}(t)$ defined as

$$\hat{\rho}(t) := |\Psi(t)\rangle \langle \Psi(t)| = \sum_{k,k'} c_k(t) c_{k'}^*(t) |E_k\rangle \langle E_{k'}| \quad (2.8)$$

where in the last equivalence we explicitly used the Hamiltonian eigenvectors as basis set. It is simple to notice that the elements of the density operator are nothing else than the product of coefficients of the wave function

$$\rho_{k,k'} = c_k(t) c_{k'}^*(t) \quad (2.9)$$

In the case of pure states of isolated systems the density matrix represents the projection operator onto the direction of the wave function and it has the

following properties:

- unit trace $\text{Tr}\{\rho(t)\} = 1$;
- hermicity $\rho(t) = \rho(t)^\dagger$;
- idempotency $\hat{\rho}(t)\hat{\rho}(t) = \hat{\rho}(t)$;
- positive definiteness $\langle \phi | \hat{\rho}(t) | \phi \rangle \geq 0$ for every $|\phi\rangle \in \mathcal{H}$.

Its time evolution is described by the Liouville-von Neumann equation

$$i\hbar \frac{\partial}{\partial t} \rho(t) = [\hat{H}, \hat{\rho}(t)] \quad (2.10)$$

where $[\hat{H}, \hat{\rho}] := \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$ is the commutator of the two operators.

Thanks to these simple definitions we have introduced two different, but equivalent, representations for the state of a quantum system, the wave function and the density matrix operator of the pure state, both equipped with their time-evolution equations. The third important ingredient in the description of quantum system is the definition of the properties we want to investigate. In quantum mechanics the observables are defined as expectation values of operators. For example, given a generic operator \hat{A}

$$a(t) := \langle \Psi(t) | \hat{A} | \Psi(t) \rangle \quad (2.11)$$

represents its expectation value and it will be, in general, time-dependent. Equation (2.11) can be also expressed in the following way

$$a(t) = \text{Tr}\{\hat{A}\hat{\rho}(t)\} = \sum_{k,k'} A_{k,k'} c_k(0) c_{k'}^*(0) e^{-\frac{i}{\hbar}(E_k - E_{k'})t} \quad (2.12)$$

where $A_{k,k'} = \langle E_k | \hat{A} | E_{k'} \rangle$. The first equivalence of equation (2.12) shows the relation between the expectation value and the density matrix while the second equivalence explicitly considers the eigenvectors coefficients. The expectation value is nothing more than an average of all the possible measures made on the quantum system where the wave function coefficients represent the probability density with respect to all the possible outcomes.

From the Liouville-Von Neumann equation (2.10) we can observe that all the operators that commute with the Hamiltonian are constant of motion be-

cause they are diagonal in the same basis of the Hamiltonian. In the particular case where the operator is the Hamiltonian, its expectation value is the energy of the system and it is a conserved quantity.

$$E = \langle \Psi(t) | \hat{H} | \Psi(t) \rangle = \sum_k |c_k(t)|^2 E_k = \sum_k |c_k(0)|^2 E_k \quad (2.13)$$

In addition, we could be not interested in the properties of the system as a whole but only on a part of it, called *subsystem*. Such a framework allows the investigation of the behavior of a subsystem S of the overall system, composed by the subsystem S and a generic environment E . In particular, since the overall system is in a pure state, its subsystem is entangled with the environment and cannot be described as wave function. The correct tool to specify the subsystem properties is the reduced density matrix $\hat{\sigma}(t)$, defined as the partial trace of the pure state density matrix operator

$$\hat{\sigma}(t) = \text{Tr}_E\{\hat{\rho}(t)\} \quad (2.14)$$

where the subscript E means that the trace is performed on the environment degrees of freedom.

The definitions and the equations above represent the core of the necessary tools for the description of the time evolution of an isolated quantum system as early described, for example, by Schrödinger [26] and Von Neumann [27]. Given the initial conditions it is possible to follow the system's dynamics as well as the time evolution of expectation values.

2.2 Quantum Mechanical Equilibrium

Since the beginning of the 20th century, scientists have been challenged by the derivation on the thermodynamic properties from a microscopic description. This issue, closely related to the foundation of statistical mechanics, was investigated mainly by focusing on the properties of a collection of systems. Only recently this fundamental topic has gained a renewed interest, both from the classical [28, 29]¹ and from the quantum perspective. This

¹The Jarzynski equality that relates equilibrium thermodynamic states with non equilibrium processes represents an example of important recent achievement on the classical framework.

rejuvenated attention is due to the technological improvements concerning investigation on single molecule properties [30], as well as because of the need of a better understanding of the mechanism underlying quantum dynamics in order to obtain nanoscale devices, this fundamental topic has gained a renewed interest. In particular the problems related to quantum computing have developed an interesting debate on the concepts of equilibrium and equilibration [25, 31, 32, 33, 34] in an isolated system. According to our point of view, it is important to point out that standard quantum statistical mechanics do not address the problem of equilibration or dynamics of a quantum isolated system [8, 9], as a matter of fact the microcanonical or canonical formalism are related to systems yet in equilibrium. Pure quantum mechanical predictions begin now to be considered more fundamental with respect to standard statistical quantum mechanics formalism [16, 35] and have recently attracted a significant amount of attention.

This represents an important change of perspective with the focus shifted from the ensemble average over a collection of systems to the predictability of single realization of a quantum system. The pure states dynamics is now widely investigated in order to get new insight into relaxation problems.

The foundation of quantum statistical mechanics themselves starts to be reconsidered and nowadays the concept of equilibrium is addressed in several ways, mainly through a comparison with the standard ensemble perspective. An isolated system, or one of its subsystems, are considered to be in equilibrium as soon as they reproduce the same results expected by the *microcanonical* or *canonical* density matrices, respectively. Although the focus is either on the overall system or in the subsystem, the argumentations are often closely related.

Before going deeper into details of different perspectives of equilibrium situation, it is useful to recall the standard statistical density matrix formalism and to briefly illustrate the main features of microcanonical and canonical density matrices.

2.2.1 Standard quantum statistical mechanics

The most important ensemble in standard quantum statistical mechanics is represented by the *microcanonical ensemble*. As in classical mechanics, it is

used in the description of isolated systems with many degree of freedom, where a complete characterization of the system state is impossible. The microcanonical ensemble is used to make predictions about the outcomes of experiments performed on systems where the energy is known. Its strength also depends on the fact that the other ensembles, like *canonical* and *gran-canonical*, can be derived from this, under some reasonable assumptions [36].

Like in the classical case, the microcanonical formalism considers that only the eigenvalues $|E_k\rangle$ within an energy interval $[E, E + \delta E]$ contributes to the systems properties. It is expressed by the *microcanonical density matrix* ρ_{mc} as

$$\hat{\rho}_{mc} = \frac{1}{\Gamma(E)} \sum_{E \leq E_k \leq E + \delta E} |E_k\rangle \langle E_k| \quad (2.15)$$

where $\Gamma(E)$ represents the number of states whose energy lies between E and $E + \delta E$, while outside of the energy range the density matrix vanishes. The energy interval selects a specific subspace of the total Hilbert space that is often called *active space*. In the case of macroscopic systems, the eigenenergies spectrum forms almost a continuum and the number of states $\Gamma(E)$ can be expressed as the integral on a selected interval as

$$\Gamma(E) = \int_E^{E+\delta E} dE \tilde{g}(E) \quad (2.16)$$

where $\tilde{g}(E)$ is the extension to the continuum of the real density of energy eigenstates

$$g(E) = \sum_k \delta(E - E_k) \quad (2.17)$$

and $\delta(E - E_k)$ is the Dirac delta function. If in addition $\delta E \ll E$ and $\tilde{g}(E)$ varies only slightly in that interval, it is possible to write

$$\Gamma(E) \simeq \tilde{g}(E) \delta E \quad (2.18)$$

In the classical case the microcanonical probability density is well motivated as the results of classical chaos that make reasonable the assumption of ergodicity. In those conditions one is easily persuaded that every initial condition for a system explores uniformly in time all the phase space compatible with the system's energy. If it is possible to demonstrate that the system is

ergodic, the Kinchin theorem provides a good explanation of the agreement between statistical mechanics predictions and experimental results. Despite these methodological foundations, one should take into account that classical systems are not ergodic, and in the quantum mechanical framework the ergodicity appears even less justified.

Due to the strictly linear time evolution, the mechanics of chaos is completely absent in the quantum dynamics and it is an open question how isolated quantum mechanical systems, prepared in an arbitrary initial state, evolve toward a state that resembles the thermodynamics in its microcanonical ensemble. Standard quantum statistical mechanics did not address such a problem [8, 9].

Another important ensemble in quantum mechanics is the so called *canonical ensemble*. It describes a system which is not isolated but in contact with a large thermal bath. The canonical density matrix has the form

$$\hat{\sigma}_{can} = \frac{\exp(-\beta \hat{H}_S)}{Z} \quad (2.19)$$

where \hat{H}_S is the subsystem Hamiltonian, Z is the partition function and $\beta = 1/k_B T$ is the inverse temperature. The partition function Z is defined as

$$Z = \text{Tr}\{\exp(-\beta \hat{H}_S)\} \quad (2.20)$$

While the microcanonical ensemble describes isolated systems, canonical ensemble allows the subsystem to exchange energy with the thermal bath and the important thermodynamic parameter is represented by the temperature. The canonical density matrix is usually obtained from the microcanonical ensemble by assuming that the subsystem S is weakly coupled with the thermal bath B [8]. Gibbs was the first who suggested this important ensemble in the classical framework [5] and it is interesting to notice the assumptions he made on the classical side are the same for obtaining its quantum equivalent.

2.2.2 Equilibrium on the wave function perspective

The new perspective places the wave function at the center of the theoretical investigation trying both to describe the emergence of thermodynamics from first principles and to understand why the standard formulation works so well

in the description of quantum systems. In this direction, the interest is focused on the mechanism that allows the equilibration to occur or on which properties the system should have in order to reproduce the standard thermal equilibrium.

Considering the last point the so called *Eigenstate Thermalization Hypothesis* (ETH) is gaining a widespread interest. The ETH, as firstly proposed by Deutsch [14] and Srednicki [15], states that a system thermalizes whenever the expectation values for an eigenstate, or for a set of eigenstates in a narrow energy interval, is able to reproduce the result obtained by using the micro-canonical density matrix. The hypothesis is largely debated [37, 16, 17, 38, 39] and proved for several systems.

Another common formulation of the equilibrium considers the system composed by a small subsystem in contact with a large thermal bath. In particular, starting from a pure state, the distance between the reduced density matrix for the subsystem and the equilibrium canonical density matrix has been investigated, accounted as the trace of the difference between their matrix representations. As long as the bath has a macroscopic dimension the canonical density matrix is recovered almost always and it allows to overcome the equal *a priori* probability principle. In this field I only want to cite two important works written by Goldstein *et al.* [21] and Popescu *et al.* [22]. It is important to point out that in these approaches the energy eigenstates of the Hamiltonian do not play any role.

In the same direction, a different approach considers the equilibrium as the result of quantum dynamics of the wave function. About this topic, interesting results were obtained by Popescu and al. [25] by focusing on the equilibration of a subsystem. They demonstrated that all the interacting large systems have a subsystem in equilibrium, in the sense that the subsystem spends almost all time in a state very close to the equilibrium state, defined as infinite time average. The underlying assumption concerns the energy distribution of the initial wave function and the dimension of the Hilbert space where the pure state is defined.

In my opinion, hypothesizing any particular properties on the Hamiltonian eigenstates, like in the ETH approach, could lead to the possible contradiction of explaining a not well understood phenomenon (the thermalization) with an hypothesis that cannot be proved, but only verified. In my opinion, the large energy distribution of the initial state is a more reasonable assumption. In the

case of complex quantum systems any actual Hilbert space has large dimensions, and a generic state will have significant overlap with many eigenstates.

2.2.3 Equilibrium from the dynamics of the wave function

In this thesis, I fully endorse the pure state quantum approach and the equilibrium properties will be related to evolution of the quantum system. Let's consider a generic time dependent observable $a(t)$. A possible definition of the correspondent equilibrium property \bar{a} could be that associated to the infinite time limits of a generic observable

$$\bar{a} = \lim_{t \rightarrow \infty} a(t) \quad (2.21)$$

However it is clear from equation (2.12) that the expectation value of a generic operator in quantum closed system has an oscillating behaviour described by the complex exponential. It means that it cannot equilibrate in the sense that it will approach a time independent stationary state, since the time dependence is of oscillating type. The system will reproduce any initial state after a certain time, called Poincaré recurrence time [40, 41] and, although it is possible that the recurrence time will be longer than the actual age of the universe, a infinite temporal limit does not exist. The only exception is represented by a system prepared in an Hamiltonian eigenstate, that is already a stationary state. Such a situation cannot be easily realised, since a slightly different initial state as well as a small perturbation in the Hamiltonian would lead to the situation of a wave function with many contributions of different eigenstates.

An alternative meaningful definition of equilibrium is the one related to the time average, as firstly suggested by Von Neumann [27] (a commentary article concerning this topic is proposed by Goldstein *et al.* in ref. [42]). The infinite time limit is substituted with the infinite-time average limit of a generic observable $a(t)$ as

$$\bar{a} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} dt a(t) = \text{Tr}(\hat{A}\bar{\hat{\rho}}) \quad (2.22)$$

where

$$\bar{\hat{\rho}} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} dt \hat{\rho}(t) \quad (2.23)$$

If we only assume the so called *non-degeneracy condition*, such that the Hamiltonian eigenstates are not degenerate, the previous limit is readily performed as $\lim_{t \rightarrow \infty} (1/t) \int_0^t d\tau e^{-i\tau(E_k - E_{k'})} = \delta_{k,k'}$. The equilibrium property of the expectation values of equation (2.12) can be expressed as

$$\bar{a} = \sum_k |c_k|^2 A_{kk} \quad (2.24)$$

This time average highlights how the square moduli of the coefficients $|c_k|^2$ represent the constants of motion of the quantum dynamical problem.

The information on the time average only partially characterizes the dynamical system that may fluctuate largely around the equilibrium values of the properties. When the fluctuation amplitude is comparable with the interval of the possible values of the property, it is meaningless to speak about equilibrium since the system does not spend much time around its time average.

Since evaluating the amplitude of the fluctuations around the time average becomes necessary in order to fully identify an equilibrium property, we introduce the deviation $\Delta a(t)$ of a quantity $a(t)$ from its average \bar{a}

$$\Delta a(t) = a(t) - \bar{a} = \text{Tr}\{\hat{A}(\hat{\rho}(t) - \bar{\rho})\} \quad (2.25)$$

from which we can quantify the amplitude of the fluctuations as time average of the squared deviation

$$\overline{|\Delta a(t)|^2} = \sum_{k \neq k'} |A_{kk'} \bar{\rho}_{kk'}|^2 \quad (2.26)$$

In particular the last equality is obtained in the so called *non resonance condition* [43, 33], that is slightly stronger with respect to the non-degenerate one because it implies also non degenerate transition frequencies.

An equilibrium property can be identified by the analysis of its infinite time average together with its mean square deviation. Two important contributions by Reinmann [44, 45] and by Bartsch and Gemmer [46] have demonstrated how the fluctuations around time average, defined as (2.26), are small for the majority of the wave functions, under the condition that the system is spread over many Hamiltonian eigenstates. In particular, the expectation values of physical interesting observables show a narrow distribution

with respect to all the possible wave functions [44] and moreover the expectation values at a given time will yields similar expectation values at any later time [46]. Given those results for complex quantum systems, it is possible to state that the dynamics of expectation values is almost always close to the average and this gives strength to the above definition of equilibrium properties (see equation (2.22)). From now on, the overbar will denote the equilibrium properties defined as infinite time average.

The non resonance condition, employed in obtaining equation (2.26), represent a general and mild condition. One needs only to think that the spectrum of real systems is characterized by a partial random character, due to very different types of interaction modulated by the interparticle distances. This avoids the degeneracy of the energy eigenstates as well as the the resonance condition of transition frequency.

If on the one hand the just presented constants of motion of the Schrödinger dynamics are fundamental in the description of equilibrium properties in quantum systems, on the other hand they represent a misty object and difficult to deal with, since the complete lack of *a priori* information about them. In my opinion, this lack of knowledge can be only treated in a statistical framework that naturally leads to the definition of a statistical ensemble of pure states.

2.3 Ensemble of Pure States

Since equilibrium properties are described only by the constants of motion $|c_k|^2$, it is useful to parametrize the wave function coefficients of equation (2.6) in their polar form

$$c_k(t) = \sqrt{P_k} e^{-i\alpha_k(t)} \quad (2.27)$$

where P_k are called *populations* and $\alpha_k(t)$ *phases*. The phases α_k are linearly dependent on time

$$\alpha_k(t) = \alpha_k(0) + E_k t/\hbar \quad (2.28)$$

while the populations represent the constants of motion. They are no more than the square modulus of the coefficients representing the wave function projection on each eigenstate $|E_k\rangle$

$$P_k := |c(t)|^2 = |c(0)|^2 \quad (2.29)$$

and they are normalized as

$$\sum_k P_k = 1 \quad (2.30)$$

The summation is extended to all the Hilbert space directions, which in principle can be infinite. If we compare the definition of population with equation (2.9) we recognize immediately, due to the wave function, that populations are the diagonal elements of the density matrix

$$P_k = \rho_{k,k} \quad (2.31)$$

The polar parametrization of coefficients c_k enables us to describe the wave function according to the sets of time-dependent phases $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_k, \dots)$ and time independent populations $P = (P_1, P_2, \dots, P_k, \dots)$. From this new parametrization, a general equilibrium property is expressed as

$$\bar{a} = \sum_k P_k A_{kk} \quad (2.32)$$

while its fluctuation

$$\overline{\Delta a} = \sum_{k k'} P_k P_{k'} |A_{k k'}|^2 \quad (2.33)$$

In addition, a deeper look into equation (2.12), shows that any property of a quantum pure state can be represented as a function of the phases $f_P(\alpha)$ parametrically dependent on the populations, where its equilibrium value is completely defined by populations

$$\overline{f_P} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt f_P(\alpha(t)) \quad (2.34)$$

Taking note of the importance of the populations variables in the description of quantum pure states, we now have to face the problem of their characterization. Since the impossibility of knowing the exact spreading on the Hamiltonian eigenstates of a quantum system, from experimental data, in my opinion, the only viable option is the statistical approach. It can be formalized through the definition of an ensemble of pure states, where *ensemble* is meant as probability distribution $p(P)$ for the populations specifying our state.

Large differences exist between this ensemble definitions and the one proposed by Gibbs in its original works [5, 47, 48]. Here no real ensemble, like

collection of systems, is ever considered, since the object of interest is the single wave function describing the quantum isolated system.

Our need of the definition of a statistical ensemble on the wave function is no more than the manifestation of our lack of knowledge on the system, i.e. the typical framework of statistical mechanics.

More formally, the ensemble is described by a sample space D of the possible sets of populations P and the corresponding probability density $p(P)$. In principle several choices are possible in order to describe the sample space, each of them can lead to different probability distribution on populations. In the following section I will briefly describe the main one, called *Random Pure State Ensemble*, showing also its connection with the thermodynamics.

2.3.1 Random Pure State Ensemble

Starting from the pure state analysis Fresch and Moro have developed the Random Pure State Ensemble (RPSE) [43, 49, 50]. Following their definitions, the wave function belongs to a N -dimensional Hilbert space \mathcal{H}_N , called *active space* where the set of eigenfunctions of the Hamiltonian $|E_k\rangle$ (with $1 \leq k \leq N$ and $k \in \mathbb{N}$) forms an orthonormal basis set for that space. The only constraint on the sample space D is the normalization and the positiveness of each population

$$D = \{(P_1, P_2, \dots, P_N) \in \mathbb{R}^N \mid \sum_k^N P_k = 1, \quad P_k \geq 0 \forall k\} \quad (2.35)$$

The populations associated with directions outside the active space vanish, such that $P_k = 0$ for $k > N$. The above sample space describes a $(N - 1)$ -dimensional simplex on the populations space. Since no *a priori* properties can be attributed to wave function, no preferential direction in the Hilbert space was considered and the populations of the unitary vector, representing the wave function, are chosen according to the uniform distribution on the simplex.

The constant probability density of RPSE statistics was derived from a geometrical analysis on the Hilbert space by considering the $N - 1$ independent populations

$$p(P_1, P_2, \dots, P_{N-1}) = (N - 1)! \quad (2.36)$$

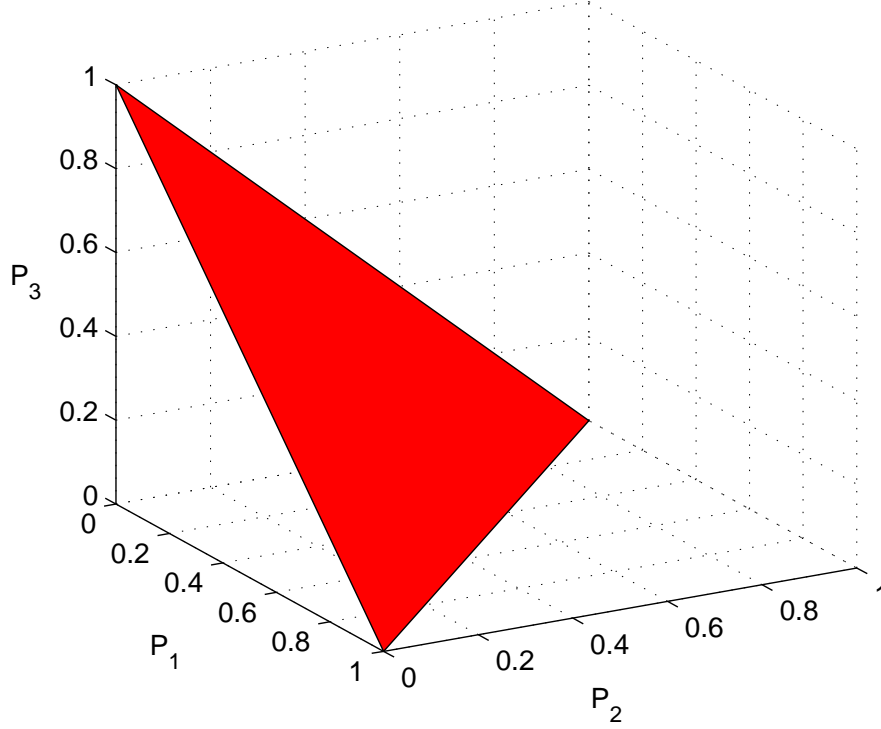


Figure 2.1: The triangle represents the two-dimensional simplex embedded in a three-dimensional space. In the 3-d case the equation (2.35) is written as $\sum_{k=1}^3 P_k = 1$. Once the first population is selected, the domain of the second one is constrained. As soon as the second one is chosen, the last one is determined by the normalization condition, such the constraint to belong to the simplex.

with normalization

$$\int dP_1 dP_2 \dots dP_{N-1} p(P_1, P_2, \dots, P_{N-1}) = 1 \quad (2.37)$$

The last population P_N is given according to the normalization condition. The explicit probability distribution, in principle, allows one to calculate the average of every function of populations f_P that will be denoted as

$$\langle f_P \rangle := \int dP_1 dP_2 \dots dP_{N-1} f(P_1, P_2, \dots, P_{N-1}) p(P_1, P_2, \dots, P_{N-1}) \quad (2.38)$$

where $\langle \cdot \rangle$ stands for ensemble average.

It should be noted that all the populations are not statistically independent due to their positiveness that constrains the domain of integration [50]. If we

consider a specific order of integration, for example from $N - 1$ to 1, the positiveness of the last population $P_N = 1 - \sum_k^{N-1} P_k > 0$ determines the allowed region for P_{N-1} as function of the previous populations $P_{N-1} \leq 1 - \sum_k^{N-2} P_k$. The positiveness also of P_{N-1} determines the upper integration limit of the previous, and so forth.

All the statistical properties of the RPSE ensemble are well characterized [43, 50] and here I report only the most interesting results for our purposes. For example the marginal distribution for a single population can be analytically derived as

$$p(P_k) = (N - 1)(1 - P_k)^{N-2} \quad (2.39)$$

The latter equation is valid for any population thanks to the invariance of the full distribution (eqn. (2.36)). The first two moments can be obtained by integration from equation (2.39) as

$$\langle P_k \rangle = \frac{1}{N} \quad \langle P_k^2 \rangle = \frac{2}{N(N + 1)} \quad (2.40)$$

Furthermore, one could be interested in the evaluation of ensemble average equation (2.38) of an equilibrium properties of eq. (2.32). This is very useful in order to understand how the system properties are affected by the statistical sampling of the wave function. As a matter of fact, one could ask if there is any particular functions that is nearly independent with respect to the choice of the wave function. In the next paragraph, it will be shown how the overwhelming majority of wave functions, within RPSE statistics, produces almost the same value for properties related to thermodynamic state functions. It represents the most important validation of the RPSE model since the thermodynamics emerges quite naturally from the picture of the wave function under a condition called *typicality*.

2.4 Emergence of Thermodynamics Properties

How a property f in each single realization of a quantum system differs from the ensemble average $\langle f \rangle$ is a very important ingredient in the characterization

of the statistical ensemble. The most appropriate tool is the variance

$$\sigma_f^2 := \langle (f - \langle f \rangle)^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2 \quad (2.41)$$

that formally quantify the typical deviation with respect to all the possible realizations within a specified ensemble. About this topic, Reimann [44] demonstrated how, for almost any quantum system, the distribution of several interesting physical properties with respect to different realizations, shows a narrow peaked behaviour. This implies that the dynamical equilibrium properties deviate negligibly from the ensemble average. In this situation, where a property manifest a typical deviation σ_f much smaller than the range of its possible values Δ_f

$$\sigma_f \ll \Delta_f \quad (2.42)$$

that property is said to be *typical*.

Under quite mild assumptions, Reimann demonstrated how several possible probability distributions on the wave function coefficients manifest the typicality behavior, i.e. a randomly sampled wave function is very likely to yield expectation values very close to the ensemble average simultaneously for a large number of observables. Since the equilibrium properties, within our formalism, are specified only by the set of populations, the previous statement assures that several equilibrium properties are almost the same even if different sets of populations are considered.

The typicality property can be considered as the natural connection between a single realization and the standard ensemble point of view of statistical mechanics, where our lack of knowledge about the precise system state is not of primary importance since almost all quantum states behave essentially in the same way.

Since equation (2.42) does not provide a quantitative criterion for the typicality property, Fresch and Moro [50] have considered a stronger formulation of typicality by considering the macroscopic limit. They assign an almost sure typicality to a property when the ratio σ_f/Δ_f tends to zero in increasing the number of components n .

$$\lim_{n \rightarrow \infty} \frac{\sigma_f}{\Delta_f} = 0 \quad (2.43)$$

where the thermodynamic limit was considered at fixed temperature. If the

condition (2.43) holds the ensemble average is a good estimate for the equilibrium properties in all the possible realizations of the quantum system. Fresch and Moro reinforced that result by considering two particular properties with a thermodynamic correspondence: *internal energy* and *entropy*.

In the microscopic framework, a natural choice would associate the expectation value of energy $E = \sum_k E_k P_k$ to internal energy U . At the same time the Shannon entropy $W = -k_B \sum_k P_k \ln P_k$ would be the natural choice for the description of the statistical disorder with respect to the decomposition of wave function in the eigenvectors. However, in general, both the latter quantities depend on the specific realization of the quantum system and consequently on the set of populations. On the contrary, the thermodynamic one should be independent from it and univocally determined. Fresch and Moro in ref. [50] have demonstrated that the internal energy and entropy assume typical values in the thermodynamic limits and this assures the identification of the typical value of this properties to the macroscopic properties, independently of the specific realization.

In addition they have demonstrated that the ensemble averaged properties are in agreement with the thermodynamic state functions, for example entropy is shown to be a convex increasing function of internal energy. These important and new results connect microscopic behaviour with the macroscopic observables in a clear and self-consistent methodological framework.

The macroscopic limit as well as the typicality behaviour represent a good test for the statistical ensemble in order to verify the agreement with the thermodynamics. In addition the focus on the wave function can lead to new insight in the dynamics of quantum system and possibly new approaches to study relaxation phenomena.

2.5 Different approaches on wave function Ensemble

Since in the rest of the thesis I fully endorse the perspective of Fresch and Moro, in the following paragraph, I briefly report some other contributions about ensembles of pure states present in literature, mainly related to typicality arguments.

The association between typicality property and ensembles of wave functions demonstrates how some features of quantum states are almost preserved when different precise realizations are considered. The words *probability distribution* or *measure* in the Hilbert space are alternatively used and a prevalent notation is still not present.

Goldstein *et al.*, in ref. [21], demonstrated how the canonical density matrix for a subsystem is typical for the overwhelming majority of wave functions chosen according to a particular probability distribution. Following the works of Schrödinger [51, 52] and Block [53], the authors introduced a uniform surface area measure on the unitary sphere in a narrow Hilbert subspace $\mathcal{H}_{[E, E+\delta]}$ [21]. The considered probability distribution is uniform over all the normalized wave functions $|\Psi\rangle$ with energy in the interval $[E, E + \delta]$, where δ is small on the macroscopic scale. Unlike Fresch and Moro approach, Goldstein *et al.* do not explicitly derive the distribution function on the wave function coefficients but a thorough inspection can show a strong similarity with RPSE statistics. Both probability distributions can be interpreted as a uniform distribution on the surface of a sphere of equation $\sum_k |c_k|^2 = 1$ (where $|c_k|^2 = P_k$). Where Goldstein *et al.* consider a narrow energy interval with two parameters E and $E + \delta$, that represent the lower and the upper limit, Fresch and Moro virtually eliminate the lower bound setting it at the lowest eigenvalue. This choice is driven principally by two reasons: first of all it is not clear why the pure state should have components only in a narrow energy interval in the, in principle, infinite Hilbert space, secondly only the upper bound limit has a strong thermodynamic interpretation in the macroscopic limit. In my opinion, a mono-parametric probability distribution should be preferred, since it provides the same results with less arbitrariness.

While Goldstein *et al.* were interested in the subsystem properties, Reimann [44, 45] focused his work on the prediction that can be performed on the isolated quantum system. In ref. [44], he demonstrated how almost every wave function sampled from a distribution function has expectation values very close to their ensemble averages. He did not consider a specific form for the ensemble average that is quite general, provided that includes many eigenstates. As he underlined, his approach include the standard formalism of Goldstein *et al.* as a special case.

I would like also to mention the work of Naudts [54] that recognized as

a difficult task the characterization of the single realization of a quantum system since no information on the constant of motions is available. However he avoided to consider a possible ensemble of wave functions by applying the maximum entropy principle. He was able to derive a single set of populations bypassing the problem of several possible wave functions. It naturally implies no more than one realization for each thermal state.

The most similar contribution to mine was suggested by Brody and Bender [55, 56] and re-elaborated by Fine [57], which consider an alternative microcanonical ensemble called *Fixed Expectation Energy Ensemble* (FEEE) by Fresch and Moro. The authors propose to derive a probability distribution on the pure state with a constraint on the expectation energy. A uniform probability distribution over all the wave functions that posses exactly the same energy show typical behaviour and can be easily interpreted as a microcanonical formulation on quantum pure state. Nevertheless some predictions of this ensemble contradict macroscopic thermodynamics [43, 58, 59]. Since there are no *a priori* information on the populations variables, different statistical models can be defined. In my opinion one of the most important criterion to the acceptability of a statistical ensemble is its agreement with the thermodynamics of macroscopic systems. Thus, due to its inconsistency in the macroscopic limit, the FEEE can not be considered as an adequate ensemble for pure states.

On the other hand it is possible to introduce different criteria in the selection of statistical ensembles and these will be the main topic of my research. I will specifically consider an invariance property in the thermalization experiment that will lead to a statistical ensemble without a uniform measure such that different directions in the Hilbert space weight differently in the pure state selection.

Thermalization Resilient Ensemble

Since the dynamics of wave function does not supply any information about populations, the definition of a probability distribution on these variables is a difficult task. At the same time, populations are strictly related with equilibrium properties on a quantum state and they represent very important variables in the description of a quantum state. Since each realization of a quantum state is characterized by different choices of the set of populations, the probability distribution points us how to select the most appropriate wave function for the system of interest. However different probability distributions on populations have been proposed [57, 49], only on the bases of reasonable assumptions.

The validation of these statistical ensembles can be performed only with *a posteriori* considerations and in ref.s [43, 58] Fresh and Moro have demonstrated as the agreement with thermodynamics can be an optimum criterion to discriminate between different probability distributions on pure states.

The important role of thermodynamics in the validation of models on wave function, combined with the need for a quantum systems to exist in different thermal states, for example associated to different temperatures, suggests that whatever probability distribution is defined, it should take into account the possibility of different thermal states with a precise thermodynamic correspondence in the macroscopic limit.

Starting from this premise I analyze how a perturbative interaction between different systems can be described and how it affects the thermal state of a quantum system. This investigation reveals the major drawback of the RPSE statistics. If we consider to bring into contact two systems, even through a perturbative interaction, we are not able to describe the equilibrium properties after the interaction within the Random Pure State Ensemble statistics, since the random uniform character is lost. It represents a shortcoming of the model from a methodological point of view, since closed systems can be always considered as the result of interaction among previously isolated systems.

On the other hand this drawback introduces a further requirement of a different nature that can be used for the definition of a new statistical ensemble.

The invariance of the thermal state in the coupling between identical system will be used as a guideline in the definition of a new probability distribution on populations. In the following, I will introduce an invariance constraint on the average populations that leads to the development of a statistical ensemble invariant with respect to the interaction of identical systems and very well resilient when a real thermalization experiment is considered.

I will also demonstrate that this new statistical ensemble is in agreement with thermodynamic predictions.

3.1 Probability distribution and thermal states

In the following some general considerations on pure state probability distributions will be reported, many of them were not clear at the beginning of my research, or at least they were never expressed in literature in terms that I will use from now on.

Whenever different realizations of quantum pure states are considered, one deals with different sets of populations and phases, characterising the system state, once the Hamiltonian eigenstates are provided. However, as explained in the previous chapter, only the set of populations is truly distinctive of a quantum state in relation to different equilibrium properties. Precisely for this reason the set of positive and normalized populations $P = (P_1, P_2, P_3, \dots)$ represents the set of statistical variables of our analysis.

In order to formally describe the statistical ensemble [60] we need to specify the probability density $p(P)$, as well as the sample space D of the variables P . While the positivity of each population together with the normalization condition constrains the sample space, for the probability distribution we have no hints.

In several statistical analyses of pure states [49, 50, 21, 44] the uniform random distribution of the populations is assumed a priori, on the premise that there are no reasons to privilege particular directions of the Hilbert space. This allows a precise identification of the probability density on the populations and the characterization of ensemble averages. Distinct implementations of this scheme derive from different rules employed for the identification of the active space. Let us consider the particular case of the Random Pure State Ensemble (RPSE) analyzed in detail in refs. [49, 43, 50, 61] and briefly exposed in paragraph 2.3.1, which is based on the active space selected according to an upper energy cutoff E_{max} only : $|E_k\rangle \in \mathcal{H}_N$ if $E_k < E_{max}$. The corresponding probability density takes the simple form $p(P) = 1/N$ where N is the dimension of the active space determined by the choice of the cutoff E_{max} . Then the same average $\langle P_k \rangle = 1/N$ is recovered for the populations within the active space, since the probability density is invariant with respect to exchange of the populations. In other words, different energy eigenvectors within the active space play an identical role and no privileged directions are present.

In addition, the typicality behaviour shows as different realizations of a quantum system does not produce substantial variations on the system properties. It means that different realizations from the same probability density correspond to realizations of the same thermodynamics state, if the systems is macroscopic, or more generally correspond to realizations of different thermal states if microscopic quantum systems are considered. Then, in general, a population distribution $p_\zeta(P)$ should be identified according to a thermal parameter ζ in order to highlight its dependence on the thermal state.

The specification of the thermal parameter has to be done on the basis of the connection between quantum statistical ensembles and thermodynamics. It is then strictly related to the emergence of thermodynamics from first principles.

Because of the uniform distribution within the active space, in the Random Pure State Ensemble, the thermal state can be modified only by changing the

dimension of \mathcal{H}_N . Thus the thermal state is parametrized by the energy cutoff, $\zeta = E_{max}$, with distinct active spaces having different distributions on the populations. Furthermore it has been shown [50] that in the thermodynamic limit, that is for systems of increasing size, the cutoff E_{max} becomes equivalent to the internal energy U . In this way, the thermal parameter gets a precise correspondence with a thermodynamic state function.

Other statistical ensembles with an uniform random distribution on the populations can be derived from alternative choices of the active space \mathcal{H}_N . The active space confined by both the lower E_{min} and the upper E_{max} energy cutoffs, like for the microcanonical density matrix, has been often considered [21, 44].

$$|E_k\rangle \in \mathcal{H}_N \quad \text{if} \quad E_{min} < E_k < E_{max} \quad (3.1)$$

It should be evident that the same statistical tools of RPSE can be applied also to this case by considering the non vanishing populations of energy eigenvectors belonging to the active space \mathcal{H}_N . Now, however, a two parameter representation of the thermal state, $\zeta = (E_{min}, E_{max})$, has to be managed, since the population distribution depends on both energy cutoffs. In the macroscopic limit one can show the equivalence of the upper energy cutoff with the internal energy, and that the thermodynamic parameters are independent from the lower one[50]. The lack of a thermodynamic correspondence for one of the parameters determining the thermal state complicates its application to finite sized system, as long as there are no evident guidelines for the choice of E_{min} . From this point of view the use of RPSE statistics appears to be more straightforward, since one has to select only the upper energy cutoff which is directly related to the internal energy.

It should be mentioned that some authors [55, 56] have proposed a variant of the uniform random statistics by imposing also the constraint of a given expectation value for the energy, but in this case the correspondence with thermodynamic parameters is not assured in the macroscopic limit [43, 58]. In agreement with Fresch and Moro perspective, I consider the absence of a clear thermodynamic interpretation of such an ensemble as a reasonable objection against its use in the statistical description of isolated quantum systems in general conditions.

Albeit appealing from different points of view, the uniform random distri-

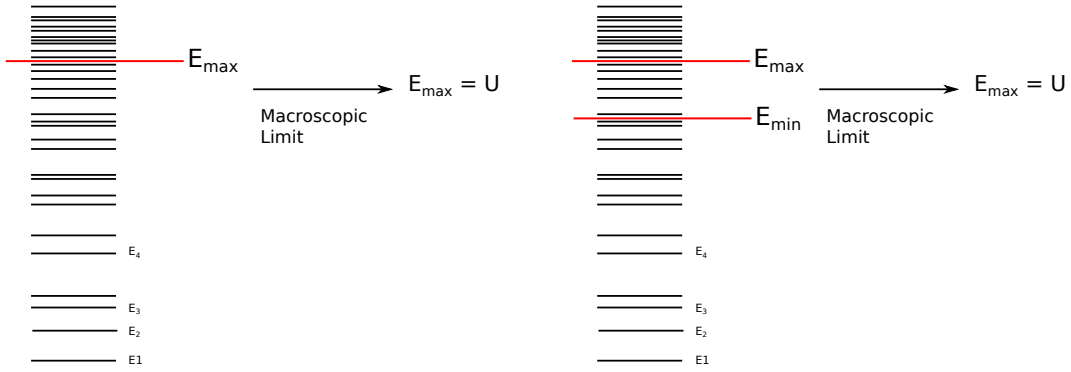


Figure 3.1: Random pure state ensembles are schematically represented. On the left, only the upper cut-off parameter E_{max} is taken into account. It corresponds to thermodynamic internal energy. when the macroscopic limit is considered. On the right a bi-parametric representation is provided. In this situation only the E_{max} is related with a thermodynamic state function, while E_{min} has no a direct thermodynamic meaning.

bution within the active space has a major drawback: it does not survive to the process of thermalization. Let us consider the simpler experiment of this type: two identical systems A and B , initially isolated and described by a statistical ensemble of this type, which are brought to interact so leading to a new equilibrium state for the overall system $A + B$. If we characterize the two systems with the same probability distribution, i.e. with the same thermal parameter $\zeta = E_{max}$, one would expect that the thermal state of the overall system should be the sum of the previous two thermal parameters, since they are related to the internal energy. It means that the probability distribution should be uniform in the new active space determined by $E_{max}^{AB} = E_{max}^A + E_{max}^B$. However, the direct analysis of the experiment (see Section 3.4) shows that the populations in the final equilibrium state are no more characterized by an identical average as it was in the statistical ensemble for the initially isolated systems A and B . The Random Pure State statistics is not able to describe the equilibrium properties after the thermalization, even if the interaction between systems is perturbative.

In this work we intend to find and characterize a statistical ensemble for populations that overcomes the drawbacks of the uniform random distribution. From the methodological point of view, the main issue concerns what a guideline should be assumed in order to recognize such an ensemble. Our choice

is that of starting precisely from the failures of the random uniform distributions. We intend to identify a statistical ensemble resilient to thermalization, or at least to its simplest realization, in the meaning that the population distribution maintains its structure after thermalization. This requirement will be employed as the guideline for the derivation of such a statistical ensemble, in the following called as Thermalization Resilient Ensemble (TRE).

A reasonable possibility in the development of the TRE statistics is to introduce a sort of constraint in the probability distribution that assures the property we want. However, it is not straightforward to identify such a constraint, since the "thermalization invariance" has not a clear formal meaning. In order to overcome this difficulties and to formalize the thermalization invariance, I have studied how a system, formed by the weak interaction between two previously separated systems, can be described. It introduces a *composition rule* for weakly interactive systems that allows a precise identification of the invariance property.

3.2 Probability density on the energy domain

The previous discussion has shown as population variables are related with the equilibrium properties of an isolated quantum system. Furthermore, when macroscopic limit is considered and if the system properties manifest the typical behavior of equation (2.43), different realizations of a quantum system for the same thermodynamic state are characterized by almost the same equilibrium value for a large number of observables. In this situations, equilibrium properties can be completely described by their ensemble average value.

At the same time, once the probability density on populations $p_\zeta(P)$ has been defined, the ensemble average $\langle h \rangle_\zeta$ of any function $h(P)$ of populations can be calculated as

$$\langle h \rangle_\zeta = \int dP h(P) p_\zeta(P) \quad (3.2)$$

where the integration is performed on the $N - 1$ independent populations, with integration domain determined by the constraints $P_k \geq 0$ and $\sum_k P_k = 1$. We denote such an average as $\langle h \rangle_\zeta$ to emphasize its dependence on the thermal state ζ brought by the choice of the probability density. As an example one could consider the ensemble average of the equilibrium value \bar{a} of equation

(2.32) for the expectation value of an operator

$$\langle \bar{a} \rangle_\zeta = \sum_k \langle P_k \rangle_\zeta A_{kk} \quad (3.3)$$

with $\langle E \rangle_\zeta = \sum_k \langle P_k \rangle_\zeta E_k$ in the case of the expectation value of the Hamiltonian, i.e., the energy. Then the ensemble average of a function $f(E)$ of the energy becomes

$$\langle f(E) \rangle_\zeta = \sum_k \langle P_k \rangle_\zeta f(E_k) \quad (3.4)$$

The central role of ensemble average populations in the characterization of quantum systems should now be clear if one considers that equations (3.3) and (3.4) can describe many different observables of the system. Precisely thanks to the last considerations, ensemble average populations $\langle P_k \rangle_\zeta$ become the main objective of our analysis.

The analysis of thermalization experiments is conveniently performed by adopting the representation in the continuum of the system's properties. This correspond to specify (3.4) as an energy integral by introducing the density of states to take into account the multiplicity of energy eigenvalues. Furthermore one needs to assume the existence of a smooth energy function $\tilde{P}_\zeta(E)$ for a given thermal state ζ , which represents the extension to the continuum of the average populations such that

$$\langle P_k \rangle_\zeta = \tilde{P}_\zeta(E_k) \quad (3.5)$$

Then the average of $f(E)$ can be specified as

$$\langle f(E) \rangle_\zeta = \int_{-\infty}^{+\infty} dE g(E) \tilde{P}_\zeta(E) f(E) \quad (3.6)$$

where $g(E)$ is the density of energy eigenstates

$$g(E) = \sum_k \delta(E - E_k) \quad (3.7)$$

and $\delta(E - E_k)$ is the Dirac delta function. From the density of states, the number of states Γ within a certain energy interval, for example $[E, E + \delta E]$,

can be easily obtained by integration

$$\Gamma(E) = \int_E^{E+\delta E} dE' g(E') \quad (3.8)$$

In the presence of a dense structure of energy eigenstates, the density of states can be replaced by its continuous extension $\tilde{g}(E)$

$$\langle f(E) \rangle_\zeta = \int_{-\infty}^{+\infty} dE \tilde{g}(E) \tilde{P}_\zeta(E) f(E) = \int_{-\infty}^{+\infty} dE \tilde{\rho}_\zeta(E) f(E) \quad (3.9)$$

which allows the identification of a probability density on the energy $\tilde{\rho}_\zeta(E)$ defined as

$$\tilde{\rho}_\zeta(E) := \tilde{g}(E) \tilde{P}_\zeta(E) \quad (3.10)$$

for the thermal state ζ .

The function $\tilde{\rho}_\zeta(E)$ alone summarizes the information on the distribution of energy states and on their average populations. It is normalized as

$$\int_{-\infty}^{+\infty} dE \tilde{\rho}_\zeta(E) = \int_{-\infty}^{+\infty} dE \tilde{g}(E) \tilde{P}_\zeta(E) = 1 \quad (3.11)$$

This implies that the average population $\tilde{P}_\zeta(E)$ is implicitly a functional of the density of states $\tilde{g}(E)$. More specifically, different systems at the same thermal state ζ cannot be described by the same energy function $\tilde{P}_\zeta(E)$ for the average populations, because in general they are characterized by different density of states $\tilde{g}(E)$. In order to preserve the normalization of equation (3.11) they have to be described by different functions $\tilde{P}_\zeta(E)$.

As an example we consider here the uniform distribution within the N -dimensional Hilbert active space \mathcal{H}_N determined by both the lower and the upper energy cut-off, so that the thermal parameter is specified as $\zeta = (E_{min}, E_{max})$. Then the same average $\langle P_k \rangle_\zeta = 1/N$ is recovered for the populations within the active space, since the probability density is invariant with respect to exchange of the populations. In other words the different energy eigenvectors within the active space play an identical role. On the other hand, vanishing averages are attributed to populations for eigenstates outside the active space. Correspondingly the function $\tilde{P}_\zeta(E)$ describing population averages is constant

within the energy range of the active space and vanishes outside

$$\tilde{P}_\zeta(E) = \begin{cases} \text{constant} & \text{for } E_{min} < E < E_{max} \\ 0 & \text{otherwise} \end{cases} \quad (3.12)$$

with the constant determined by the normalization Eq. (??). When multiplied to $\tilde{g}(E)$ to generate the energy probability density $\tilde{\rho}_\zeta(E)$, it simply selects the portion of the density of states belonging to the active space. Figure 3.2 illustrates this behaviour for the system scribed by the following density of states

$$\tilde{g}(E) = \begin{cases} \frac{A}{E_s} \left(\frac{E}{E_s}\right)^M & \text{for } E \geq 0 \\ 0 & \text{otherwise} \end{cases} \quad (3.13)$$

which is often employed in the statistical mechanics of ideal systems [9]. Notice that it is implicitly assumed that $E = 0^+$ is the ground state. The parameter E_s represents the energy unit, while by modifying the parameter A one controls the number of states for a given energy interval without changing the overall profile of the density of states. In our applications we use an unitary value for the constant A .

3.3 Composition rule for interacting systems

In this section we analyze the average populations for the composite system $(A+B)$ deriving from the interaction between system A and system B , which are supposed to be initially isolated. The previously introduced formalism is adopted to describe statistically the pure state (wave-function) of both the isolated systems A and B .

System A is defined within its Hilbert space \mathcal{H}^A and it is characterized by its Hamiltonian \hat{H}^A and its density of states $g^A(E) = \sum_{k^A} \delta(E - E_{k^A}^A)$ where $E_{k^A}^A$ denotes the corresponding eigenenergy:

$$\hat{H}^A |E_{k^A}^A\rangle = E_{k^A}^A |E_{k^A}^A\rangle \quad \text{with} \quad |E_{k^A}^A\rangle \in \mathcal{H}^A \quad (3.14)$$

Furthermore, we assume that isolated system A is characterized by well defined ensemble average populations for the thermal state ζ^A , which are described

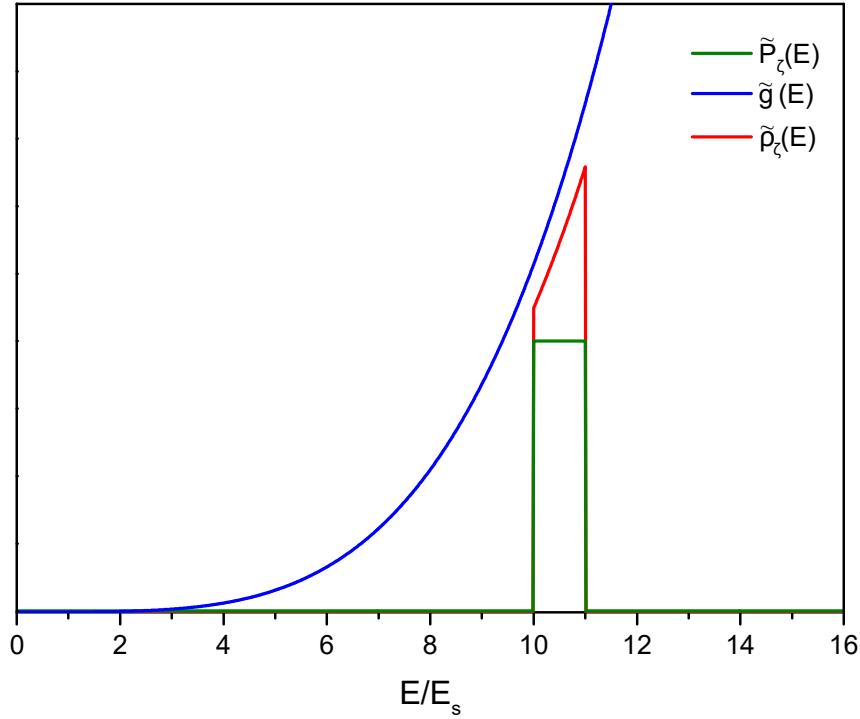


Figure 3.2: Average population function $\tilde{P}_\zeta(E)$ (green line) and energy probability density $\tilde{\rho}_\zeta(E)$ (red line) for the uniform statistical distribution with density of states $\tilde{g}(E)$ equation (3.13) (blue line) for $M = 4$, $E_{min} = 10E_s$ and $E_{max} = 11E_s$. These functions have been scaled by suitable multiplicative factors in order to allow a visual comparison.

by the function $\tilde{P}_{\zeta^A}^A(E)$. Correspondingly one can introduce the probability density

$$\tilde{\rho}_{\zeta^A}^A(E) = \tilde{P}_{\zeta^A}^A(E) \tilde{g}^A(E) \quad (3.15)$$

on the energy variable E by invoking the extension to the continuum of the density of states, $\tilde{g}^A(E)$. An analogous formal description, with B replacing the superscript A , is adopted for the pure states of isolated system B supposed to be in the thermal state ζ^B and with average populations described by function $\tilde{P}_{\zeta^B}^B(E)$.

Let us now consider the composite system deriving from system A and system B in the presence of a weak interaction. Then independent pure states for systems A and B do not exist any more, and a pure state description can be employed only for the overall system in the Hilbert space

$$\mathcal{H}^{A+B} := \mathcal{H}^A \otimes \mathcal{H}^B \quad (3.16)$$

If the interaction is weak enough, the eigenenergies tend to be additive with respect to contributions $E_{k^A}^A$ and $E_{k^B}^B$ of systems A and B , respectively, and they can be evaluated as $E_{k^A}^A + E_{k^B}^B$. Correspondingly the density of states $g^{A+B}(E)$ of the composite system can be calculated as

$$\begin{aligned} g^{A+B}(E) &= \sum_{k^A} \sum_{k^B} \delta(E - E_{k^A}^A - E_{k^B}^B) \\ &= \int_{-\infty}^{+\infty} dE' \left[\sum_{k^A} \delta(E - E' - E_{k^A}^A) \right] \left[\sum_{k^B} \delta(E' - E_{k^B}^B) \right] \end{aligned} \quad (3.17)$$

that is by the convolution of the density of states of isolated A and B systems accounted by the two summation within the square brackets in the previous equation:

$$g^{A+B}(E) = \int_{-\infty}^{+\infty} dE' g^A(E - E') g^B(E') \quad (3.18)$$

By substituting the density of states of systems A and B with their extensions to the continuum $\tilde{g}^A(E)$ and $\tilde{g}^B(E)$, we derive the density of states $\tilde{g}^{A+B}(E)$ for the composite system by means of the convolution rule.

The central issue is now what a structure on the populations P^{A+B} for the composite system will be produced by the interaction between A and B . It is important to remind that only interactions with a perturbative strength are considered, such that the density of states in the overall system can be described with equation (3.18). In this situation, the interaction contribution on the energy is negligible with respect to the energy of the two systems and the overall energy E in the composite system $A+B$ can be described as the sum of the energies of systems A and B , $E = E^A + E^B$. In addition, each system is characterized by an independent probability density $\tilde{\rho}^A(E)$ and $\tilde{\rho}^B(E)$ where the energy can be considered as the stochastic variable of the problem. The most appropriate variable for the composite system, after the interaction, is the sum of the energy contributions of the two systems. It leads to the definition of the probability density $\tilde{\rho}^{A+B}(E)$ on the energy of the composite system as the convolution of its components, according to standard probability rules [62],

$$\tilde{\rho}^{A+B}(E) = \int_{-\infty}^{+\infty} dE' \tilde{\rho}_{\zeta^A}^A(E - E') \tilde{\rho}_{\zeta^B}^B(E') \quad (3.19)$$

Moreover, the corresponding function $\tilde{P}^{A+B}(E)$ for the average populations of the composite system can be evaluated as

$$\tilde{P}^{A+B}(E) = \frac{\tilde{\rho}^{A+B}(E)}{\tilde{g}^{A+B}(E)} = \frac{1}{\tilde{g}^{A+B}(E)} \int_{-\infty}^{+\infty} dE' \tilde{g}^A(E-E') \tilde{g}^B(E') \tilde{P}_{\zeta^A}^A(E-E') \tilde{P}_{\zeta^B}^B(E') \quad (3.20)$$

in agreement with equation (3.10).

We emphasize that such a treatment represents the simplest way to recover the probability on the energy for the composite system under the condition of perturbative effects of the interaction on the energy, but this does not assure that the resulting population distribution has a well defined thermal state described by parameter ζ . For this reason we do not assign a thermal parameter ζ to the energy probability density $\tilde{\rho}^{A+B}(E)$, and to average population function $\tilde{P}^{A+B}(E)$ as well, in opposition to the initially isolated systems.

It is important to focus on the underlying assumption of the just presented formulation of the problem, beyond the weakness of the interaction. Here we state that the generic effect of the interaction in a thermalization process can be described with the use of the convolution law on the probability density of the energy in a quantum isolated system. Even if it appears very reasonable, the lack of a specific analysis of the effect of interactions may represent a limit of our procedure. In order to overcome this objection, in appendix 3.A, an analysis of interaction effects which supports the convolution rule is presented.

Moreover, the convolution rule of probability theory, even if it does not describe the interaction mechanisms responsible of the resulting probability density, assures a general and self-consistent treatment of the problem. As a matter of the effects of interactions between quantum systems are not easily represented in a general form without reference to the specific structure of the interaction Hamiltonian. A discussion about such an issue can be found in ref. [63] where it is shown that the equipartition inside the energy shell centered at $E = E^A + E^B$ justifies the convolution rule.

In conclusion, given the average populations $\tilde{P}_{\zeta^A}^A(E)$ and $\tilde{P}_{\zeta^B}^B(E)$ of the initially isolated systems, the convolution of the probability densities on the energy allows a direct calculation of the average population $\tilde{P}^{A+B}(E)$ of the composite system. This *thermalization criterion* will be used in order to derive a Thermalization Resilient expression for the average population.

3.4 RPSE drawback

In order to visualize in a simple case the consequences of the interaction described by the convolution rule, we consider a model system formed by two initially isolated identical systems, characterized by a density of states $\tilde{g}^A(E)$ and average population $\tilde{P}_{\zeta^A}^A(E)$.

In particular for the density of states we employ (3.13) and for the average population $\tilde{P}_{\zeta}(E)$ we choose the uniform random distribution of population with the same thermal state specified by the boundary of the active space $\zeta^A = \zeta^B = (E_{min}, E_{max})$. Therefore the initially isolated systems are characterized by the same stepwise profile equation (3.12). It corresponds to describe the behaviour of random pure state statistics in the thermalization experiment. If $E_{min} = E_1$ we recover the RPSE situation described by Fresch and Moro [49].

The specific case of identical, initially isolated, systems can be formalized by considering the same energy density

$$\tilde{g}^A(E) = \tilde{g}^B(E) = \tilde{g}(E) \quad (3.21)$$

and the same average population function

$$\tilde{P}_{\zeta}^A(E) = \tilde{P}_{\zeta}^B(E) = \tilde{P}_{\zeta}(E) \quad (3.22)$$

for both systems.

Now the convolution integrals of equations (3.18) and (3.20) can be easily performed. In particular for $E < 2E_{min}$ and $E > 2E_{max}$ the population vanishes as well as the system energy density ρ^{A+B} . The energy density is positive only within the interval $[2E_{min}, 2E_{max}]$ and two different integration domains has to be considered.

For $E \in [2E_{min}, E_{max} + E_{min}]$ we obtain

$$\begin{aligned} \rho^{A+B}(E) &= \frac{A}{E_s} \int_{\frac{E_{min}}{E_s}}^{\frac{E}{E_s} - \frac{E_{min}}{E_s}} dE' \left(\frac{E}{E_s} - \frac{E'}{E_s} \right)^M \left(\frac{E'}{E_s} \right)^M \quad (3.23) \\ &= \frac{A}{E_s} \sum_{k=0}^M s(M, k) \left(\frac{E}{E_s} \right)^{M-k} \left[\left(\frac{E}{E_s} - \frac{E_{min}}{E_s} \right)^{M+k+1} - \left(\frac{E_{min}}{E_s} \right)^{M+k+1} \right] \quad (3.24) \end{aligned}$$

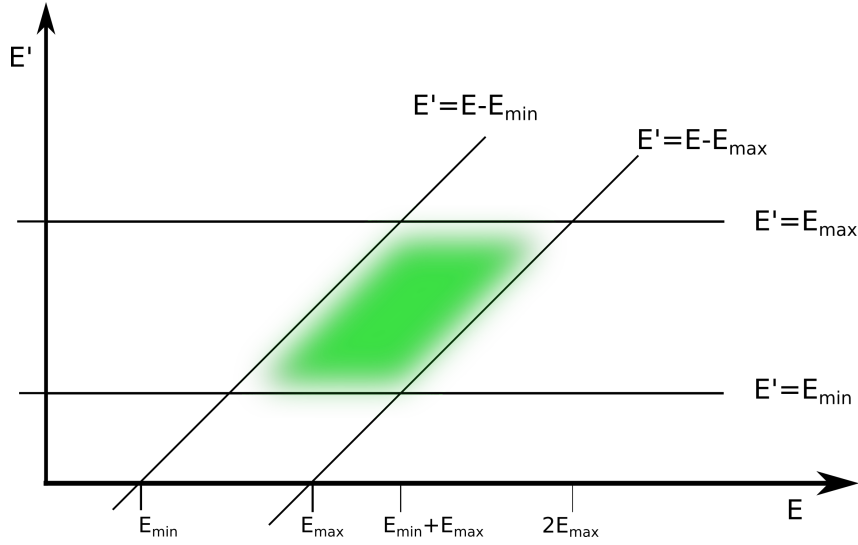


Figure 3.3: Schematic representation of the integration domain. The convolution integral is non vanishing where RPSE populations are different from zero. It can be displayed in a x-y plane, where the axes are respectively E and E' . The convolution integral is performed in the E' domain and the interesting plane region can be determined through two constraints: $E'_{min} < E' < E'_{max}$ selects an horizontal stripe while $E_{min} < E - E' < E_{max}$ defines the region between the two lines. The constraint just mentioned define the integration domain highlighted in green.

while for the interval $E \in [E_{max} + E_{min}, 2E_{max}]$

$$\rho^{A+B}(E) = \frac{A}{E_s} \int_{\frac{E - E_{max}}{E_s}}^{\frac{E_{max} + E_{min}}{E_s}} dE' \left(\frac{E}{E_s} - \frac{E'}{E_s} \right)^M \left(\frac{E'}{E_s} \right)^M \quad (3.25)$$

$$= \frac{A}{E_s} \sum_{k=0}^M s(M, k) \frac{E^{M-k}}{E_s} \left[\left(\frac{E_{max}}{E_s} \right)^{M+k+1} - \left(\frac{E}{E_s} - \frac{E_{max}}{E_s} \right)^{M+k+1} \right] \quad (3.26)$$

where, for both cases

$$s(M, k) = \binom{M}{k} (-1)^k \frac{1}{M + k + 1} \quad (3.27)$$

We can easily obtain the mean populations function $P^{A+B}(E)$, according to equation (3.10), by dividing the previous equation for the convoluted density

of states

$$g^{A+B}(E) = \left(\frac{A}{E_s}\right)^2 \left(\frac{E}{E_s}\right)^{2M+1} \sum_{k=0}^M s(M, k) \quad (3.28)$$

Figure 3.4 shows the profiles of average populations for the RPSE statistical ensemble ($E_{max}/E_s = 10$ and $E_{min}/E_s = 0$) in increasing number of components, represented by different growths of density of states (values of M parameter). At the same time, in Figure 3.5 the same type of profiles are displayed for the active space with both the lower and upper energy cutoffs, in particular $E_{min}/E_s = 4$ and $E_{max}/E_s = 10$.

The uniform random distributions has been developed under the hypothesis of equivalence of each direction within the active space of the total Hilbert space. It corresponds to a step functions in a plot like figures (3.4) (3.5) where $\tilde{P}^{A+B}(E)$ vs E/E_s is considered. Thermalization experiments break this equivalence on populations leading to an average population with an explicit dependence on the energy. This, as emphasized in the introduction, is a fundamental shortcoming of the uniform distribution considered as the statistical tool describing isolated systems, as long as isolated systems can be produced by interaction between initially isolated parts. Once the systems are brought into contact, equilibrium properties cannot be described anymore by uniform statistics.

3.5 Thermalization Resilient mean populations

Thermalization by interaction can be realized in different situations depending on the thermal state of the two initially isolated systems. Here we consider the simplest case when two isolated systems are identical and have the same thermal state. According to Thermodynamics, their thermal state is not modified by putting them in contact and, as happen at macroscopic level, no change of temperature would be detected. This is a peculiar case of thermalization because of the absence of a net energy flux between the two systems. The main effect of the interaction is that of producing an entanglement between the two pure states of the initially isolated systems. On the other hand it is precisely in this situation that the drawbacks of random ensembles of pure

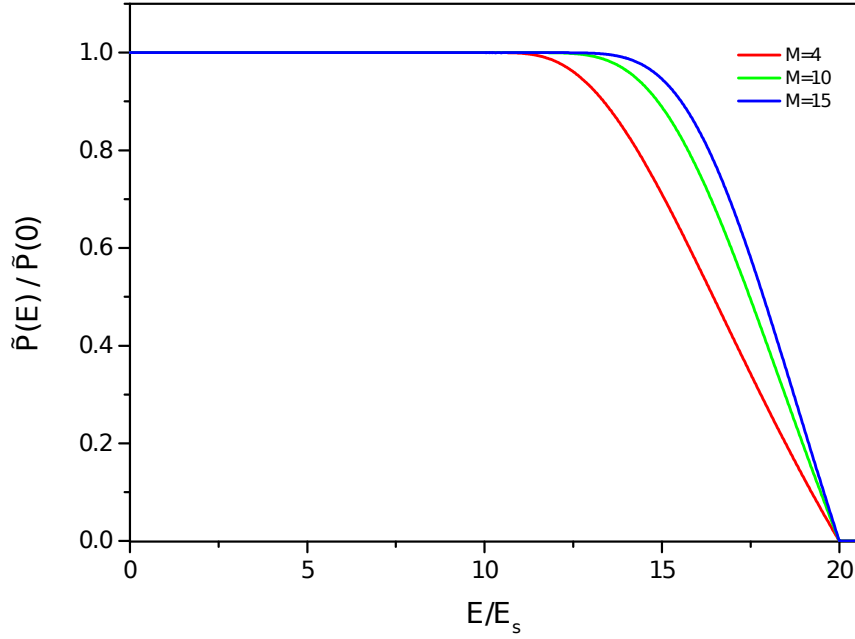


Figure 3.4: Average population function $\tilde{P}(E)$ is obtained after the interaction between two identical systems with the same thermal parameter $E_{max}/E_s = 10$ for both systems. Model density of states of equation (3.13) has been employed with $M = 4$ (blue line), $M = 10$ (green line) and $M = 15$ (blue line)

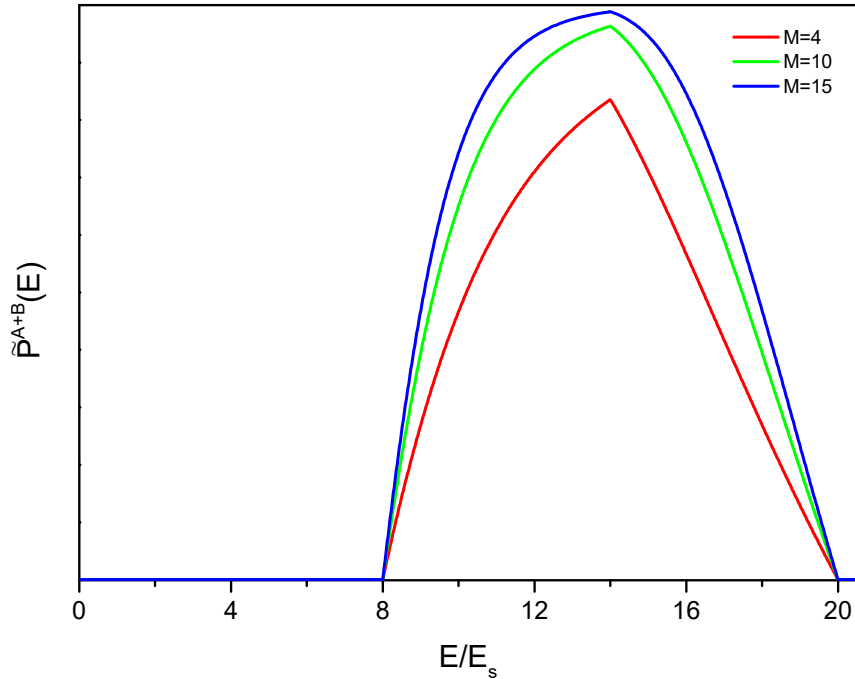


Figure 3.5: $\tilde{P}(E)/\tilde{P}(E_0)$ obtained through the interaction between two identical systems. Each starting system is characterized by lower and upper limits cut-offs, $E_{min}/E_s = 4$ and $E_{max}/E_s = 10$. Model density of states of equation (3.13) has been employed with $M = 4$ (blue line), $M = 10$ (green line) and $M = 15$ (blue line), with the corresponding average population scaled by suitable factors in order to allow a visual comparison

states clearly emerge. As shown in Figure 3.4 and 3.5, the uniform average populations of this type of statistical ensemble does not survive to such a type of thermalization and the uniform statistics cannot describe this experiment.

In this section we intend to recognize a new statistical ensemble that overcomes these drawbacks, just by imposing the condition that the functional dependence on the energy of the mean populations should be invariant in the interaction between two identical systems characterized by the same thermal state.

In the first place we characterize the two initially isolated systems according to their density of states and average populations. The same density of states, $\tilde{g}^A(E) = \tilde{g}^B(E) = \tilde{g}(E)$, is employed for the two systems in order to impose the condition of their physical equivalence. We assume also that their density of states is a continuous function of the energy with the following behaviour

$$\tilde{g}(E) \begin{cases} =0 & \text{for } E \leq 0 \\ >0 & \text{for } E > 0 \end{cases} \quad (3.29)$$

with $E \rightarrow 0^+$ as the energy of the ground state. Then, according to equation (3.18), the following density of states is recovered for the overall $(A + B)$ system,

$$\tilde{g}^{A+B}(E) = \int_0^E dE' \tilde{g}(E - E') \tilde{g}(E') \quad (3.30)$$

for $E \geq 0$. Furthermore we assume that the two systems are in the same thermal state ζ and they are characterized by the same energy dependent average population: $\tilde{P}_\zeta^A(E) = \tilde{P}_\zeta^B(E) = \tilde{P}_\zeta(E)$.

Let us now consider the thermalization induced by a weak perturbation as described in the section 3.3. Of course, given the premises, the thermal state of the overall system $(A + B)$ is the same of the initially isolated systems. It means that we assume that it is described by the same parameter ζ of the systems before thermalization, so attributing to parameter ζ an intensive character: systems in the same thermal state are described by the same value of parameter ζ independently of their size. This legitimates us to denote the resulting average populations as $\tilde{P}_\zeta^{A+B}(E)$, whose functional dependence on

the energy is evaluated according to equation (3.20), that is

$$\tilde{P}_\zeta^{A+B}(E) = \frac{1}{\tilde{g}^{A+B}(E)} \int_0^E dE' \tilde{g}(E - E') \tilde{g}(E') \tilde{P}_\zeta(E - E') \tilde{P}_\zeta(E') \quad (3.31)$$

for $E > 0$. Notice that because of the vanishing of the density of states for $E \rightarrow 0^+$, the ground state population of the thermalized system is simply the square of the ground state population of the initially isolated systems:

$$\tilde{P}_\zeta^{A+B}(0) = \lim_{E \rightarrow 0^+} \tilde{P}_\zeta^{A+B}(E) = \tilde{P}_\zeta(0)^2 \quad (3.32)$$

where $\tilde{P}_\zeta(0) := \lim_{E \rightarrow 0^+} \tilde{P}_\zeta(E)$.

The condition of invariance cannot be imposed directly to energy functions $\tilde{P}_\zeta(E)$ and $\tilde{P}_\zeta^{A+B}(E)$ for the average populations, because they have to be considered as functional of the density of states, which are different in the two case, i.e., $\tilde{g}(E)$ and $\tilde{g}^{A+B}(E)$, respectively. We recall that such a functional dependence is imposed by the normalization condition (3.11). For this reason we introduce the energy functions for the scaled populations with respect to the ground state

$$\tilde{h}_\zeta^{A(B)}(E) := \frac{\tilde{P}_\zeta^{A(B)}(E)}{\tilde{P}_\zeta^{A(B)}(0)} \quad \tilde{h}_\zeta^{A+B}(E) := \frac{\tilde{P}_\zeta^{A+B}(E)}{\tilde{P}_\zeta^{A+B}(0)} \quad (3.33)$$

which are not constrained by the normalization, but only by unitarity in correspondence of the ground state energy: $\tilde{h}_\zeta^{A(B)}(0) = 1$, $\tilde{h}_\zeta^{A+B}(0) = 1$.

These scaled populations are independent of the density of states of the system and that they are invariant in the thermalization process here considered, that is they should be described by the same energy function $\tilde{h}_\zeta(E)$ dependent only on the thermal state ζ :

$$\tilde{h}_\zeta^A(E) = \tilde{h}_\zeta^B(E) = \tilde{h}_\zeta^{A+B}(E) = \tilde{h}_\zeta(E) \quad (3.34)$$

This is precisely the invariance condition which allows us to describe the desired population distribution.

By specifying in equation (3.31) the populations according to $\tilde{h}_\zeta(E)$, and

by taking into account equation (3.32), the following expression is derived

$$\tilde{h}_\zeta(E) = \frac{1}{\tilde{g}^{A+B}(E)} \int_0^E dE' \tilde{g}^A(E-E') \tilde{g}^A(E') \tilde{h}_\zeta(E-E') \tilde{h}_\zeta(E') \quad (3.35)$$

This is a non-linear integral equation whose solution, if unique, identifies the invariant form of population distribution. In Appendix 3.B, by using standard methods of solution of integral equation through discretization [64], we show that it has only one solution of exponential form

$$\tilde{h}_\zeta(E) = e^{-\lambda E} \quad (3.36)$$

parametrized by coefficient λ . Such a solution can be easily recognized by replacing $\tilde{g}^{A+B}(E)$ in equation (3.35) in according to equation (3.30), reorganizing it as

$$\int_0^E dE' [\tilde{h}_\zeta(E) - \tilde{h}_\zeta(E-E') \tilde{h}_\zeta(E')] \tilde{g}(E-E') \tilde{g}(E') = 0 \quad (3.37)$$

A sufficient condition for a solution is that the term within the square brackets vanishes for $0 \leq E' \leq E$, that is if

$$\tilde{h}_\zeta(E' + E'') = \tilde{h}_\zeta(E') \tilde{h}_\zeta(E'') \quad (3.38)$$

where we have replaced $(E - E')$ with E'' , and this implies that $\ln[\tilde{h}_\zeta(E)]$ is a linear function of the energy and, therefore, that equation (3.36) is the solution satisfying the constraint $\tilde{h}_\zeta(0) = 1$.

The scaled populations given by equation (3.36) together with the ground state population, determines the distribution of average populations for the allowed energies depending on the parameter λ . Different values of λ correspond to different distributions of populations, that is to different thermal states. The identification of λ with parameter ζ denoting the thermal state is then compelling, so that

$$\tilde{P}_\zeta(E) = \tilde{P}_\zeta(0) \exp(-\zeta E) \quad (3.39)$$

Furthermore the normalization equation (3.11) supplies the value of the ground

state population. In conclusion the following relation is recovered for the average populations having the appropriate invariance with respect the thermalization here considered

$$\tilde{P}_\zeta(E) = \frac{e^{-\zeta E}}{\int_{-\infty}^{+\infty} dE' \tilde{g}(E') e^{-\zeta E'}} \quad (3.40)$$

for energies E exceeding the ground state. The dependence on the physical system is brought by the density of states $\tilde{g}(E')$. It can be used to evaluate the populations $\tilde{P}_\zeta(E)$ of the initially isolated systems, and of the thermalized system $\tilde{P}_\zeta^{A+B}(E)$, by inserting $\tilde{g}(E)$ and $\tilde{g}^{A+B}(E)$, respectively. These populations share the same exponential dependence on the energy and, therefore, they assure the required invariance, so that the same profile would be obtained if employed for a plot like Figure 3.4 or Fig. 3.5.

In the previous derivation we have assumed, according to equation (3.29), that the ground state is at energy $E \rightarrow 0^+$. By introducing an energy shift, $E \rightarrow E - E_0$, the previous results can be generalized to a system with the ground state at energy $E \rightarrow E_0^+$. Notice, however, that equation 3.40 does not change because the new exponential term $\exp(\zeta E_0)$ at the numerator is eliminated by an identical term generated by the change of variable in the integral. Of course the population distribution has an implicit dependence on the ground state energy deriving from the boundary of the integration domain where the density of states is non vanishing.

Given the population distribution, one can evaluate also the probability density $\tilde{\rho}_\zeta(E)$ on the energy according to the definition equation (3.10). In Figure 3.6 I have reported the density of states, the average populations and the energy probability density for a particular case of the model system described by equation (3.13) ($\zeta = 0.1/E_s$, $M = 4$). As expected, even if the average population is an exponentially decreasing function of the energy, the resulting energy probability density is a function localized in a small energy range because of the quickly increasing density of states. It might be compared with the energy probability density in the random pure state ensemble having a step like behavior: in this case it has the profile of the density of states $\tilde{g}(E)$, but truncated at $E = E_{max}$.

The description of the system through a continuous function $\tilde{g}(E)$ for the

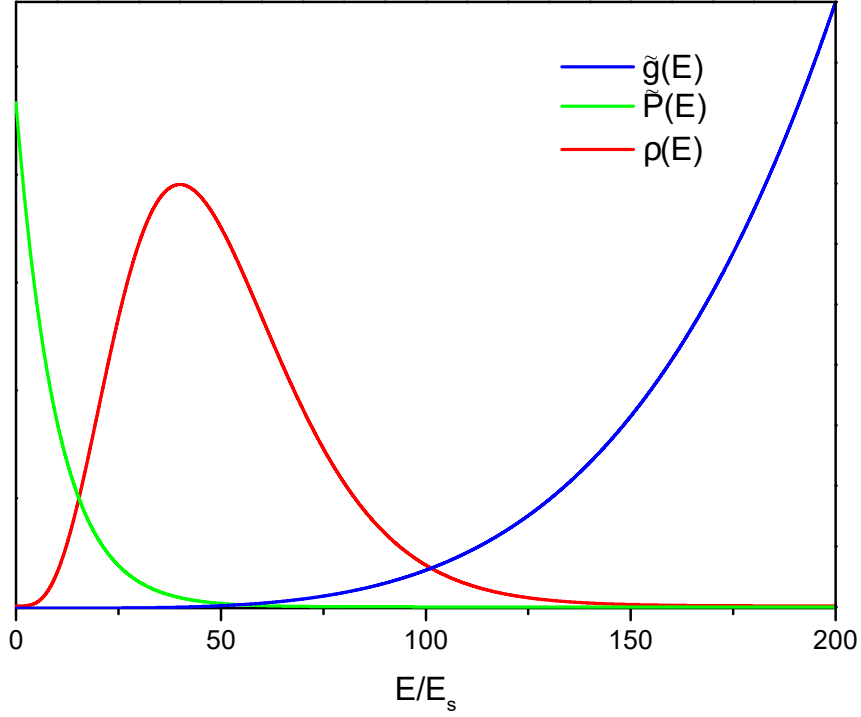


Figure 3.6: Energy density in the TRE model (red line) and its contributions. The blue line represents the density of states of equation (3.13) ($M = 4$) while the green line shows the exponential dependence on population due to equation (3.40) ($\zeta = 0.1/E_s$).

density of states allows the derivation of the invariant average population $\tilde{P}_\zeta(E)$ in the form of the continuous function equation (3.40) of the energy E . On the other hand, any fully microscopic representation of quantum systems should employ the discrete set (E_1, E_2, \dots) of eigenenergies of its Hamiltonian. However, equation (3.40) is easily converted to such a representation by imposing to the average population $\langle P_k \rangle_\zeta$ the same exponential dependence on its energy E_k

$$\langle P_k \rangle_\zeta = \frac{e^{-\zeta E_k}}{\sum_{k'} e^{-\zeta E_{k'}}} \quad (3.41)$$

with the suitable normalization.

Hereafter the statistical ensemble with mean populations given by equation (3.41) will be denoted as Thermalization Resilient Ensemble (TRE). In section 3.6 we will show that such a distribution tends to be preserved in the thermalization between two systems having initially a different thermal states. In other words such a distribution of populations displays to some degree an

intrinsic resistance to modifications in the thermalization, in opposition to the behaviour of statistical ensemble due to random pure states (see figures 3.4 and 3.5).

As one can observe from Figure 3.6, the energy density profile $\tilde{\rho}_\zeta(E)$ shows a bell shape that, in first approximation, can be described by a Gaussian function $N_{(\mu,\sigma)}(E)$.

$$\rho_\zeta(E) \cong N_{(\mu,\sigma)}(E) \quad (3.42)$$

with μ being the energy of the maximum and σ^2 the variance. It corresponds to perform a Taylor expansion, truncated to the second order, on the function $f(E)$ defined as

$$\rho_\zeta(E) = P_\zeta(E) g(E) = \text{const} \cdot e^{f(E)} \cong \text{const} \cdot e^{\left(f(\mu) - \frac{(E-\mu)^2}{2\sigma^2}\right)} \quad (3.43)$$

By using the density of states of equation (3.13) we obtain

$$\mu = M/\zeta \quad \sigma = \sqrt{M}/\zeta \quad (3.44)$$

In particular, in the limit of infinite increasing density of states ($M \rightarrow \infty$) we can demonstrate that the energy distribution narrows around the maximum

$$\lim_{M \rightarrow \infty} \frac{\sigma}{\mu} = \lim_{M \rightarrow \infty} \frac{1}{\sqrt{M}} = 0 \quad (3.45)$$

Up to now, I have obtained a thermalization resilient dependence on the energy for the population variables, under the assumption that the thermalization experiment between two systems can be described by using the convolution law on the energy density of the separated systems. This result has been obtained by the use of reasonable considerations and can be validated only *a posteriori*. As explained by Fresch and Moro [43, 58], the comparison with the thermodynamics can be an optimum criterion in order to discriminate between different probability distributions on pure states and, in our problem can also be used to provide a physical meaning to the thermal parameter ζ .

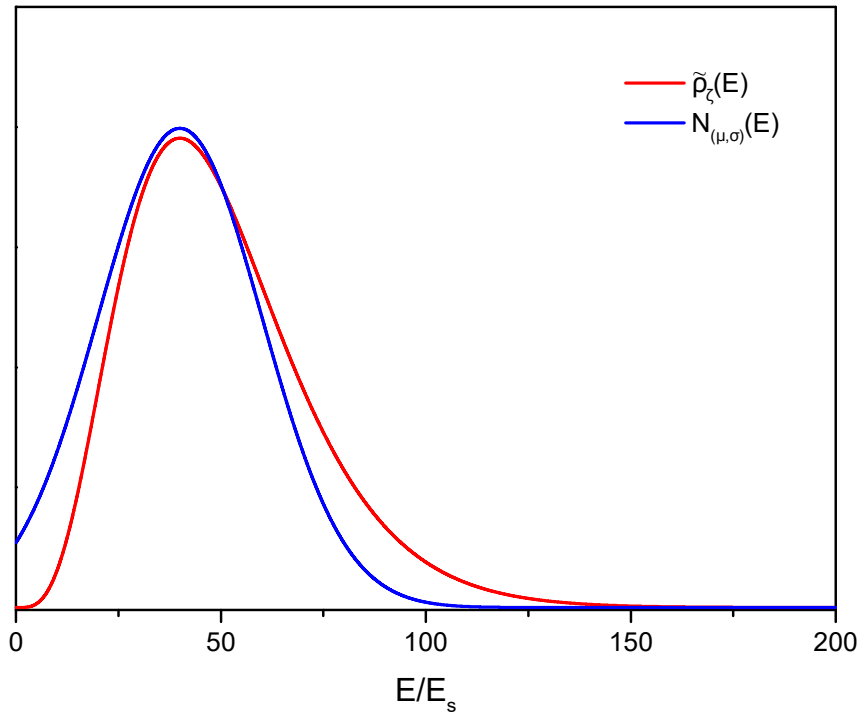


Figure 3.7: energy density profile for a system with $M = 4$ and $\zeta = 0.1/E_s$ (red line) compared to its gaussian approximation, where the maximum $\mu = M/\zeta = 40$ and variance $\sigma = 20$.

3.6 Thermodynamic properties from mean population

The idea of statistical distribution of pure states is relatively recent [22, 21, 44, 65, 57] and it represents an important change of perspective on the description of isolated quantum systems. One shifts the attention from the standard approach with the density matrix [9], representing the average on an ideal collection of many equivalent copies of the system, to the statistical ensemble for the probability density on stochastic variables that parametrize the wave function.

In principle different ensembles of pure state are possible on the basis of constraints on the wave function or on its properties but, once the distribution probability on stochastic variables is provided, it is possible to statistically characterize any observable, like expectation values of relevant operators, so obtaining not only their average values but also their distribution. If the macroscopic limit is considered for an increasing number of components, i.e.

in increasing the density of states for fixed thermal state, some properties can manifest typicality behaviour and therefore their distribution narrows around the average value. In this situation the thermodynamic description is recovered and a single value only is associated to the equilibrium property.

In the following I will discuss the emergence of thermodynamic state functions from the Thermalization Resilient Statistics by elucidating what can be considered as criteria in order to control the agreement between the microscopic quantum picture and thermodynamics. We will be able to attribute a physical meaning to the parameter ζ that accounts for the thermal state.

3.6.1 TRE and Canonical density matrix

Clearly the main feature of TRE ensemble previously derived at the level of average populations (3.41), is the exponential dependence on the energy. This might suggest its equivalence with the canonical statistics of ordinary quantum statistical mechanics [9], which is described by the following canonical density matrix

$$\hat{\sigma}_{can} = \sum_k |E_k\rangle \frac{e^{-E_k/k_B T}}{\sum_{k'} e^{-E_{k'}/k_B T}} \langle E_k| \quad (3.46)$$

where k_B is the Boltzmann constant. In this case, however, the exponential dependence is specified according to the temperature. Indeed the canonical statistics describes a quantum system in contact with a thermal bath at the given temperature T . Implicitly one must assume a weak enough, but non vanishing, interaction between them in order to assure the thermal equilibrium for the overall system so that the same temperature of the thermal bath can be attributed to the quantum system. In such a situation the quantum system is no more isolated and it cannot be in a pure state, that is it cannot be described by a wave function: a wave function could exist only for the overall system including both the quantum system and the thermal bath. Thus the canonical density matrix $\hat{\sigma}_{can}$ should be interpreted as reduced density matrix deriving from the partial trace on the thermal bath states of the pure state density matrix for the overall system.

In the derivation of TRE ensemble, on the contrary, no thermal bath is invoked and, therefore, the exponential weight of average populations in equation (3.41) has no reference to temperature, and it is specified according to a generic parameter ζ for the thermal state of the isolated quantum system. As

a matter of fact, the TRE statistical ensemble is developed for pure states of the quantum system, this implying the absence of interactions with any other system, for instance a thermal bath.

In conclusion, the canonical density matrix and TRE statistical ensemble refers to a quantum system in completely different situations, and this excludes any a priori equivalence between them. On the other hand the shared exponential dependence on the energy suggests that a relation between them should exist. Such an issue calls for the identification of the temperature, and in general of thermodynamic parameters, in the case of TRE statistical ensemble.

3.6.2 Does thermodynamics emerge from Thermalization Resilient Populations?

The aim of recovering thermodynamics from a quantum mechanical description of microscopic systems is widely discussed and several points of view are nowadays present [10, 14, 37]. For example, a particular line of investigation, where typicality holds a key role, has been recently developed [21, 22, 44]. Whenever a property manifests typicality in the meaning of equation (2.43), a clear connection between microscopic and macroscopic description of equilibrium properties is provided. In this work I fully adopt this perspective and in particular I have employed a similar procedure of reference [50] in order to show the emergence of thermodynamics from Thermalization Resilient populations.

The definition of statistical rules in order to obtain a realization of a quantum system, although reasonable, does not provide a direct information on the value of an equilibrium property in an actual system. In fact, a given probability distribution $p(P)$ on populations is compatible with different sets of populations P , each of them representing a possible equilibrium state, correspondingly different values can be attributed to a properties described by a function $f(P)$. It means that from the probability density on populations,

one obtains a distribution of equilibrium properties, without the possibility to assign to them a precise value. However, the emergence of a typical value of an equilibrium property for an isolated quantum system can be determined by investigating the large size limit of the system's properties.

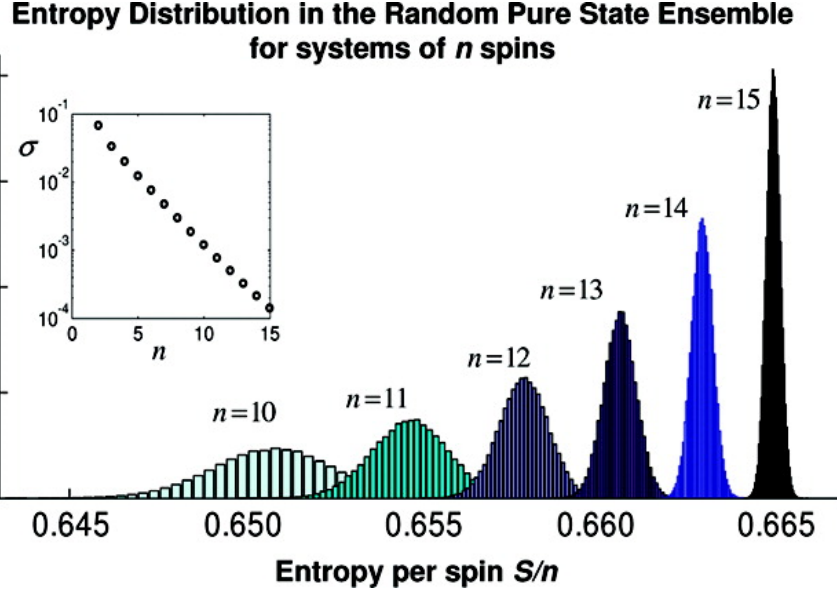


Figure 3.8: the image is taken from *Typicality in Ensembles of Quantum States: Monte Carlo Sampling versus Analytical Approximations* by Fresch and Moro, *J. Phys Chem. A* **2009** 113 (52), in order to show the typicality effect on system properties. In particular the distribution of the entropy per spin S/n for different numbers of spins is shown as obtained by numerical sampling (10^5 sampled points) of the RPSE distribution of systems composed of $n = 11, 13,$ and 15 spins. In the inset, the standard deviation of the fitting Gaussian distributions is reported as a function of the number of spins which constitute the system.

In order to obtain a thermodynamic description of quantum properties it is important to identify microscopic observables that can be related to thermodynamic state functions. In the following, I will propose again and expand the argumentations reported in paragraph 2.4. As already discussed by Fresch and Moro [43, 50] in the case of uniform statistics, the internal energy of thermodynamics should be associated to the energy of the quantum system given as expectation value of the Hamiltonian (2.13)

$$E = \sum_k P_k E_k \quad (3.47)$$

In the presence of typicality behaviour, the energy in a single realization should be very close to the ensemble average property U_Q which can be considered as representative for the system. Then, for the microscopic internal energy we obtain

$$U_Q(\zeta) = \langle E \rangle_\zeta = \sum_k \langle P_k \rangle_\zeta E_k = \frac{\sum_k E_k e^{-\zeta E_k}}{\sum_k e^{-\zeta E_k}} \quad (3.48)$$

where the $\langle \cdot \rangle_\zeta$ indicates the ensemble average with respect to the probability density $p_\zeta(P)$ depending on the thermal state ζ . In equation (3.48), I have substituted to average populations $\langle P_k \rangle_\zeta$ its thermalization resilient expression of equation (3.41). It is important to point out as microscopic internal energy should be considered as functions of parameter ζ because the ensemble average depends on the thermal state of the system. We stress that this quantity is defined for all isolated quantum systems independently of the size, for instance also for a two level system. Therefore it represents the quantum microscopic counterparts of thermodynamic properties. It should be recalled that this microscopically defined state function needs to behave as true thermodynamic properties, for instance in relation to the extensivity, only in the large size limit of the system. For this reason in definitions equation (3.48) we have modified the thermodynamics symbols U by adding the label 'Q' in order to pinpoint its quantum microscopic nature. The thermodynamics internal energy can be recovered in the macroscopic limit

$$U = \lim_{n \rightarrow \infty} U_Q(\zeta) \quad (3.49)$$

where n is the number of components for a fixed thermal state.

The second microscopic quantity considered by Fresch and Moro, which is essential for a thermodynamic description, is the microscopic entropy S_Q . The Shannon entropy W is the best candidate to describe the disorder associated to a distribution of pure states.

$$W = -k_B \sum_k P_k \ln P_k \quad (3.50)$$

where k_B is the Boltzmann constant. In particular, it quantifies the disorder with respect the decomposition on the eigenvectors of a quantum system. By the use of the typicality argument we can associate its ensemble average with

the microscopic entropy

$$S_Q(\zeta) = \langle W \rangle_\zeta = -k_B \sum_k \langle P_k \ln P_k \rangle_\zeta \quad (3.51)$$

Given the formal definitions of these quantum microscopic parameters (equations (3.48) and (3.51)), one can derive the corresponding temperature. Indeed the function $S_Q = S_Q(U_Q)$ is obtained by mutually eliminating the functional dependence of $U_Q(\zeta)$ and $S_Q(\zeta)$ on the thermal state parameter ζ , and this allows the identification of the temperature according to the fundamental differential (at constant volume) of thermodynamics:

$$\frac{1}{T_Q} := \frac{dS_Q}{dU_Q} = \frac{\partial S_Q(\zeta)/\partial \zeta}{\partial U_Q(\zeta)/\partial \zeta} \quad (3.52)$$

We stress that this is the formal definition of quantum microscopic temperature, and that the correspondence with the temperature of macroscopic systems has still to be addressed.

I think that one should appreciate the capability of TRE statistical ensemble to allow a formal definition of a microscopic temperature which can be applied to any quantum system, independently of its size, even in the extreme case of a two level system. As a matter of fact such a procedure cannot be directly transferred to random pure state ensembles. We recall that in this case the thermal parameter ζ should be identified with the cut-off energy $\zeta = E_{max}$, or equivalently with the dimension N of the active space \mathcal{H}_N (see paragraph 3.1). Then, by using definitions equations (3.48) and (3.51), one recovers parameters $U_Q(\zeta)$ and $S_Q(\zeta)$ which are not continuous functions of ζ , since they display step-like increments when the active space dimension N increases (see Fig. 3 of ref.[50]). Therefore the function $S_Q = S_Q(U_Q)$ resulting from the elimination of ζ variable is not continuous, and definition equation (3.52) is not directly applicable. In order to define the temperature one should consider the continuous extension of $S_Q = S_Q(U_Q)$ in the macroscopic limit when the step increments of U_Q and S_Q are no more relevant. But this, of course, prevents the identification of the microscopic temperature of small quantum with the statics of random pure state ensembles.

The possibility to define a quantum temperature does not directly means that it behaves according to what we expect from the thermodynamics and

further requirements have to be considered. In particular entropy should be a convex increasing function of internal energy, in fact only in this case one can recover, from equation (3.52), a temperature that increases with the internal energy.

Morover the extensivity of both internal energy and entropy has to be assured in order recover a quantum temperature having an intensive character.

The agreement between the properties obtained with TRE populations and the behaviour of material systems requires also that the standard canonical form of equation (3.46) for the equilibrium reduced density matrix $\hat{\sigma}$ of a subsystem can be derived. Only in this case the global comparison between the global and the local temperature become equivalent.

To summarise, several requirements have to be verified in order to assume the agreement between the quantum properties (equations (3.48) and (3.51)) and the thermodynamic state functions U and S . This is necessary in order to recover a physically reasonable description of quantum system from the statistical ensemble point of view. I report here as a list the requirements we have just considered

- typicality of internal energy U_Q and entropy S_Q
- $S_Q(U_Q)$ as an increasing convex function
- U_Q and S_Q has to be extensive properties in the limit of macroscopic systems
- canonical reduced density matrix
- equivalence between local and global temperature

3.6.3 Approximated evaluation of entropy

The explicit dependence of TRE average populations on energy, that is equation (3.41), allows the direct calculation of the microscopic internal energy U_Q , however the same direct evaluation cannot be performed on the microscopic entropy S_Q

$$S_Q = -k_B \sum_k \langle P_k \ln P_k \rangle = -k_B \sum_k \int dP P_k \ln P_k p(P) \quad (3.53)$$

since the probability distribution on populations variables $p(P)$ is needed. At the same time, the absence of the exact probability distribution for a certain statistical problem is a common situation in statistics and it can be solved by considering that each probability distribution derives from the constraints of the problem that represent the information content. If we approximate these constraints we are able to derive an approximate probability distribution $D(\eta)$ and check a posteriori the goodness of the approximation.

The methodological ingredient we introduce is based on the maximum entropy principle, developed by Jaynes [1, 66] in the framework of information theory and already used with some differences by Wooters [67], Naudts [54] and Fresch and Moro [49] on the ensemble of wave functions. We replace the populations parameters $P = (P_1, P_2, \dots, P_k, \dots)$ with a set of random variables $\eta = (\eta_1, \eta_2, \dots, \eta_k, \dots)$ each of them defined in the interval $[0, \infty)$ and characterized by the probability density

$$\int_0^\infty d\eta D(\eta) = 1 \quad (3.54)$$

that allows the calculation of average values $\langle f(\eta) \rangle$ of any function $f(\eta)$

$$\langle f(\eta) \rangle = \int_0^\infty d\eta D(\eta) f(\eta) \quad (3.55)$$

In addition, we require that the distribution function $D(\eta)$ is such that the average value $\langle \eta_k \rangle$ of each η_k reproduces the Thermalization Resilient Populations.

$$\langle \eta_k \rangle = \langle P_k(E_k) \rangle_\zeta = \frac{e^{-\zeta E_k}}{\sum_{k'} e^{-\zeta E_{k'}}} \quad (3.56)$$

We can immediately see as a single realization of η variables does not have to satisfy the normalization condition, for this reason η set is not strictly a set of populations. This represents the major approximation. Furthermore, the constraint of equation (3.56) alone does not select a unique probability distribution and no strong physical reasons are available to select one with respect some others. In fact, there would be additional constraints if this is the case.

The problem is now how to select an appropriate probability distribution with a low information content represented by the set of constraints (3.54), (3.56). Thanks to the development of information theory, Jaynes proposed the

maximum entropy principle as a solution for this problem. He stated that the best probability distribution to represent the state of knowledge for a given set of data is the one that has maximum entropy [1, 66]. In particular, within the infinite set of $D(\eta)$ functions that satisfy the given constraints, we choose the one that minimizes the information functional

$$I[D] = \int d\eta D(\eta) \ln D(\eta) \quad (3.57)$$

where $I[D]$ is the functional that describe the information content I of the distribution $D(\eta)$. The minimization of the information functional corresponds to the maximization of the entropy since maximum entropy is associated with lowest information on a given situation.

The minimization of the functional (3.57) under the constraints (3.54) and (3.56) is performed by the use of Lagrange multipliers method. By introducing the Lagrange multipliers λ_k we obtain the actual functional that has to be minimized

$$F[D] = I[D] + \sum_k \lambda_k \langle \eta_k \rangle \quad (3.58)$$

$$= \int d\eta D(\eta) \ln D(\eta) + \int d\eta D(\eta) \sum_k \lambda_k \eta_k \quad (3.59)$$

$$= \int d\eta \left[D(\eta) \ln D(\eta) + \sum_k \lambda_k \eta_k D(\eta) \right] \quad (3.60)$$

where the number of lagrange multipliers correspond to the dimension of the Hilbert space, since each Hamiltonian eigenvector has different TRE average population. In order to minimize the functional we evaluate its variation for the change $D(\eta) \rightarrow D(\eta) + \epsilon h(\eta)$ of the distribution

$$F[D + \epsilon h] = \int d\eta (D(\eta) + \epsilon h) \ln (D(\eta) + \epsilon h) + \int d\eta \sum_k \lambda_k \eta_k (D(\eta) + \epsilon h) \quad (3.61)$$

and then we expand it in series of ϵ up to the first order so obtaining

$$F[D + \epsilon h] = F[D] + \left(\ln D(\eta) + 1 + \sum_k \lambda_k \eta_k \right) \epsilon h \quad (3.62)$$

Thus we impose the first order functional derivative equal to zero in order to

find its maximum

$$\frac{\delta F}{\delta D} = \lim_{\epsilon \rightarrow 0} \frac{F[D + \epsilon h] - F[D]}{\epsilon h} = \ln D(\eta) + 1 + \sum_k \lambda_k \eta_k = 0 \quad (3.63)$$

The resultant normalized distribution function is

$$D(\eta) = \frac{e^{-\sum_k \lambda_k \eta_k}}{\int d\eta e^{-\sum_k \lambda_k \eta_k}} \quad (3.64)$$

where the λ_k parameters are the Lagrange multipliers. Their explicit identification can be performed through the evaluation of $\langle \eta_k \rangle$ leading to

$$\frac{1}{\lambda_k} = \frac{e^{-\zeta E_k}}{\sum_k e^{-\zeta E_k}} \quad (3.65)$$

The approximate probability distribution of equation (3.64) is factorised and all the variables result to be statistically independent.

The microscopic entropy (3.51) can be now evaluated according to the approximated variables η as

$$S_Q = -k_B \sum_k \langle \eta_k \ln \eta_k \rangle = -k_B \sum_k \int d\eta \eta_k \ln \eta_k D(\eta) \quad (3.66)$$

The result can be expressed in terms of Lagrange multipliers as

$$S_Q = -k_B \sum_k \frac{1 - \gamma - \ln \lambda_k}{\lambda_k} \quad (3.67)$$

where γ is the constant of Eulero-Mascheroni, or by inserting equation (3.65) for the lagrange multipliers

$$S_Q = -k_B \left[1 - \gamma - \frac{\sum_k \zeta E_k e^{-\zeta E_k}}{\sum_k e^{-\zeta E_k}} - \ln \sum_k e^{-\zeta E_k} \right] \quad (3.68)$$

In particular from the last equality it can be easily shown that the average $\langle \eta_k \ln \eta_k \rangle$ corresponds to the product of the averages $\langle \eta_k \rangle \ln \langle \eta_k \rangle$ with a constant additive term to entropy

$$S_Q = -k_B \sum_k \langle \eta_k \ln \eta_k \rangle = -k_B \sum_k \langle \eta_k \rangle \ln \langle \eta_k \rangle - k_B(1 - \gamma) \quad (3.69)$$

Furthermore, if we consider small enough values for the thermal parameter ζ , we obtain average populations effectively distributed over a large number of eigenstates and in this case the additive terms $k_B(1 - \gamma)$ becomes negligible so that

$$S_Q \cong -k_B \sum_k \langle \eta_k \rangle \ln \langle \eta_k \rangle \quad (3.70)$$

3.6.4 Quantum Temperature

The explicit relation for the microscopic internal energy together with the approximate equation for the entropy allows the evaluation of the temperature according to equation (3.52). By taking into account that $\sum_k d\langle P_k \rangle_\zeta / d\zeta = 0$ because of the normalization of the populations, the derivative of the entropy can be specified as

$$\frac{dS_Q(\zeta)}{d\zeta} \cong -k_B \sum_k [\ln \langle P_k \rangle_\zeta + 1] \frac{d\langle P_k \rangle_\zeta}{d\zeta} = k_B \zeta \sum_k E_k \frac{d\langle P_k \rangle_\zeta}{d\zeta} \quad (3.71)$$

where the logarithmic term has been evaluated according to equation (3.41). At the same time we can evaluate the derivative of internal energy with respect the thermal parameter

$$\frac{dU_Q(\zeta)}{d\zeta} = \sum_k E_k \frac{d\langle P_k \rangle_\zeta}{d\zeta} \quad (3.72)$$

Thus, the r.h.s. of equation (3.71) is proportional to the derivative of the internal energy (3.48) through $k_B \zeta$. In conclusion the direct identification of the thermal state parameter ζ , which up to now was left unspecified, and the inverse of the thermal factor is recovered:

$$\zeta \cong \frac{1}{k_B T_Q} \quad (3.73)$$

We emphasize that this is not an equivalence since it is valid only in the limit assuring typicality. As an alternative, which will be exploited in a subsequent chapter, one can evaluate exactly the quantum microscopic temperature $T_Q(\zeta)$ as a function of the thermal parameter ζ according to equation (3.52). Moreover, if typicality is assumed in relation to the macroscopic limit, the very simple and useful relation (3.73) is assured, as supposed in the following.

Thanks to the identification of the thermal parameter with the inverse of the quantum analogue of temperature, we can now understand why a large number of eigenstates with non-negligible population corresponds to a small thermal parameter. In fact, due to the inverse proportionality, lower thermal parameter means an higher temperature and more eigenstates with significant population.

The formal connection between the quantum systems parameter ζ and the state function temperature represents an important result. In fact given the Hamiltonian of the system and the correspondent energy spectrum, the ζ parameter takes into account how the eigenstates are populated on the average in a given thermodynamic state of the microscopic system. The importance of this result is amplified in the case of few level systems, for example the two level systems where TRE statistics allows for the description of all the possible thermal states. In opposition, Random Pure State statistics allows the description of only two thermal states when one or both levels have non vanishing population. TRE statistics, instead, allows the existence of all the possible thermal states with variable populations and uniform random statistics is recovered as limit situations: if temperature approaches zero, only the ground state is populated while if infinite temperature is considered equal mean populations of both levels are obtained.

Furthermore, equation (3.73) allows us to specify the mean in the TRE ensemble of the time averaged density matrix operator of equation (2.23)

$$\langle \bar{\hat{\rho}} \rangle_{\zeta} = \sum_k |E_k\rangle \langle P_k \rangle_{\zeta} \langle E_k| = \sum_k |E_k\rangle \frac{e^{-\zeta E_k}}{\sum_{k'} e^{-\zeta E_{k'}}} \langle E_k| \quad (3.74)$$

Then if approximation (3.73) is inserted, the equivalence between the mean density matrix of TRE statistical ensemble and the canonical form equation (3.46) is recovered

$$\langle \bar{\hat{\rho}} \rangle_{\zeta} \cong \hat{\rho}_{can} \quad (3.75)$$

Therefore all the properties of thermodynamic state functions which are derivable from the canonical statistics, can be transferred to the TRE statistical ensemble. In this way one obtains that 1) the entropy $S_Q = S_Q(U_Q)$ is a convex function of the internal energy U_Q so that the temperature $T_Q = T_Q(U_Q)$ is an increasing function of the internal energy, that 2) both internal energy U_Q

and entropy S_Q are extensive, so that the temperature T_Q is an intensive state function and that 3) if the quantum system is partitioned into a subsystem of interest and its environment, then the subsystem is described by a canonical reduced density matrix.

3.7 Resilience to Thermalization

In the previous paragraphs I have obtained the ensemble average populations characterized by a thermal state ζ (see equation (3.40)). I have also demonstrated the emergence of thermodynamic properties by considering the typicality behaviour of the internal energy and of the entropy. All this results, however arise from average population eq. (3.40) which derives from the condition of thermalization invariance applied to the particular case when two identical systems in the same thermal state are brought in contact. In this situation, no neat energy flux can be detected, differently from the standard thermodynamic experiment of thermalization. Then the following questions naturally arise. What happens if the systems have different temperatures? Are the TRE populations able to describe the equilibrium state after the equilibration process? These are the question I try to answer in the following. In particular, in this paragraph I want to consider a real thermalization experiment by putting in interaction systems in different thermal states. I will show as TRE populations are resilient to thermalization since they tends to preserve the TRE energy dependence.

One can show that the interaction modifies the TRE energy dependence of population averages only when the two interacting systems start from different thermal state. As a matter of fact, the invariance condition used to derive TRE average populations, is satisfied also in the case of two different systems, that is systems described by different densities of states $g^A(E)$ and $g^B(E)$, but at the same thermal state $\zeta^A = \zeta^B = \zeta$. Indeed by specifying in Eq. (3.31) both $P_{\zeta^A}^A$ and $P_{\zeta^B}^B$ according to Eq. (3.40) so that $P_{\zeta^A}^A(E - E')\tilde{P}_{\zeta^B}^B(E') \propto \exp(-\zeta E)$, the same energy dependence of Eq. (3.40) is recovered for the the population averages $\tilde{P}^{A+B}(E)$ after the interaction.

The resilience can be estimated on the basis of the equilibrium mean populations $\tilde{P}^{A+B}(E)$ when two systems, A and B , with the same energy spectrum ($\tilde{g}^A(E) = \tilde{g}^B(E) = \tilde{g}(E)$), but different quantum temperatures ($\zeta_A \neq \zeta_B$), are

brought in contact. We assume that the initially isolated systems A and B have TRE average of equation (3.40)

$$\tilde{P}_{\zeta_A}^A(E) = \frac{e^{-\zeta_A E}}{n^A(\zeta_A)} \quad \tilde{P}_{\zeta_B}^B(E) = \frac{e^{-\zeta_B E}}{n^B(\zeta_B)} \quad (3.76)$$

where $n(\zeta_A)$ and $n(\zeta_B)$ are the normalization factors

$$n^A(\zeta_A) = \int_{-\infty}^{+\infty} dE \tilde{g}(E) e^{-\zeta_A E} \quad n^B(\zeta_B) = \int_{-\infty}^{+\infty} dE \tilde{g}(E) e^{-\zeta_B E} \quad (3.77)$$

Furthermore, we suppose the interaction between systems is perturbative with respect to the single system energies. In addition we use the model (3.13) for the density of states that leads to a density of states $\tilde{g}^{A+B}(E)$ of equation (3.28)

The perturbative character of the interaction allows one to describe the overall system on the base of single system eigenstates and, in addition, to define the energy density $\tilde{\rho}^{A+B}(E) = \tilde{P}^{A+B}(E)\tilde{g}^{A+B}(E)$ in according to equations (3.19) as a convolution of the energy density of systems A and B

$$\tilde{\rho}^{A+B}(E) = \int_0^E dE' \tilde{P}_{\zeta_A}^A(E - E') \tilde{g}(E - E') \tilde{P}_{\zeta_B}^B(E') \tilde{g}(E') \quad (3.78)$$

The energy density of the overall system from the convolution is given as

$$\tilde{\rho}^{A+B}(E) = \frac{A^2}{E_s^2} \frac{e^{-\zeta_A E}}{n^A(\zeta_A) n^B(\zeta_B)} \cdot \left[\sum_{k=0}^M \binom{M}{k} \frac{(-1)^k}{(\zeta_B - \zeta_A)^{M+k+1}} \left(\frac{E}{E_s}\right)^{M-k} \gamma(M+k+1, (\zeta_B - \zeta_A)E) \right] \quad (3.79)$$

where $\gamma(M+k+1, (\zeta_B - \zeta_A)E/E_s)$ is the lower incomplete gamma function

[68] that, for $M \in \mathbb{N}$, has an analytic expression

$$\begin{aligned} \gamma(M+k+1, (\zeta_B - \zeta_A) \frac{E}{E_s}) &= \int_0^{(\zeta_B - \zeta_A)E/E_s} dx x^{M+k} e^{-x} \\ &= (M+k)! \left(1 - e^{-(\zeta_B - \zeta_A)E} \cdot \sum_{r=0}^{M+k} \left(\frac{E}{E_s} \right)^r \frac{\zeta_B - \zeta_A}{r!} \right) \end{aligned} \quad (3.80)$$

In Fig. 4 we have represented the resulting energy dependence of $\tilde{P}^{A+B}(E)$ in the case of thermal state parameters differing by a factor of two, $\zeta^A = 0.1/E_s$ and $\zeta^B = 0.2/E_s$, with the model density of states Eq. (3.13) with $M = 4$. Even if an exponential scale has been used for populations, the deviations from TRE behaviour, $\ln[\tilde{P}^{A+B}(E)] \propto E$, are not evident. In order to quantify these deviations we need to characterize the thermal state of the overall system $A + B$ resulting from the interaction. This is naturally done according to thermodynamics, by identifying the temperature of the $A + B$ system. Given the model density of states Eq. (3.13), from the TRE average of the energy one derives the internal energy $U_Q(\zeta) = (M+1)/\zeta$ which, according to the assignment Eq. (3.73), implies a linear dependence on the temperature of the internal energy, i.e. a constant thermal capacity. On the other hand the thermodynamical equilibration of two identical bodies with constant thermal capacities initially at temperatures T_Q^A and T_Q^B , leads to the mean temperature $T_Q^{A+B} = (T_Q^A + T_Q^B)/2$ as the thermalization temperature of the final state. By invoking again the assignment Eq. (3.73), this allows the identification of the thermal parameter for the TRE average populations in the thermal state

$$\zeta^{A+B} = \frac{1}{k_B T_Q^{A+B}} = \frac{2}{k_B T_Q^A + k_B T_Q^B} = \frac{2}{1/\zeta^A + 1/\zeta^B} = \frac{2\zeta^A \zeta^B}{\zeta^A + \zeta^B} \quad (3.81)$$

Therefore, for the sake of comparison, in Fig. 4 we have plotted also the TRE average populations $\tilde{P}_{\zeta^{A+B}}^{A+B}(E)$ for the mean temperature, that is for $\zeta^{A+B} = 0.4/(3E_s)$. In this way one clearly detects the deviations produced by the interactions with respect to the TRE predictions at the thermalization temperature. In the same Figure we have also represented the correspondent probability densities, $\tilde{\rho}^{A+B}(E)$ and $\tilde{\rho}_{\zeta^{A+B}}^{A+B}(E)$, which allow the identification of the most probable range of energies. Then one clearly see that the two average

populations $\tilde{P}^{A+B}(E)$ and $\tilde{P}_{\zeta^{A+B}}^{A+B}(E)$ are nearly coincident in the most relevant range of energies, and that the deviations appears neatly only when the energy probability density is small. The overall effect is that, even if the interaction does not lead exactly to TRE average population averages, the TRE profile well reproduces the behaviour of average populations in correspondence of the most probable energies. In this sense we consider TRE to be resilient with respect to thermalization.

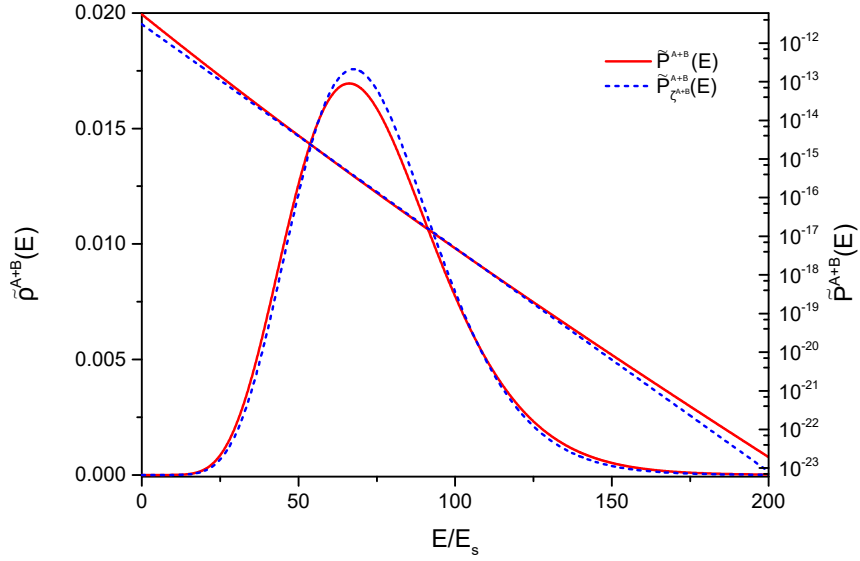


Figure 3.9: Energy dependence of average populations $\tilde{P}^{A+B}(E)$ (right scale) and energy distribution $\tilde{\rho}^{A+B}(E)$ (left scale) for the interaction of two systems A and B with different thermal state, $\zeta^A = 0.1/E_s$ and $\zeta^B = 0.2/E_s$, but with the same density of states Eq. (3.13) with $M = 4$. Continuous red lines: average populations $\tilde{P}^{A+B}(E)$ from Eq. (?). Dashed blue lines: TRE average populations $\tilde{P}_{\zeta^{A+B}}^{A+B}(E)$ for the mean temperature, $\zeta^{A+B} = 0.4/(3E_s)$.

In order to quantify with an unique quantity the TRE resilience in this kind of thermalization processes, we have employed the following parameter:

$$\Delta_{TRE} := \frac{1}{2} \int_0^{+\infty} dE \left| \tilde{\rho}^{A+B}(E) - \tilde{\rho}_{\zeta^{A+B}}^{A+B}(E) \right| \quad (3.82)$$

that is half the energy integral of the absolute difference between the energy probability density $\tilde{\rho}^{A+B}(E)$ evaluated according to the convolution rule, and the TRE energy probability density $\tilde{\rho}_{\zeta^{A+B}}^{A+B}(E)$ for the mean temperature. Of course a vanishing value is recovered when the effects of the interaction is

exactly reproduced by the TRE ensemble, for instance when the two systems start from the same thermal state, $\zeta^A = \zeta^B$. The largest deviation occurs in the absence of superposition between the two energy probability densities, in which case $\Delta_{TRE} = 1$ since both probability densities are normalized. By evaluating numerically the integral of Eq. (3.82), we have determined Δ_{TRE} for fixed $\zeta^A = 0.1/E_s$ and increasing values of ζ^B with two values of the exponent M of the model density of states Eq. (3.13). The results reported in Fig. 5 show as expected that deviations from TRE increase with the difference in the thermal state of the two systems. It should be stressed, however, that these deviations appear somehow limited, since a fourfold difference in the thermal parameter (or, correspondingly, in the temperature) produces an effect less than 10%. This is another evidence that confirms the resilient character of TRE statistics. Moreover this conclusion is rather general, as long as the results displayed in Fig. 5 are rather insensitive to the model density of states, i.e. parameter M of Eq. (3.13). Further results not reported here have shown also the weak dependence on the mean temperature.

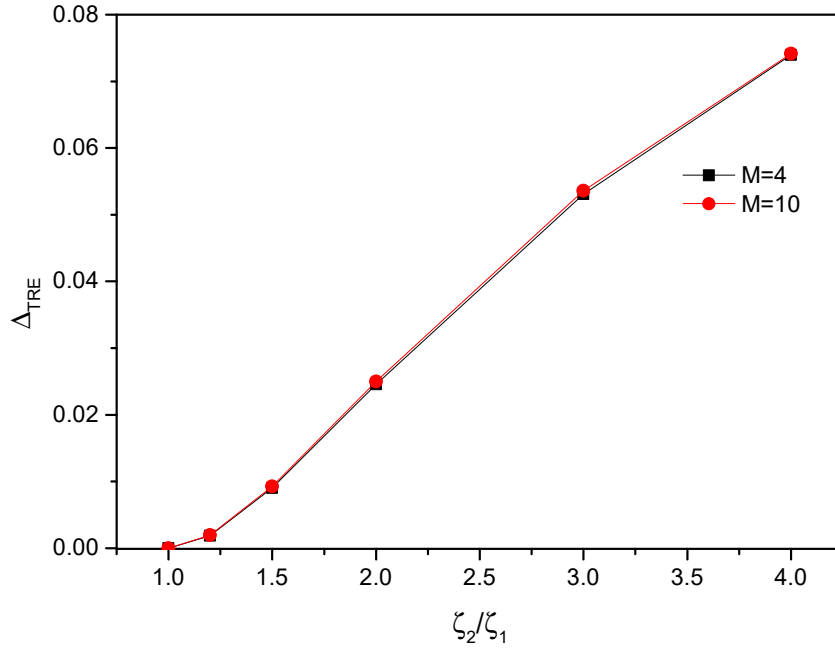


Figure 3.10: results for the resilience parameter Δ_{TRE} obtained for $\zeta^A = 0.1/E_s$ and increasing values of ζ^B with the model density of states of Eq. (3.13) for $M = 4$ (black squares) and $M = 10$ (red circles).

3.A Weak interaction model between systems

Let's consider a generic quantum system characterized by its energy spectrum (E_1, E_2, \dots) and described by its density of states

$$g(E) = \sum_k \delta(E - E_k) \quad (3.83)$$

where the summation run on each k -th Hamiltonian eigenstate. In the presence of typicality behaviour of the equilibrium properties, they are described by ensemble average populations only (equation (3.3)). Furthermore, by following the discussion in the main text, as long as the systems is complex enough one can introduce the continuous representation in the energy domain both for average populations $\tilde{P}(E)$ and for the density of states $\tilde{g}(E)$. The calculation of the equilibrium value of all functions $f(E)$ of the energy can be easily performed as energy integral, like in equation (3.4).

For practical purpose, it is also possible to introduce a discretized picture of the energy variable in intervals of ΔE width, each centered in ε_i , such that the continuous representation is recovered for $\Delta E \rightarrow 0$. In this framework, we define the number of energy levels ω_i in the i -th interval as the integral on the density of states

$$\omega_i = \int_{\varepsilon_i - \Delta E/2}^{\varepsilon_i + \Delta E/2} dE \tilde{g}(E) \quad (3.84)$$

The system is then represented as equally spaced energy levels ε_i made by ω_i degenerate states and having $P_i = P(\varepsilon_i)$ as average population per level. The ground state corresponds to the level ε_{i_0} such that $\omega_{i_0} \neq 0$ and $\omega_i = 0$ for $i < i_0$.

This representation is very useful in the calculation of energy integral. If we consider the generic function of energy $f(E)$, its ensemble average values $\langle f(E) \rangle$ can be expressed in according to equations (3.4) and (3.84), as

$$\langle f(E) \rangle = \sum_{k=-\infty}^{+\infty} P_i f(\varepsilon_i) \int_{\varepsilon_i - \Delta E/2}^{\varepsilon_i + \Delta E/2} dE \tilde{g}(E) \quad (3.85)$$

that allows one to obtain a discrete counterpart of the continuum representa-

tion of the average $\langle f(E) \rangle$

$$\langle f(E) \rangle = \sum_{i=-\infty}^{+\infty} f(\varepsilon_i) \omega_i P_i \quad (3.86)$$

This is nothing else than the Simpson rule for the discretization of integrals. It's important to point out that in the limits of infinitesimal width of energy interval the continuous representation is perfectly recovered.

We consider now the interaction among two generic systems A and B . Each system is characterized by its own Hamiltonian \hat{H}^A and \hat{H}^B , that determines the energy spectrum and so the density of states $\tilde{g}^A(E)$, $\tilde{g}^B(E)$. By dividing the energy axes of each system in intervals of the same length ΔE , we obtain the same discrete representation for both systems, characterized by degenerate levels ω_i^A and ω_i^B for each energy level ε_i . In full generality, the differences in the density of states between the two systems are taken into account by the values of ω_i^A and ω_i^B .

In order to describe the equilibrium situation deriving from the interaction between these two systems, we suppose the presence of an interacting Hamiltonian \hat{H}^{int} in the overall Hilbert space $\mathcal{H} = \mathcal{H}^A \otimes \mathcal{H}^B$, such that its contribution to the overall energy is negligible. This allows one to describe the overall system eigenenergies E_k^{AB} and eigenvectors $|E_k^{AB}\rangle$ according to populations of the initially isolated systems

$$E_k^{AB} = \varepsilon_i^A + \varepsilon_j^B \quad |E_k^{AB}\rangle = |\varepsilon_i^A\rangle |\varepsilon_j^B\rangle \quad (3.87)$$

where $k = i + j$. We can also describe the deneneration in the overall system Ω_k in terms of number of levels of the separated systems ω_i^A and ω_i^B .

$$\Omega_k = \sum_{s=0}^k \omega_{k-s}^A \omega_s^B \quad (3.88)$$

Although the contribution of the interaction Hamiltonian is negligible in terms of energy, we suppose that it gives rise to the energy redistribution between the systems. In particular we suppose then an entangled state derives such that the interaction mixes the population among levels with the same energy. The redistribution of the population within the multiplets can be seen as a manifestation of the conservation energy principle. The mean population of

the overall system is then derived as the cumulative population on a multiplet over its degeneration

$$P_k = \frac{\sum_{s=0}^k P_{k-s}^A \omega_{k-s}^A P_s^B \omega_s^B}{\Omega_k} \quad (3.89)$$

One can immediately notice that the mean population derives from the discrete convolution of the two separated system population. The role of the convolution is discussed and generalized in the main text.

3.B Solution of the integral equation

To find the solution of Eq. (3.35), we adopt the discretization procedure of integral equations which allows their transformation into algebraic equations [64]. Let us partition the domain for the energy variable, $E \geq 0$ into intervals having $E_j = j\Delta E$ as borders for $j = 0, 1, 2, \dots$ with a given increment ΔE . Then, by applying the Simpson rule, one obtains the discrete counterpart of the integral equation (3.35)

$$h_j = \frac{\sum_{j'=1}^{j-1} g_{j-j'} g_{j'} h_{j-j'} h_{j'}}{\sum_{j'=1}^{j-1} g_{j-j'} g_{j'}} \quad (3.90)$$

where $\tilde{g}^{A+A}(E)$ has been specified according Eq. (??) in discretized form and $h_j := \tilde{h}_\zeta(E_j)$, $g_j := \tilde{g}^A(E_j)$. Notice that in the discretization of convolution integrals, the borders of the integration domain do not contribute because $g_0 = \tilde{g}^A(0) = 0$ according to Eq. (??). The algebraic equations (3.90) allow the calculation of the unknown h_j given the lower order coefficients h_{j-1}, h_{j-2}, \dots , while $h_0 = \tilde{h}_\zeta(0) = 1$ because of definition Eq. (??).

Since Eq. (3.90) is missing for $j = 1$, the ensemble of algebraic equations has a solution parametrically dependent of the unknown coefficient h_1 . More specifically, one can demonstrate that $h_j = (h_1)^j$ is their solution. Indeed, this is obviously true for $j = 2$, and then one can verify it with a recursive procedure directly from Eq. (3.90). By replacing the unknown h_1 with the free parameter $\lambda = -\ln(h_1/\Delta E)$, the discrete solution takes the form

$$\tilde{h}_\zeta(E_j) = h_j = \exp\{-\lambda j \Delta E\} = \exp\{-\lambda E_j\} \quad (3.91)$$

Finally the full continuous solution Eq. (3.36) is recovered by considering the limit of a vanishing increment ΔE .

CHAPTER 4

From sphere to ellipsoid

In the previous chapter I have illustrated about the drawbacks of uniform statistics on pure states, suggesting the thermalization invariance as a new guideline in the identification of a suitable probability distribution on populations. As a matter of fact, the thermalization experiment represents a very common and interesting physical-chemical process whenever two systems are brought in contact and allowed to exchange their energy. Starting from the statistical invariance in the thermalization, I have obtained and characterized the thermalization resilient average populations.

The main results of this approach are twofold: on the one hand, unlike uniform random ensembles population, TRE average populations can describe the equilibrium after the thermalization experiments and, on the other hand, from TRE populations a clear equilibrium thermodynamics emerges with well defined thermal states even in the microscopic realm.

However, this does not represent a complete statistical description of the problem. Even if the set of average populations pinpoints a well determined thermal quantum state, the lack of a probability distribution does not allow the sampling of quantum pure states, which is indispensable in order to perform quantum dynamical simulations. As a matter of fact, the unbiased random sampling of quantum states is a necessary tool in the development of the quantum analogue of molecular dynamics simulations.

In this chapter I will obtain a probability distribution on pure states with the use of a geometrical analysis on the Hilbert space. The surface elements of an ellipsoidal manifold will be related to the probability density on populations.

4.1 What does geometry say about statistics?

Following the perspective of Fresch and Moro [49], I will develop and explain how to obtain a probability distribution on population parameters through the analysis of a surface embedded in the Hilbert space. In particular I am going to consider how a uniform density of points in a surface of an ellipsoid is deformed by its projection to the unitary hypersphere, representing the domain of normalized wavefunctions.

I recall that a generic quantum mechanical state can be described as a vector in the Hilbert space, very much like the state of a classical system can be interpreted as a point in the phase space for the ensemble of position and momenta. Then the properties of the system select the subspace of the total space where the system is defined. Every additional constraint corresponds to further restrictions of the phase space. This correspondence between constraints on system properties and subsets of the phase space is completely general and valid both for classical and quantum systems. For example, when a classical isolated system is introduced with a given value of the energy, the appropriate subspace corresponds to all the values for positions and momenta that are in agreement with the constraint on the energy. It selects a manifold (surface) in the classical phase space such that different system's energies correspond to different surfaces. If in addition some other properties of the systems are considered, like constraints on the distances between atoms, the manifold is further limited to all the point that satisfy the energy and the distance constraints.

In the same way, constraints on the wave function correspond to the selection of a surface in the Hilbert space that can be described by the use of geometrical tools. For example, by employing the normalization condition on the wave function, Fresch and Moro were able to constrain the wave function to the surface of hypersphere of unitary radius in the Hilbert space[49]. Then from the measure of a surface element they have obtained a uniform probability density for the Random Pure State ensemble that is characterized by

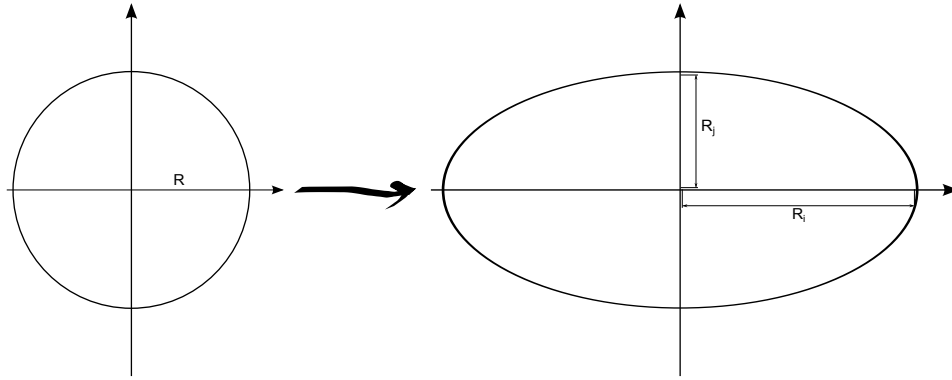


Figure 4.1: normalized wave functions are represented by points on the surface of sphere in the Hilbert space. A uniform sampling from the surface of an ellipsoid, inscribed in the sphere, is considered in order to break up the equivalence of all the Hilbert space directions, with the final goal of obtaining TRE average populations. The sampled vector is then normalized to restore the normalization condition.

the equivalence of all the directions in the Hilbert space where the sphere is embedded. As we shall see in the following, the geometrical perspective is very useful in the definition of the suitable probability distribution on populations due to the strictly related concepts of probability and measure on a closed manifold.

By following Fresch and Moro [49], I recognize the normalized wave function as a vector in the surface of an unitary sphere embedded in the Hilbert space, however I consider to uniformly sample it on the surface of an ellipsoid. The surface element of the ellipsoid, except for the normalization constant, will be related with the probability density on populations. Unlike RPSE statistics, it generates a probability distribution on populations that privileges lower energy eigestates. As far as we are able to control the anisotropy, we are able to reproduce the TRE populations of equation (3.41) as well.

I wish to clarify here that the following chapter is not about quantum geometry, that represents a very large set of mathematical concepts developed to describe quantum systems with the tools of mathematical *geometry*. As a matter of fact I will use only few basic definitions in order to obtain a correspondence between probability and volume measure. I will briefly introduce the volume in the Hilbert space with the use of metric tensor and then I will report the connection between volume and probability, showing how metric tensor can be a useful tool. The paragraph 4.2 will present how to obtain the

anisotropic probability distribution on populations starting from an ellipsoid embedded in a unitary sphere in the Hilbert space, in order to reproduce the TRE average populations.

4.1.1 Volume elements in the Hilbert space

In the following I will define the volume in the Hilbert space. In order to achieve such an objective, I will confine the attention to finite dimensional Hilbert spaces. As a matter of fact, whenever one wants to perform numerical simulations, it is mandatory to restrict the Hilbert space up to have a finite dimension N , where the vectors representing the wave function can be described by a finite number of parameters. At the same time, recalling that TRE populations decrease with the increasing of energy, it is acceptable to limit the Hilbert space to those eigenstates with significant populations that influence the properties of the systems, and to exclude the remaining directions. It should also be mentioned that the description of the infinite dimensional Hilbert space is recovered by applying at the end the infinite limit on the chosen dimension N of the calculated properties.

Let's start by considering an orthonormal basis set $u = (u_1, u_2, \dots, u_N)$ in the N dimensional Hilbert space

$$\langle u_k | u_{k'} \rangle = \delta_{k,k'} \quad (4.1)$$

where $\langle \cdot | \cdot \rangle$ is the scalar product and $\delta_{k,k'}$ is the Kronecker delta. A generic vector ψ can be always expressed as a linear combination of basis vectors

$$\psi = \sum_k^N c_k u_k \quad \text{with } c_k \in \mathbb{C} \quad (4.2)$$

where the set $c = (c_1, c_2, \dots, c_N) \in \mathbb{C}^N$ of complex coefficients corresponds to the coordinates with respect the basis set u . By varying the c coefficients it is possible to describe all the vectors in the N -dimensional Hilbert space.

At the same time, an equivalent description can be obtained through a different representation of the same space by expressing the c vector as a real vector r

$$r = (\text{Re}(c), \text{Im}(c)) \in \mathbb{R}^{2N} \quad (4.3)$$

where $\text{Re}(c)$ and $\text{Im}(c)$ are the real and imaginary part, respectively, of the c vector. The c or r representations of the vector ψ contain the same amount of information and can be used to describe all the points in the Hilbert space.

In addition, if we consider two different states, $\psi = \sum_k^N c_k u_k$ and $\psi' = \sum_k^N c'_k u_k$, also their scalar product can be expressed equivalently in c or in x representations as

$$\langle \psi | \psi' \rangle = \sum_k^N c_k^* c'_k \qquad \langle \psi | \psi' \rangle = \sum_j^{2N} r_j r'_j \qquad (4.4)$$

and if $\psi = \psi'$ the scalar product defines the square of the vector norm $|\psi|$

$$|\psi|^2 = \langle \psi | \psi \rangle = \sum_j^{2N} r_j^2 \qquad (4.5)$$

that can be interpreted as the square of its vector length. Thus, a change on the representation of points in the space does not change the lengths of the vectors or the angles between them, which are determined by the way to measure elements on the space, called *metric*. In particular the natural metric in the Hilbert space is the Euclidean metric [69] and the norm of equation (4.5) is said *euclidean norm*.

The same metric is employed for the well known Euclidean xyz -space or \mathbb{R}^3 -space where a generic vector $v_1 \in \mathbb{R}^3$ can be express as linear combination of the vectors of the basis set u_x, u_y, u_z

$$v = x u_x + y u_y + z u_z \qquad (4.6)$$

where (x, y, z) are the coefficients with respect the basis set. Furthermore, the square of the norm of the vector, that is its squared length, is simply the summation of the square of the coefficients

$$|v|^2 = x^2 + y^2 + z^2 \qquad (4.7)$$

that is clearly the scalar product of the v vector with itself $\langle v | v \rangle$ and can be interpreted as the squared distance between the origin and the point v . In \mathbb{R}^3 the definition of the volume V of a region $\Sigma \in \mathbb{R}^3$ is defined as the integral of

its differential form dV on the region Σ .

$$V = \int_{\Sigma} dV = \int_{\Sigma} dx dy dz \quad (4.8)$$

In conclusion, the metric is the way to define distances, from which it is possible to define volumes and the Hilbert space can be considered as an extension of the xyz -space as far as metric is concerned. A compact and useful notation to store all the information about the metric is the so called *metric tensor* g whose elements $g_{ij}^{(r)}$ in the r representation of the Hilbert space takes the unitary form [69]

$$g_{ij}^{(r)} = \delta_{ij} \quad (4.9)$$

where δ is the Kronecker delta and can be interpreted as the scalar product $\langle r_i | r_j \rangle$.

The introduction of the metric tensor allows one to simplify the change of coordinates and the calculation of distances and volumes in the Hilbert space. As a matter of fact, whenever a change of coordinates is introduced, for example $r \rightarrow w$, it can be expressed as a change in the metric tensor following the relation

$$g_{i'j'}^{(w)} = \sum_i^{2N} \sum_j^{2N} \frac{\partial r_i}{\partial w_{i'}} g_{ij}^{(r)} \frac{\partial r_j}{\partial w_{j'}} \quad (4.10)$$

that, in turn, can be used to evaluate volumes as

$$V = \int_{\Sigma} dV = \int_{\Sigma} |\det(g^{(w)})| dw_1 dw_2 \dots dw_{2N} \quad (4.11)$$

where $\Sigma \in \mathbb{R}^{2N}$ is a region of the full space and $|\det(g^{(w)})|$ is the determinant of the metric tensor. As far as r coordinates is employed, where the metric tensor is euclidean (see equation (4.9)), we recover the standard form $dV = dr_1 dr_2 \dots dr_{2N}$ for the volume elements, in agreement with equation (4.8).

Furthermore, since the measure of a volume element dV in the space is invariant with respect to different representations of the space, a generic change of coordinates $r \rightarrow w$ implies the equivalence

$$\sqrt{|\det(g^{(r)})|} dr_1 dr_2 \dots dr_{2N} = \sqrt{|\det(g^{(w)})|} dw_1 dw_2 \dots dw_{2N} \quad (4.12)$$

and from (4.10) we obtain

$$\sqrt{\frac{|\det(g^{(w)})|}{|\det(g^{(r)})|}} = \left| \det \left(\frac{\partial r_i}{\partial w_j} \right) \right| \quad (4.13)$$

which is just the Jacobian determinant for the change of variables.

In conclusion, the knowledge about the metric tensor allows the calculation of the volume in the Hilbert space, once the integration domain is determined. As far as our purpose is concerned, this well known result of differential geometry is important since it allows a simple method to connect probability density and parametrization of Hilbert space, as it will be better explained in the next section.

4.1.2 Connection between volume and probability

Since we have defined the volume on the Hilbert space, we can now clarify the connection between probability and volume measure. Let us consider a generic stochastic variable X whose possible outcomes belong to the sample space Ω . Once a probability density $p(X)$ is defined, it is possible to calculate the probability for the variable to belong to a certain subset $\Delta \subset \Omega$ as

$$P(X \in \Delta) = \int_{X \in \Delta} p(X) dX \quad (4.14)$$

We have implicitly assumed that the probability density $p(X)$ is positive and normalized as

$$P(X \in \Omega) = \int_{X \in \Omega} p(X) dX = 1 \quad (4.15)$$

If we now assume that the $p(X)$ is uniform in the sample space, we are stating that the probability for the variable to belong to the subspace Δ is the ratio between the sizes of the subspace and of the total space Ω . In addition, if we consider that the region Δ as well as the sample space Ω have infinitesimal volumes given as $dV = \sqrt{|\det(g^{(r)})|} dr_1 dr_2 \dots dr_{2N}$, we can specify the probability density as

$$p(X)dX = \frac{dV}{\int_{\Omega} dV} = \frac{\sqrt{|\det(g^{(r)})|} dr}{\int_{\Omega} \sqrt{|\det(g^{(r)})|} dr} \quad (4.16)$$

In conclusion, being the probability a measure on a set, it can be connected with the concept of volume and due to the relation between volume and metric tensor, the probability density can be identified as

$$p(X) \propto \sqrt{|\det(g^{(x)})|} \quad (4.17)$$

whichever χ -representation is employed, up to a normalization factor. In particular we will choose as privileged representation the one with phases and populations, from which we will obtain a probability distribution on the desired parameters.

It is important to point out preliminarily that, instead of a generic volume, we will use the surface of an ellipsoid in order to develop the probability density on populations.

4.1.3 Metric induced on a surface

The capability to calculate generic volumes in Hilbert space is not enough in order to obtain a probability distribution on populations that produces the TRE averages. We need to define how to measure surfaces belonging to a manifold embedded in the Hilbert space. For this reason, it is important to notice as a K -dimensional manifold in a domain of the $2N$ -dimensional space is defined by a set of $(2N - K)$ equations, which have to be interpreted as constraints for the points belonging to the surface.

$$\begin{aligned} f_1(x_1, x_2, \dots, x_{2N}) &= 0 \\ f_2(x_1, x_2, \dots, x_{2N}) &= 0 \\ &\vdots \\ f_{2N-k}(x_1, x_2, \dots, x_{2N}) &= 0 \end{aligned} \quad (4.18)$$

At each point $P = (x_1, x_2, \dots, x_{2N})$ belonging to the surface it is then possible to introduce a local set of coordinates (z_1, z_2, \dots, z_K) which parametrically

identifies points on the manifold

$$\begin{aligned}
 x_1 &= z_1 \\
 &\vdots \\
 x_K &= z_K \\
 x_{K+1} &= x_{K+1}(z_1, \dots, z_K) \\
 &\vdots \\
 x_{2N} &= x_{2N}(z_1, \dots, z_K)
 \end{aligned} \tag{4.19}$$

The metric tensor can be now used to describe the metric induced on the manifold from the metric on the entire space. In particular the corresponding induced metric tensor can be specified [69] as

$$g_{kk'}^{(z)} = \sum_j^{2N} \sum_j^{2N} \frac{\partial x_i}{\partial z_k} g_{ij}^{(x)} \frac{\partial x_j}{\partial z_{k'}} \tag{4.20}$$

where $k, k' = 1, \dots, K$. As before, once the metric tensor is defined, it is possible to determine the volume elements.

The case we are examining provides only a single constraint: the wave function vector should belong to the surface of an ellipsoid. Thus, we deal with a $(2N-1)$ -dimensional manifold embedded in the $2N$ -dimensional Hilbert space. The determinant of the metric tensor will be proportional to the surface element dS (see equation (4.11)) of the ellipsoid and will be related to the probability density on populations (see equation (4.17)).

4.2 Probability distribution and ellipsoid surface

In this section we outline the derivation of the probability distribution on populations, through the use of the measure of the surface element of an ellipsoid in the Hilbert space.

The main methodological ingredient is the connection between the probability that system wave function belongs to a certain set, and the measure that this set has with respect to the whole ensemble of possible wave functions. By

following and generalizing the strategy of Fresch and Moro [49], we consider the normalized wave function as a random vector on the $(2N - 1)$ -dimensional unitary sphere embedded in the $2N$ -dimensional space

$$S^{2N-1} := \left\{ r \in \mathbb{R}^{2N} \mid \sum_k |r_k|^2 = 1 \right\} \quad (4.21)$$

but, differently from the previous approach, we consider a uniform sampling of the wave function on an ellipsoid inscribed in the sphere

$$T^{2N-1} := \left\{ r \in \mathbb{R}^{2N} \mid \sum_k \frac{|r_k|^2}{R_k^2} = 1, \quad \text{with } R_k \in \mathbb{R} \quad \forall k \right\} \quad (4.22)$$

where the R_k parameters represent the ellipsoid axes. It is important to notice that if the wave function vector is chosen on the surface of the ellipsoid, it is not normalized

$$|\Psi\rangle \in T^{2N-1} \Rightarrow \sum_k |r_k|^2 < 1 \quad (4.23)$$

where we have used (4.5) for the norm. By decreasing the length of ellipsoid axes for increasing eigenvalues associated to that Hilbert space directions, the uniform sampling on the ellipsoid surface produces an anisotropic distribution when the corresponding unitary vector is considered through the normalization. The vectors on the surface of the sphere, that represent the system states, are no more uniformly distributed, and wave functions with higher population at lower energy eigenstates are privileged, in agreement with our purposes.

In order to go deeper into details, we recall that the representation of Hilbert space with cartesian r coordinates is characterized by a unit metric tensor 4.9 [69]. However, a more convenient representation y of the \mathbb{R}^{2N} space makes use of the polar coordinates of rays and phases, $y = (\rho, \alpha)$ where

$$\text{Re}(c_k) = \sqrt{\rho_k} \cos \alpha_k \quad \text{Im}(c_k) = \sqrt{\rho_k} \sin \alpha_k \quad (4.24)$$

The rays represent the generalization of populations variables without the normalizations constraint and the population can be recovered as

$$P_k = \frac{\rho_k}{\sum_k \rho_k} \quad (4.25)$$

The Jacobian matrix associated to the transformation $r \rightarrow y$ is

$$\begin{pmatrix} \frac{\partial \operatorname{Re}(c_k)}{\partial \rho_k} & \frac{\partial \operatorname{Im}(c_k)}{\partial \rho_k} \\ \frac{\partial \operatorname{Re}(c_k)}{\partial \alpha_k} & \frac{\partial \operatorname{Im}(c_k)}{\partial \alpha_k} \end{pmatrix} = \begin{pmatrix} \frac{1}{2\sqrt{\rho_k}} \cos \alpha_k & \frac{1}{2\sqrt{\rho_k}} \sin \alpha_k \\ -\sqrt{\rho_k} \sin \alpha_k & \sqrt{\rho_k} \cos \alpha_k \end{pmatrix} \quad (4.26)$$

and the new metric tensor $g^{(y)}$ in the system with polar coordinates can be obtained as

$$g_{i'j'}^{(y)} = \sum_i^{2N} \sum_j^{2N} \frac{\partial r_i}{\partial y_{i'}} g_{ij}^{(r)} \frac{\partial r_j}{\partial y_{j'}} = \sum_i^{2N} \frac{\partial r_i}{\partial y_{i'}} g_{ii} \frac{\partial r_i}{\partial y_{j'}} \quad (4.27)$$

where we have eliminated a summation thanks to diagonal form of the metric tensor $g^{(r)}$. The metric tensor in the new representation is still diagonal with elements

$$g_{\rho_i \rho_i}^{(y)} = \frac{1}{4\rho_i} \quad g_{\alpha_i \alpha_i}^{(y)} = \rho_i \quad (4.28)$$

In this representation the ellipsoid (4.22) is parametrized as

$$T^{2N-1} = \{(\rho, \alpha) \in \mathbb{R}^{2N} \mid \sum_k \frac{\rho_k}{R_k^2} = 1, \quad \text{with } R_k \in \mathbb{R} \quad \forall k\} \quad (4.29)$$

and depends only on the rays parameters, for this reason it is easier to impose the constraint by considering the last ray ρ_N as a function of the other independent variables

$$\rho_N = \left(1 - \sum_{k=1}^{N-1} \frac{\rho_k}{R_k^2}\right) R_N^2 \quad (4.30)$$

The $(2N - 1)$ independent coordinates $z = (\rho_1, \rho_2, \dots, \rho_{N-1}, \alpha_1, \alpha_2, \dots, \alpha_N)$ represent a point on the ellipsoid surface and the metric induced on this manifold can be described through the corresponding metric tensor $g^{(z)}$, to be calculated according to equation (4.20). It can be partitioned in two diagonal blocks having in correspondence of the phases only diagonal elements whereas in correspondence with rays a full block.

$$g_{\alpha_i \alpha_i}^{(z)} = \rho_i \quad g_{\alpha_N \alpha_N}^{(z)} = \left(1 - \sum_{k=1}^{N-1} \frac{\rho_k}{R_k^2}\right) R_N^2 \quad (4.31)$$

$$g_{\rho_i \rho_j}^{(z)} = \frac{1}{4\rho_i} \delta_{i''j''} + \frac{R_N^4}{R_{i''}^2 R_{j''}^2} \frac{1}{4\rho_N} \quad (4.32)$$

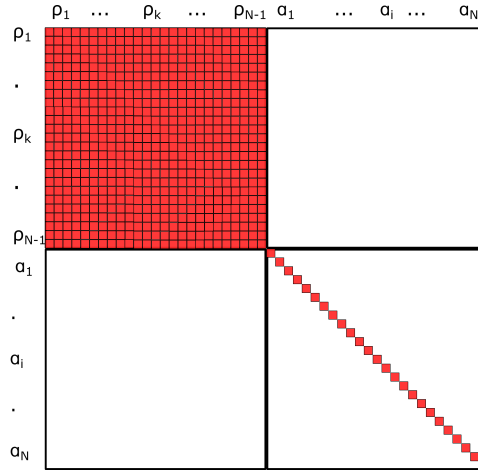


Figure 4.2: schematic representation of the induced metric tensor $g^{(z)}$ on the ellipsoidal surface. The block concerning the phases elements $g_{\alpha_i, \alpha_j}^{(z)}$ is diagonal whereas the block on rays $g_{\rho_i, \rho_j}^{(z)}$ has off-diagonal elements.

The volume dS of the surface elements can now be calculated as

$$dS = \sqrt{|\det(g^{(z)})|} d\rho_1 \dots d\rho_{N-1} d\alpha_1 d\alpha_N \quad (4.33)$$

by means of the determinant of the metric tensor $g^{(z)}$. Thanks to the block structure of the latter we can factorize the determinant calculation as

$$\det(g^{(z)}) = \det(g_{\rho_i \rho_j}^{(z)}) \det(g_{\alpha_i \alpha_j}^{(z)}) \quad (4.34)$$

that corresponds to a product of surface elements $dS = dS_\rho dS_\alpha$. The block for the phases is diagonal and its determinant is

$$\det(g_{\alpha_i \alpha_j}^{(z)}) = \left(1 - \sum_{k=1}^{N-1} \frac{\rho_k}{R_k^2}\right) R_N^2 \prod_{k=1}^{N-1} \rho_k = \rho_N \prod_{k=1}^{N-1} \rho_k \quad (4.35)$$

The block for the rays has a more complex structure and for the calculation of its determinant we employ the following property of the matrices.

$$\det(A + uv^T) = (1 + v^T A^{-1}u) \det(A) \quad (4.36)$$

where A is a non-singular matrix and u and v two column vectors [70]. Let us identify $(A + uv^T)$ with the ray block of the metric tensor, with matrix A describing only its diagonal elements $g_{\rho_i \rho_i}^{(z)} = \frac{1}{4\rho_i}$ and the column vectors given

as

$$u = \begin{pmatrix} \frac{R_N^4}{R_1^2} \frac{1}{4\rho_N} \\ \vdots \\ \frac{R_N^4}{R_i^2} \frac{1}{4\rho_N} \\ \vdots \\ \frac{R_N^4}{R_{N-1}^2} \frac{1}{4\rho_N} \end{pmatrix} \quad v = \begin{pmatrix} \frac{1}{R_1^2} \\ \vdots \\ \frac{1}{R_i^2} \\ \vdots \\ \frac{1}{R_{N-1}^2} \end{pmatrix} \quad (4.37)$$

The two contributions at the r.h.s of (4.36) are easily evaluated:

$$(1 + v^T A^{-1} u) = 1 + \sum_{i=1}^{N-1} \frac{\rho_i}{R_i^4} \frac{R_N^4}{\rho_N} = \frac{R_N^4}{\rho_N} \sum_{i=1}^N \frac{\rho_i}{R_i^4} \quad (4.38)$$

$$\det(A) = \prod_{i=1}^{N-1} \frac{1}{4\rho_i} = \left(\frac{1}{2^{N-1}} \right) \prod_{i=1}^{N-1} \frac{1}{\rho_i} \quad (4.39)$$

Then from their product one obtains the determinant of metric of the ray block of the metric tensor

$$\det(g_{\rho_i \rho_j}^{(z)}) = \frac{R_N^4}{\rho_N} \sum_{i=1}^N \frac{\rho_i}{R_i^4} \cdot \left(\frac{1}{2^{N-1}} \right)^{2^{N-1}} \prod_{i=1}^{N-1} \frac{1}{\rho_i} \quad (4.40)$$

The determinant of the full metric tensor is finally evaluated according to equation (4.34)

$$\det(g^{(z)}) = \left(\frac{1}{2^{N-1}} \right)^2 \left(\sum_{i=1}^{N-1} \rho_i \left(\frac{R_N}{R_i} \right)^4 + \rho_N \right) \quad (4.41)$$

Once the determinant of the matrix tensor is obtained, it is possible to calculate the surface element, according to equation (4.33), and to obtain the probability distribution on $p(z)$

$$p(z) dz = \frac{1}{Q(z)} \sqrt{\left(\sum_{i=1}^{N-1} \rho_i \left(\frac{R_N}{R_i} \right)^4 + \rho_N \right)} d\rho_1 \dots d\rho_{N-1} d\alpha_1 \dots d\alpha_N \quad (4.42)$$

where $Q(z)$ is the normalization factor of the statistical distribution.

The representation $z = (\rho, \alpha)$ of the Hilbert space is particularly convenient thanks to the statistical independence of rays and phases, leading to the previously described partitioning of the metric tensor, that allows me to factorise

the probability density

$$p(\rho, \alpha) = p(\rho)p(\alpha) = p(\rho)/(2\pi)^N \quad (4.43)$$

In the last equality we have employed a result of Fresch and Moro [49], that have demonstrated, under mild and realistic assumptions, how the phases variables are uniformly distributed in their domain with a probability density

$$p(\alpha) = \frac{1}{(2\pi)^N} \quad (4.44)$$

From the previous considerations we deduce the marginal probability distribution on rays

$$p(\rho)d\rho = \frac{1}{Q(\rho)} 2\pi^N \sqrt{\left(\sum_{i=1}^{N-1} \rho_i \left(\frac{R_N}{R_i}\right)^4 + \rho_N\right)} d\rho_1 \dots d\rho_{N-1} \quad (4.45)$$

Finally by performing the change of variables from rays ρ_i to populations P_i according to (4.25)

$$p(P)dP = \frac{1}{Q(P)} \sqrt{\frac{\sum_{i=1}^{N-1} P_i}{\sum_{i=1}^{N-1} \frac{P_i}{R_i^2} - \frac{1 - \sum_{i=1}^{N-1} P_i}{R_N^2}}} \frac{1}{\left(\sum_{i=1}^{N-1} \frac{P_i}{R_i^2} - \frac{1 - \sum_{i=1}^{N-1} P_i}{R_N^2}\right)^N} dP \quad (4.46)$$

where the normalization factor $Q(P)$ includes the Jacobian matrix determinant of the transformation.

We started by describing a generic volume element in the \mathbb{R}^{2N} Hilbert space by the use of the metric tensor. Then we noticed that the phases and rays representation is much more manageable as soon as a constraint on the norm of the wave function vector has to be considered, as in our case. Once the induced metric tensor on the ellipsoid has been obtained we can describe area elements on the surface that are directly related to the probability. As a matter of fact the probability that the wave function belongs to a certain set, in particular that belonging to an ellipsoidal surface element, is described by the measure of that surface with respect whole surface (all the possible wave functions). In this way one defines the probability distribution $p(\rho, \alpha)$ on rays and phases. From that probability distribution, with a simple change of variable $(\rho, \alpha) \rightarrow (P, \alpha)$ (4.25), we are able to evaluate how populations behave

when sampled uniformly in an ellipsoidal surface. The probability distribution on population is not uniform and the different Hilbert space directions are no longer equivalent. The control on the anisotropy of the probability distribution assumes now the central role in order to obtain the TRE average populations. As a matter of fact, only by controlling the ellipsoid axes it is possible to sample a wave function from a probability distribution where the thermal state is well known, having so a unbiased sampling of a quantum state with a well determined thermodynamic reference.

4.3 Montecarlo sampling of probability distribution

In the previous paragraph we have obtained a probability distribution on populations by considering a uniform sampling of wave function on the surface of an ellipsoid embedded in the Hilbert space. It represents a very useful result, since it allows the evaluation of ensemble average of a property $f(P)$ of populations as

$$\langle f(P) \rangle = \int dP p(P) f(P) \quad (4.47)$$

and as well as its variance

$$\sigma_{f(P)}^2 = \langle f(P)^2 \rangle - \langle f(P) \rangle^2 \quad (4.48)$$

In particular, the last quantity is very important in order to confirm the typicality when different realizations of the quantum state behave essentially in the same way as far as the given property is concerned. I would like to stress again as the typicality of microscopic internal energy and entropy leads to the emergence of equilibrium thermodynamics in a self consistent framework.

At the same time, the existence of an explicit form of the probability distribution on populations allows one to generate at random a single realization of the quantum state of the system. This is of primary importance whenever one wants to perform dynamical experiments, like in Classical Molecular Dynamics Simulations where the initial state is randomly sampled from the suitable ensemble for the considered thermodynamic state.

In this paragraph I want to characterize the statistical properties of the just

derived probability distribution in order to evaluate the role of the lengths R_k of the ellipsoid axes in determining the average populations $\langle P_k \rangle$ with the final goal of obtaining TRE average populations. Therefore we need to know how to select the ellipsoid axes in order to obtain the desired ensemble average properties.

The multidimensional integral of equation (4.47) which is necessary to obtain average of any function of populations, has not an analytical solution and it has to be evaluated numerically through a Montecarlo algorithm. In the following I will briefly outline the generic features of the Metropolis-Hastings algorithm and afterwards I will present the results of the numerical calculations for the properties of the distribution of populations.

4.3.1 Metropolis-Hastings algorithm

Metropolis-Hastings is a computational algorithm firstly developed by Metropolis et. al [71] in the field of Montecarlo-integration schemes, in order to approach statistical mechanical problems. However, it turned out to be a rather general procedure with a large applicability in several statistical issues. The algorithm was then generalized, some years later, by Hastings [72] and nowadays is very common in the evaluation of properties form complex probability distributions.

Metropolis-Hastings algorithm is able to generate numbers, for example a set of coordinates $x = (x_1, x_2, \dots, x_n)$, according to a known probability distribution $p(x)$, called target distribution. Once the statistical samples are generated, then the average of every function $f(x)$ can be numerically computed. In particular Metropolis-Hastings algorithm is very powerful because it requires only the functional dependence of the probability distribution independently of proportionality coefficient. This means that the normalization factor of the probability distribution, often very difficult to compute, is unnecessary.

The algorithm generates a sequence of statistical samples of the stochastic variables and with the use of acceptance (or rejection) criterion produces the desired probability distribution which allows the evaluation of averages. Its generic implementation consists in the following steps

- choice a random initial state for the variable of interest within its sample space;

- generation of a subsequent point sampled according to a proposal distribution $h(x'|x)$, that is the conditional probability of obtaining x' given the previous state x ;
- evaluation of the probability $a(x'|x)$ of making the step from x to x' , also called *acceptance probability*, as

$$a(x'|x) = \min \left(1, \frac{p(x')h(x|x')}{p(x)h(x'|x)} \right) \quad (4.49)$$

where $p(x')$ and $p(x)$ are the probability of being in the state x' or x evaluated from the target probability distribution;

- acceptance or rejection of the step according to the rules:
 - if $a(x'|x) > 1$ the step is automatically accepted and the new point is x'
 - if $a(x'|x) \leq 1$, generation of a random uniform r variable within the interval $[0, 1]$. If $r < a$ the new state is accepted, otherwise one generates a new state x' ;
- the algorithm restarts from the second step.

The property whose average we want to compute is evaluated on each generation of a new sample, after the acceptance or rejection step. If the step is accepted the properties is evaluated in the new point, otherwise it is evaluated in the previous one. It can be immediately noticed as the calculation of $a(x'|x)$ does not need the normalized target distribution $p(x)$ since only the ratio $p(x')/p(x)$ has to be computed. In addition, if the proposal distribution is symmetric, such that $h(x'|x) = h(x|x')$ like in the situation we are going to consider later, the acceptance probability is reduced to $p(x')/p(x)$, that is the original proposal of Metropolis [71].

Our target distribution is the probability density on populations given by equation (4.46). However, the probability distribution on rays of equation (4.45) is simpler to compute and population can be easily recovered with equation (4.25).

We start from the uniform sampling on a sphere embedded in a N -dimensional Hilbert space, as already performed in [49]. It has been shown [73, 74, 75] that a set of uniformly distributed sampling of points $Q = (Q_1, Q_2, \dots, Q_N)$ on a hyper-sphere surface can be achieved by the use of $N - 1$ auxiliary

$(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_{N-1})$ variables, uniformly distributed in $(0, 1]$, as

$$\begin{aligned}
 Q_1 &= 1 - \varepsilon_1^{1/(N-1)} \\
 &\vdots \\
 Q_j &= (1 - \varepsilon_j^{1/(N-j)}) \prod_{i=1}^{j-1} \varepsilon_i^{1/(N-i)} \\
 &\vdots \\
 Q_N &= \prod_{i=1}^{N-1} \varepsilon_i^{(1/N-i)}
 \end{aligned} \tag{4.50}$$

From the latter sampling, and by considering the appropriate change of variable $\rho_i = Q_i R_i^2$, where the set of R_i corresponds to the length of the ellipsoid axes, it is possible to obtain a symmetric proposal distribution $h(\rho'|\rho)$ on the ellipsoid surface. The algorithm proceeds through the evaluation of the acceptance probability

$$a(\rho'|\rho) = \min \left(1, \frac{p(\rho')}{p(\rho)} \right) \tag{4.51}$$

for the acceptance or rejection step. By an additional scaling of the rays from the surface of the sphere to the ellipsoid surface, it is possible to study the properties of the distribution function on populations.

4.3.2 Mean populations from the uniform sampling of the ellipsoid

The algorithm just presented is quite simple and, at the same time, very powerful in the study of our target distribution. We consider a 100 dimensional Hilbert space where the ellipsoid axes R_i are selected randomly but uniformly in the interval $[10^{-6}, 1]$.

The anisotropy of statistical distribution on the Hilbert space directions can be highlighted by marginal distributions, defined as the probability distribution on a subset of the stochastic variables. In particular we consider the probability distribution on a single population that can be obtained by integration on all the remaining populations, for example, the marginal distribution $p(P_1)$ on the

population P_1 reads

$$p(P_1) = \int dP_2 \dots dP_i \dots P_{N-1} p(P_1, \dots, P_i, \dots, P_{N-1}) \quad (4.52)$$

Because of the impossibility to analytically evaluate such an integral, we made use of the Montecarlo algorithm through a sampling of 10^6 points.

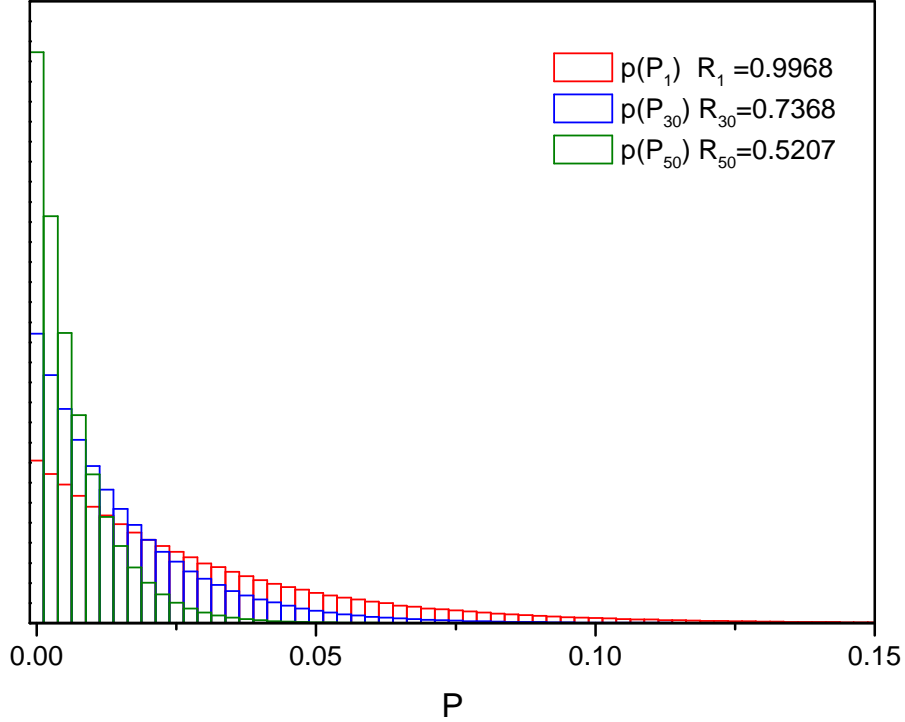


Figure 4.3: Marginal distributions of three representative populations are shown. The histograms refer to a Montecarlo sampling of 10^6 points generated by the algorithm explained in the text, for a system of 100 states.

In Figure 4.3 I have reported as an example some marginal distributions for populations of different energy eigenstates. The shape of each marginal distribution depends on ellipsoid axis length, in particular the shorter is the ellipsoid axis the narrower is the marginal distribution leading to lower values of mean populations. Thus, there is no equivalence amongst the different Hilbert space directions. In Figure 4.4 I have reported the dependence of the mean populations on the squared length of the correspondent ellipsoid axis, suggesting a proportionality between them. The rationalization of such a relation is of fundamental importance since that the average populations are

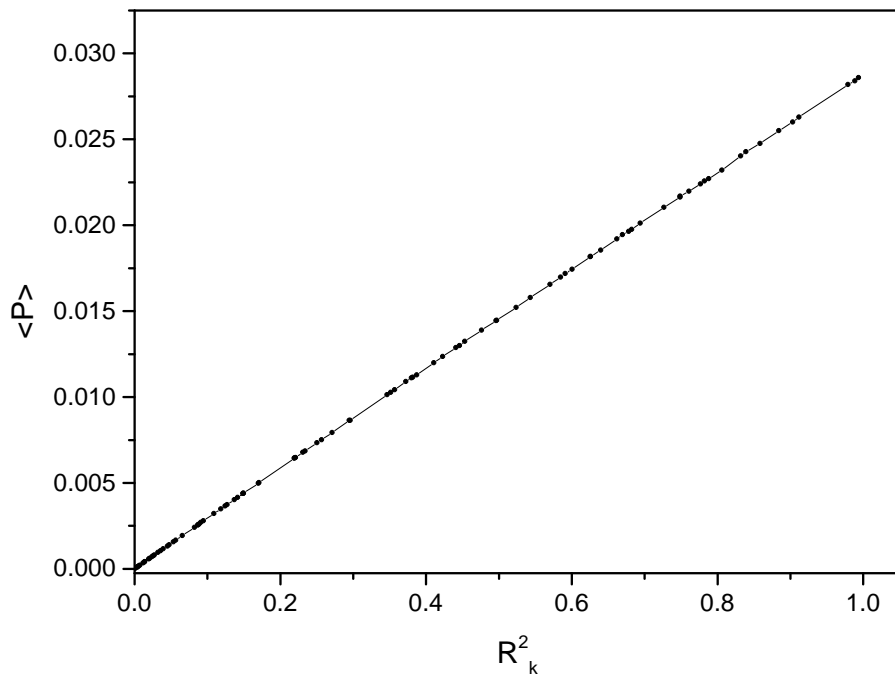


Figure 4.4: Average populations $\langle P_k \rangle$ plotted against the square length of ellipsoid axes. The line connecting the points is only a guide to the eye.

related to the thermodynamic systems properties. Once we are able to identify and control the parameters R_i^2 in order to obtain TRE average populations, we will be also able to characterize the quantum system of interest with a well defined thermal state ζ . Such an objective is very important in order to control the physical situation where we want to perform dynamical simulations.

The definition of a function $R_k(E_k)$, that relates ellipsoid axes with the eigenvalues associated to the Hilbert space principal directions $|E_k\rangle$, allows to sample populations with a statistical weight that reproduce, on average, the TRE ensemble. In principle, whenever the system Hamiltonian is provided as well as the function $R_k(E)$, representing the energy function of axis in order to obtain TRE averages, it is possible to perform dynamical simulation in whichever thermal condition.

4.4 Weakness of the model

In this chapter I have obtained a probability distribution on the set of populations starting from a geometrical analysis on the Hilbert space. The surface

element of an ellipsoid has been related to the probability density on ray parameters, from which the probability distribution on population has been derived. It is important to notice that TRE average populations are defined in all the Hilbert space directions while the geometrical analysis has to be performed on a finite dimensional Hilbert space which has to be considered as a subspace of the full Hilbert space of a system with an unbounded spectrum.

In this finite domain, the connection between axes of the ellipsoid and populations through probability density (4.46) is very complex and the function

$$\langle P_k \rangle = f(R_k) \quad (4.53)$$

is far from being analytically derivable but, at the same time, it represents the most important information in order to be able to sample a well defined quantum state. Even if it might be obtained through a multi-variable optimization procedure, which has not been carried out, its limit form for an arbitrary dimensional Hilbert space cannot be easily performed. The absence of a clear limit where both, the ensemble average population and its probability distribution with well defined R_k^2 parameters, are characterized, could be considered a weakness of the just presented model. For this reason we have preferred to change the strategy to obtain a sampling of TRE populations with a controlled convergence and the new strategy will be presented in the next chapter.

TRE populations from uniform sampling

The energy dependence of average population within the TRE ensemble has been very useful in order to analyse several important properties of the ensemble, however it is not sufficient to fully characterize it. As a matter of fact, the knowledge of average populations alone cannot provide the identification of the underlying distribution of populations. In other words, one can imagine the existence of different distributions of populations having the the same TRE averages. At the same time only the identification of the probability distribution on populations $p(P)$ would supply, for example, the information on the typicality for the thermodynamic properties. Moreover the probability distribution on populations is essential to perform directly numerical experiments about the dynamics of the thermalization on model systems, since one needs a statistical sampling of the set of populations on the basis of a well defined distribution of them. In this chapter I intend to identify the most convenient and simplest form of population distribution which can be easily implemented in the applications.

The starting point is the RPSE (Random Pure State Ensemble) population distribution whose statistical properties are well characterized [49, 43, 50] and for which a simple algorithm is available to generate a statistical sample of the set of populations [50, 74]. The aim of the following analysis is the identification of a suitable set of coefficients that, when used to scale RPSE populations,

generates TRE populations. In this way the rather complex problem of TRE statistics is reduced to the simpler case of RPSE ensemble.

The next chapter will practically use the sampling method in order to study the dynamics of the energy exchange between two quantum systems, initially at different temperatures. It will be clear as many of the considerations in the next chapter can be formulated only thanks to the possibility to obtain a random sampling from a statistical distribution that on average guarantees the TRE populations.

5.1 TRE populations from the uniform distribution

Let us first recall the notation for the problem. By considering an isolated system whose quantum states belong to the infinite dimensional Hilbert space \mathcal{H} , and whose energy eigenvalues are supposed to be rationally independent and unbounded, the set of populations associated to Hamiltonian eigenstates is denoted as

$$P := (P_1, P_2, \dots, P_k, \dots) \quad (5.1)$$

with $P_k \geq 0 \forall k$ and with normalization condition

$$\sum_{k=1}^{\infty} P_k = 1 \quad (5.2)$$

In order to describe the statistical distribution of populations we introduce the probability density $p(P)$ on the set P of populations with normalization

$$\int dP p(P) = 1 \quad (5.3)$$

where $dP = dP_1 dP_2 \dots$, and $P_k \geq 0$ is the integration domain for each population. Notice that such a probability density should include the Dirac delta factor

$$\delta\left(1 - \sum_{k=1}^{\infty} P_k\right) \quad (5.4)$$

in order to constraint the integration domain in equation (5.3) to population sets satisfying the condition (5.2). Correspondingly the average $\langle f(P) \rangle$ within

the ensemble of a generic function $f(P)$ of the population set P is calculated as

$$\langle f(P) \rangle = \int dP p(P) f(P) \quad (5.5)$$

The characterization of the statistical ensemble needs a probability density with respect to an infinite number of parameters, i.e. the infinite set of populations. It has to be defined as the limit $N \rightarrow \infty$ of the sequence of finite dimensional distributions with respect to the first N populations (P_1, P_2, \dots, P_N) . This is conveniently done by introducing the probability densities $p^{(N)}(P)$, each of them includes the Dirac delta factors

$$\delta \left(1 - \sum_{k=1}^N P_k \right) \prod_{k=N+1}^{\infty} \delta(P_k) \quad (5.6)$$

in order to enforce the condition that $P_k = 0$ for $k > N$ but, at the same time, to continue to employ the integration on the full set P of population like in equation (5.4). Then the ensemble average of function $f(P)$ is specified according to the following limit

$$\langle f(P) \rangle = \lim_{N \rightarrow \infty} \int dP p^{(N)}(P) f(P) \quad (5.7)$$

where it is conventionally assumed that $\int dP_k F(P_k) \delta(P_k) = F(0)$ even if the lower boundary of integration domain is at $P_k = 0$.

Our objective is that of recognizing a suitable probability density $p(P)$ under the constraint that its mean populations are exactly the TRE average populations given as

$$\langle P_k \rangle = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} \quad (5.8)$$

where E_k for $k = 1, 2, \dots$ denote the energy eigenvalues, E_1 being that of the ground state. The parameter ζ describes the thermal state of the system and, as shown in part I, it is related to the microscopic quantum temperature T_Q as $\zeta \simeq 1/k_B T_Q$. Equation (5.8) includes the normalization factor specified through

$$n(\zeta) := \sum_{k=1}^{\infty} e^{-\zeta(E_k - E_1)} \quad (5.9)$$

Such a quantity, considered as a function of the thermal state, in the following analysis plays the role of control parameter and, therefore, it is important to

recognize its physical meaning. Its definition (equation (5.9)) represents the count of energy eigenstates weighted by the thermal factor $\exp\{-\zeta(E_k - E_1)\}$ quantifying the contribution to statistical averages of the k -th state with respect to the ground state $k = 1$ having an unitary weight. This is somehow equivalent to partition the infinite set of eigenstates in groups having a cumulative TRE average population nearly equal to that of the ground state, and to count the number of these groups. For this reason parameter $n(\zeta)$ can be identified with the effective dimensionality of thermally populated eigenstates, and in the following we will designate it in this way. Notice that its counterpart for the uniform distribution of populations within an active space which includes eigenstates with the same statistical weight, would be simply the dimension of the active space. The behavior of such an effective dimensionality $n(\zeta)$ by changing the thermal state is rather obvious, since it is a decreasing function of ζ between the limits: $\lim_{\zeta \rightarrow 0^+} n(\zeta) = \infty$ and $\lim_{\zeta \rightarrow \infty} n(\zeta) = 1$. A more significant picture is recovered by considering the microscopic temperature $T_Q \propto 1/\zeta$ since the effective dimensionality is unitary for $T_Q \rightarrow 0$ when only the ground state is populated, and it grows indefinitely by increasing T_Q as more and more eigenstates become significantly populated.

In order to characterize statistically TRE populations, we intend to develop a scaling procedure applied to populations of a completely different statistical ensemble with an uniform distribution. With this procedure one can exploit the simple description of statistical properties with the uniform distribution, which has been already reported in past works by Fresch and Moro [49, 43, 50]. In order to clearly recognize the populations with an uniform distribution and to distinguish them from TRE populations P specified as in equation (5.1), we denote them differently as

$$Q := (Q_1, Q_2, \dots, Q_k, \dots) \quad (5.10)$$

with the normalization condition like in Eq. (5.2). The statistical ensemble with uniform distribution can be implemented in different forms depending on the choice of the active space allowed to pure states. For the present purposes, one must employ the Random Pure State Ensemble (RPSE) where the N -dimensional active space \mathcal{H}_N is given by linear combinations of the first N eigenstates. For a given dimensionality N of the active space, the RPSE

ensemble is characterized by the following probability density on populations [49]

$$p_{RPSE}^{(N)}(Q) = (N-1)! \delta\left(1 - \sum_{k=1}^N Q_k\right) \prod_{k=N+1}^{\infty} \delta(Q_k) \quad (5.11)$$

where the Dirac delta factors enforce the normalization on these populations and their vanishing outside the active space. It allows the calculation of RPSE ensemble average of functions $f(Q)$ of the populations according to the integral

$$\langle f(Q) \rangle_{RPSE}^{(N)} = \int dQ p_{RPSE}^{(N)}(Q) f(Q) \quad (5.12)$$

The distinctive features of RPSE statistics are the equivalence of mean populations (within the active space)

$$\langle Q_k \rangle_{RPSE}^{(N)} \begin{cases} = 1/N & \text{for } k \leq N \\ = 0 & \text{for } k > N \end{cases} \quad (5.13)$$

and the identical correlation between different populations, which is induced by the constraints on the integration domain

$$\langle \Delta Q_k \Delta Q_{k'} \rangle_{RPSE}^{(N)} = -\frac{1}{N^2(N+1)} \quad (5.14)$$

for $k \neq k'$ and $k, k' \leq N$, where $\Delta Q_k := Q_k - \langle Q_k \rangle_{RPSE}^{(N)} = Q_k - 1/N$.

For a given infinite set of real positive coefficients

$$x = (x_1, x_2, \dots, x_k, \dots) \quad (5.15)$$

with $x_k \geq 0 \forall k$ and finite 1-norm $\|x\|_1 = \sum_{k=1}^{\infty} x_k$, one can introduce a scaling procedure of RPSE populations according to the relation

$$P_k := \frac{x_k Q_k}{\sum_{k'=1}^{\infty} x_{k'} Q_{k'}}, \quad (5.16)$$

$\forall k \geq 0$, which generates an infinite set of parameters $P = (P_1, P_2, \dots, P_k, \dots)$ having the character of populations since $P_k \geq 0$ and $\sum_{k=1}^{\infty} P_k = 1$ and whose average can be calculated according to RPSE statistics

$$\langle P_k \rangle_{RPSE}^{(N)} = \left\langle \frac{x_k Q_k}{\sum_{k'=1}^{\infty} x_{k'} Q_{k'}} \right\rangle_{RPSE}^{(N)} \quad (5.17)$$

By choosing coefficients x_k decreasing in magnitude with k we get average populations P_k also decreasing in magnitude like TRE population averages of equation (5.8). Our purpose is that of recognizing the set of coefficients x which leads to scaled populations P_k having the same averages of TRE. Then by random sampling RPSE populations Q followed by the scaling procedure of equation (5.16), we get a statistical sample of populations P with TRE mean value, and we can consider them as possible realizations of TRE populations. However, as a preliminary condition, we must perform the infinite dimensional limit $N \rightarrow \infty$ on the RPSE average in equation (5.17) in order to fulfill the equivalence with equation (5.8). Indeed, for finite dimensions N , the average (5.17) of populations P_k for $k > N$ vanishes while equation (5.8) leads always to values greater than zero and, therefore, only in the limit $N \rightarrow \infty$ we could find the set x of coefficients assuring the equivalence on the averages.

In the asymptotic limit $N \rightarrow \infty$ of the active space, the RPSE populations Q in a statistical sample tend to vanish as a consequence of their normalization, $\sum_{k=1}^{\infty} Q_k = 1$. On the other hand, in order to perform the integration required by equation (5.17) in such an asymptotic limit, we need integration variables which remain finite on the average. For this reason we replace RPSE populations Q with their unnormalized counterparts $\hat{Q} = (\hat{Q}_1, \hat{Q}_2, \dots)$,

$$\hat{Q}_k := NQ_k, \quad (5.18)$$

having a constant average independent of the dimension of the active space: $\langle \hat{Q}_k \rangle_{RPSE}^{(N)} = 1$ for $k \leq N$. Notice that the definition (5.16) of population P for TRE ensemble can be rewritten in term of these parameters \hat{Q} :

$$P_k := \frac{x_k \hat{Q}_k}{\sum_{k'=1}^{\infty} x_{k'} \hat{Q}_{k'}} \quad (5.19)$$

Therefore, in order to evaluate Eq. (5.17) in the limit $N \rightarrow \infty$, we need to perform the average of a function $f(\hat{Q})$ of unnormalized RPSE populations in the asymptotic limit:

$$\langle f(\hat{Q}) \rangle := \lim_{N \rightarrow \infty} \langle f(\hat{Q}) \rangle_{RPSE}^{(N)} \quad (5.20)$$

where we have omitted at the l.h.s. the reference to RPSE statistics and to the

asymptotic limit of N because in the following this is the only kind of average which is explicitly considered. In Appendix 5.A it is shown that such an average is simply given by the integral on these parameters with an exponential weight function without any constraint on the integration variables:

$$\langle f(\hat{Q}) \rangle = \int d\hat{Q} \exp \left\{ - \sum_{k=1}^{\infty} \hat{Q}_k \right\} f(\hat{Q}) \quad (5.21)$$

where

$$\int d\hat{Q} \dots := \left(\prod_{k=1}^{\infty} \int_0^{\infty} d\hat{Q}_k \right) \dots \quad (5.22)$$

The exponential weight function can be interpreted as the probability density for the asymptotic problem with independent contributions for each variable corresponding to uncorrelated parameters \hat{Q}_k .

All this procedure relies on the set x of coefficients that, from unnormalized RPSE populations \hat{Q} and by means of equation (5.16), allows the calculation of populations P having TRE average values of equation (5.8). Therefore, for a given thermal state specified by parameter ζ , one has to find the solution of the set of equations

$$\left\langle \frac{x_k \hat{Q}_k}{F(x, \hat{Q})} \right\rangle = \langle P_k \rangle = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} \quad (5.23)$$

for $k = 1, 2, \dots$, where we have introduced the function

$$F(x, \hat{Q}) := \sum_{j=1}^{\infty} x_j \hat{Q}_j \quad (5.24)$$

Of course the solution of Eqs. (5.23) are thermal state dependent, that is $x = x(\zeta)$.

On the other hand, if the formal solution $x(\zeta)$ is available, then the statistical properties of TRE populations is reduced to the distribution of unnormalized RPSE populations \hat{Q} . In particular, given a statistical sample of unnormalized RPSE populations \hat{Q} , by means of equation (5.16) one determines the correspondent set of TRE populations P , which can be considered as randomly chosen possible realizations of the quantum pure state for the given thermal state ζ of the system, and which can be used to evaluate the average of any property $f(P)$ depending on pure state populations P . In the

following two sections we specifically address the issue of the procedures for solving equations (5.23).

5.2 Infinite effective dimensionality

The solution in all generality of equation (5.23) is not a trivial task because of the non linearity with respect to the unknowns x . Therefore, in the first instance we look for a simple approximation of the solution of the problem. Let us suppose that function $F(x, \hat{Q})$ is statistically nearly constant when sampling unnormalized RPSE populations \hat{Q} . Then the average of the fraction at the l.h.s. of equation (5.23) can be approximated by the ratio of the correspondent averages,

$$\left\langle \frac{x_k \hat{Q}_k}{F(x, \hat{Q})} \right\rangle \simeq \frac{\langle x_k \hat{Q}_k \rangle}{\langle F(x, \hat{Q}) \rangle} \quad (5.25)$$

which are immediately evaluated:

$$\langle x_k \hat{Q}_k \rangle = x_k, \quad \langle F(x, \hat{Q}) \rangle = \sum_{j=1}^{\infty} x_j \langle \hat{Q}_j \rangle = \|x\|_1 \quad (5.26)$$

Then we obtain the following simple solution of Eq. (5.23)

$$x_k = \langle P_k \rangle = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} \quad (5.27)$$

which implies that by scaling RPSE populations according to TRE mean populations, we get from equation (5.16) populations P following the TRE statistics.

The following question naturally arises: is this an exact solution in some suitable conditions? An answer requires the quantification of the variability of function $F(x, \hat{Q})$ in the ensemble through its variance

$$\sigma_F := \langle \Delta F(x, \hat{Q})^2 \rangle^{1/2} \quad (5.28)$$

where

$$\Delta F(x, \hat{Q}) := F(x, \hat{Q}) - \langle F(x, \hat{Q}) \rangle = \sum_{j=1}^{\infty} x_j \Delta \hat{Q}_j \quad (5.29)$$

with $\Delta \hat{Q}_j := \hat{Q}_j - \langle \hat{Q}_j \rangle = \hat{Q}_j - 1$. By taking into account that according to

the distribution in equation (5.20) the parameters $\Delta\hat{Q}_k$ are uncorrelated and have unitary variance, the following relation is derived

$$\sigma_F^2 = \sum_{j=1}^{\infty} x_j^2 = \|x\|_2 \quad (5.30)$$

so providing the following relative measure of $F(x, \hat{Q})$ variability depending coefficients x

$$\frac{\sigma_F}{\langle F \rangle} = \frac{\|x\|_2^{1/2}}{\|x\|_1} \quad (5.31)$$

In particular it can be applied to the solution Eq. (5.27):

$$\frac{\sigma_F}{\langle F \rangle} = \frac{1}{n(\zeta)} \left[\sum_{k=1}^{\infty} e^{-2\zeta(E_k - E_1)} \right]^{1/2} = \frac{n(2\zeta)^{1/2}}{n(\zeta)} \quad (5.32)$$

Since $1 < n(2\zeta) < n(\zeta)$ for $\zeta > 0$ according to definition (5.9), we obtain an upper bound on the basis of the effective dimensionality $n(\zeta)$ of thermally populated eigenstates

$$\frac{\sigma_F}{\langle F \rangle} < \frac{1}{n(\zeta)^{1/2}} \quad (5.33)$$

In the limit of a system with an infinite number $n(\zeta)$ of effective states, the function $F(x, \hat{Q})$ tends to be statistically constant because of the vanishing of its relative variance

$$n(\zeta) \rightarrow \infty : \quad \sigma_F / \langle F \rangle \rightarrow 0 \quad (5.34)$$

and, therefore, the solution (5.27) becomes exact since this was the condition invoked to derive it.

The naturally related issue concerns the physical conditions assuring the infinite limit for the effective dimensionality, $n(\zeta) \rightarrow \infty$. The definition of equation (5.9) provides an obvious answer for the infinite temperature state of the system, $\zeta \rightarrow 0$. A second, may be more interesting, case arises if we consider the system composed by an ensemble of identical components (say, molecules). Under the assumption of a weak coupling between components, the overall energy can be considered as additive with respect to the energies of the components. Correspondingly, according to definition (5.9), the effective dimensionality $n^{(M)}(\zeta)$ of the composite system with M components at a given

thermal states ζ can be specified as

$$n^{(M)}(\zeta) = n_c(\zeta)^M \quad (5.35)$$

where $n_c(\zeta)$ is the effective dimensionality of a component in the same thermal state. Then an infinite effective dimensionality $n^{(M)}(\zeta) \rightarrow \infty$ is recovered if we consider the infinite size limit $M \rightarrow \infty$ of the composite system at a given thermal state, provided that $n_c(\zeta) > 1$ at a non vanishing temperature. In conclusion the simplest solution (5.27) for the scaling coefficients of RPSE populations can be safely employed in the evaluation of thermodynamic properties of macroscopic systems.

On the other hand it should be stressed that also for finite sized systems, or even small ones as those amenable to quantum dynamical simulations, equation (5.27) represents an useful solution for the scaling coefficients besides the infinite temperature limit, which is practically uninteresting. If the effective dimensionality is large enough, at any rate equation (5.27) can be taken, instead of the exact solution, as a good approximation depending on the magnitude of $n(\zeta)$. As a matter of fact it can be considered as the first order solution in the suitable framework for the perturbational treatment of equations (5.23), which will be presented in the next section.

5.3 Finite effective dimensionality

The objective of the following analysis is the solution of the system of equations (5.23) by means of a perturbation expansion with respect to the case of infinite effective dimensionality for which the analytical solution of equation (5.27) is available. Let us rewrite the equations to be solved as

$$g_k(x) = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} \quad (5.36)$$

for $k = 1, 2, \dots$, where

$$g_k(x) := \left\langle \frac{x_k \hat{Q}_k}{F(x, \hat{Q})} \right\rangle \quad (5.37)$$

represents a set of functions of the unknowns x . It should be stressed that the system of Eqs. (5.36) has a multiplicity of solutions since, taking into account

the definition (5.24) for $F(x, \hat{Q})$, functions $g_k(x)$ are invariant by scaling the unknowns by a common factor, $x_k \rightarrow ax_k$. In order to avoid such an ambiguity about the solution of the problem, in the following we assume that the set x of unknowns is normalized according to an unitary 1-norm

$$\|x\|_1 = \sum_{k=1}^{\infty} x_k = 1 \quad (5.38)$$

Correspondingly the function $F(x, \hat{Q})$ has unitary average

$$\langle F(x, \hat{Q}) \rangle = \sum_{k=1}^{\infty} x_k \langle \hat{Q}_k \rangle = \sum_{k=1}^{\infty} x_k = 1 \quad (5.39)$$

Explicit evaluation of functions $g_k(x)$ according to their definition Eq. (5.37) is impossible because of the non linear coupling between unnormalized populations \hat{Q}_k introduced by $F(x, \hat{Q})$ at the denominator. Therefore a suitable series expansion should be performed on the function to be averaged, in order to generate powers of unnormalized populations whose averages are easily evaluated thanks to the independent distribution on the integration variables of Eq. (5.20). On the other hand the deviations of function $F(x, \hat{Q})$ from its average tend to vanish in the limit of an infinite effective dimensionality and, in the spirit of a perturbative approach, we can introduce a series expansion with respect to $\Delta F(x, \hat{Q}) := F(x, \hat{Q}) - \langle F(x, \hat{Q}) \rangle = F(x, \hat{Q}) - 1$. Then functions $g_k(x)$ are recast as

$$g_k(x) = \left\langle \frac{x_k \hat{Q}_k}{1 + \Delta F(x, \hat{Q})} \right\rangle = \left\langle x_k \hat{Q}_k \sum_{j=0}^{\infty} [-\Delta F(x, \hat{Q})]^j \right\rangle \quad (5.40)$$

where averages are now required only for the powers of unnormalized populations. In Appendix 5.B I have reported the details of the procedure for their evaluation.

In order to generate a practical scheme of solution for equation (5.36), one needs to recognize the perturbational parameter of the expansion with respect to the limit of infinite effective dimensionality, $n(\zeta) \rightarrow \infty$. The suitable parameter is

$$\epsilon := 1/n(\zeta) \quad (5.41)$$

and it should be employed to identify the contributions of different orders in

functions $g_k(x)$ organized as

$$g_k(x) = \sum_{m=1}^{\infty} g_k^{(m)}(x) \quad (5.42)$$

with $\mathcal{O}(g_k^{(m)}) = \epsilon^m$ for $\epsilon \rightarrow 0^+$. By taking into account that equation (5.27) is the solution of the problem in the limit $\epsilon \rightarrow 0^+$, one identifies the order of the unknowns, $\mathcal{O}(x_k) = \epsilon$ and of their powers:

$$\mathcal{O}(x_k^n) = \epsilon^n \quad (5.43)$$

This is the typical order of magnitude for the ensemble of these coefficients deriving from the denominator of equation (5.27), without considering their differences due to the energy eigenvalues E_k . To attribute an order to the n -norm of the unknowns, on the basis of the physical meaning of effective dimensionality $n(\zeta)$, one could consider the summation as equivalent to $n(\zeta) = 1/\epsilon$ times the order of magnitude of x_k^n , that is

$$\mathcal{O}(\|x\|_n) = \mathcal{O}\left(\sum_k x_k^n\right) = n(\zeta)\mathcal{O}(x_k^n) = n(\zeta)\epsilon^n = \epsilon^{n-1} \quad (5.44)$$

By means of the order assignments equations (5.43) and (5.44), from the contributions (5.75) reported in Appendix 5.B one can recognize the lower order contributions to equation (5.42)

$$\begin{aligned} g_k^{(1)}(x) &= x_k \\ g_k^{(2)}(x) &= x_k \|x\|_2 - x_k^2 \\ g_k^{(3)}(x) &= x_k (3\|x\|_2^2 - 2\|x\|_3) - 3x_k^2 \|x\|_2 + 2x_k^3 \end{aligned} \quad (5.45)$$

Notice that

$$\sum_k g_k^{(m)}(x) = \delta_{m,1} \quad (5.46)$$

because of the normalization $\|x\|_1 = 1$. Higher order contributions can be obtained by integrating with these rules the computer program which produces the linear combinations for functions $G_k^{(j)}(x)$ (see Appendix 5.B). One should notice also that the expansion terms of equation (5.45) have an universal character since they are independent of the physical system and of its thermal state

as well. This means that the ensemble of functions $g_k^{(m)}(x)$ can be identified once for all.

For a given physical system, specified through the sequence of energy eigenvalues E_1, E_2, E_3, \dots , in a given thermal state ζ , equations (5.36) have to be solved with respect to the unknowns x by specifying functions $g_k(x)$ according to the series expansion (5.42). In practice, however, one can calculate solutions of equations (5.36) only at a given order ϵ^M on the perturbational parameter. This corresponds to employ in equation (5.36) the expansion truncated for $m > M$, that is

$$\sum_{m=1}^M g_k^{(m)}(x) = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} \quad (5.47)$$

Let us denote with $x^{(M)} = (x_1^{(M)}, x_2^{(M)}, \dots)$ such a solution of M -order. Since $g_k^{(1)}(x) = x_k$, the first order solution $x^{(1)}$ is precisely equation (5.27) that we have already found in the limit of an infinite effective dimensionality. Higher order results requires the solution of a system of non linear equations in the unknowns as derived from Eq. (5.47) for $M > 1$. As a matter of fact they are computationally easily accessible by solving iteratively equation (5.47) rewritten as

$$x_k = \frac{e^{-\zeta(E_k - E_1)}}{n(\zeta)} - \sum_{m=2}^M g_k^{(m)}(x) \quad (5.48)$$

By inserting at the r.h.s. an approximation to $x^{(M)}$, say $x^{(1)}$, we calculate new values for the unknowns, which can replace the previous approximation, and so on up to convergence. We have found that such a procedure is very efficient. Notice also these finite order solutions $x^{(M)}$ preserve the normalization of the unknown, $\|x^{(M)}\|_1 = 1$, because of Eq. (5.46).

5.4 Convergence of the series

Once a physical system, specified by its energy spectrum, is provided in a given thermal state ζ , TRE populations P_k can be obtained by solving equation (5.36) with respect to the unknown x , according to the series (5.42). However the evaluation of the entire series is obviously impossible and a description of its convergence is necessary in order to be able to understand how many contributions of different orders $g_k^{(m)}$ have to be taken into account to perform a simulation where the average properties for the system are close to TRE

averages.

The convergence has been evaluated for a given system through the deviations of the ensemble average of the system energy $\langle E(\zeta) \rangle$, computed on a sample of 10^6 points, from the internal energy of the TRE ensemble $U_Q(\zeta)$ from equation (3.48).

$$\frac{\Delta_U}{U_Q(\zeta)} = \frac{U_Q(\zeta) - \langle E(\zeta) \rangle}{U_Q(\zeta)} \quad (5.49)$$

in particular the system I have considered is formed by 100 eigenstates selected according to the computational algorithm described in the next chapter 6.2.

In Figure 5.1 the convergence is reported for different truncation of orders m of equation (5.47), in function of the effective dimensionality $n(\zeta)$, since it is the privileged parameter in the control of the scaling evaluation. As long

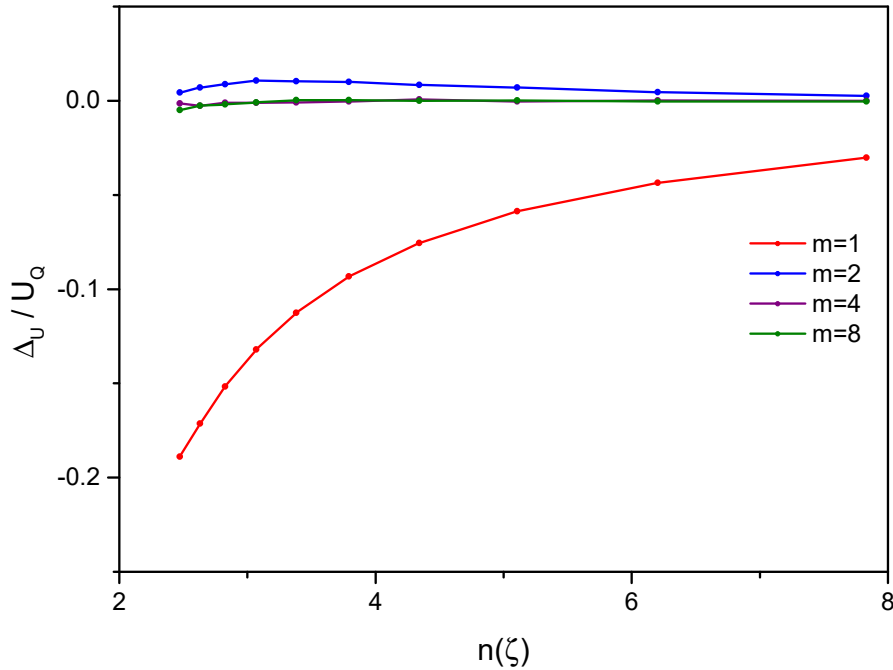


Figure 5.1: Convergence of the series accounted as the relative difference Δ_U / U_Q (5.49), computed on a system of 100 states, is reported versus the effective dimensionality $n(\zeta)$. The ensemble average of energy is computed on a sampling of 10^6 sets of populations. Different truncation orders m are shown.

as the systems is fixed, the control parameter depends only from the quantum temperature, so the increasing on the effective dimension corresponds to the increase of the system quantum temperature and to a faster convergence of the series. Such a behaviour is more evident for $m = 1$ (red points) where only

the first term of the series is considered. It is in agreement with the result of paragraph 5.2 where the first term of the series is sufficient to provide the exact solution for an infinite effective dimensionality. In Figure 5.1 a very fast convergence can be also noticed in the increasing of the truncation order m where $m = 1, 2, 4, 8$ have been reported.

The main result shown in figure is that low contributions in the series expansion are sufficient to produce a good accuracy in thermodynamic properties and so an unbiased sampling of the TRE ensemble.

5.5 Thermodynamic properties

In this section we analyze the thermodynamic behavior of the previously introduced statistical ensemble in the limit of a very large effective dimensionality $n(\zeta)$. Thus such a treatment is relevant for macroscopic systems, but it can be employed also to finite systems independently of their size if $n(\zeta)$ is large enough. Outside these conditions, the thermodynamic properties are accessible by numerical evaluation of the suitable averages which are introduced in the following.

Thus we shall adopt the first order solution of equation (5.27) for the coefficients x scaling RPSE populations. As discussed in paragraph 3.6.2, the quantum microscopic counterparts U_Q (eqn. (3.48)) and S_Q (eqn. (3.51)) of the internal energy and of the entropy, respectively, are defined as the ensemble averages

$$U_Q := \langle E \rangle = \left\langle \sum_k E_k P_k \right\rangle \quad (5.50)$$

$$S_Q := -k_B \left\langle \sum_k P_k \ln P_k \right\rangle \quad (5.51)$$

of the expectation energy and of the Shannon entropy, k_B being the Boltzmann constant. By replacing TRE populations P by scaled RPSE populations, $P_k =$

$x_k \hat{Q}_k$, one obtains

$$U_Q = \sum_k E_k x_k \langle \hat{Q}_k \rangle = \sum_k E_k x_k \quad (5.52)$$

$$S_Q = -k_B \sum_k x_k \langle \hat{Q}_k \ln(x_k \hat{Q}_k) \rangle = -k_B \sum_k x_k \ln x_k - k_B \sum_k x_k \langle \hat{Q}_k \ln \hat{Q}_k \rangle \quad (5.53)$$

The average at the r.h.s. of Eq. (5.53) with an exponential distribution of \hat{Q}_k is done analytically

$$\langle \hat{Q}_k \ln \hat{Q}_k \rangle = 1 - \gamma \quad (5.54)$$

where γ is the Euler-Mascheroni constant, and the following explicit relation is found for the entropy

$$S_Q = -k_B \sum_k x_k \ln x_k - k_B(1 - \gamma) \quad (5.55)$$

It should be stressed that because of equation (5.27), the internal energy $U_Q(\zeta)$ and the entropy $S_Q(\zeta)$, and coefficients $x_k(\zeta)$ as well, should be considered as functions of the thermal parameter ζ . Such a thermal dependence allows the identification of the quantum temperature parameter T_Q according to the fundamental differential of thermodynamics

$$\frac{1}{T_Q(\zeta)} := \frac{dS_Q}{dU_Q} = \frac{dS_Q(\zeta)/d\zeta}{dU_Q(\zeta)/d\zeta} \quad (5.56)$$

The derivative of the entropy of equation (5.55), by taking into account that coefficients X are normalized as $\|x\|_1 = 1$, can be specified as:

$$\frac{dS_Q(\zeta)}{d\zeta} = -k_B \sum_k \frac{dx_k(\zeta)}{d\zeta} (1 + \ln x_k) = k_B \sum_k \frac{dx_k(\zeta)}{d\zeta} [\zeta(E_k - E_1) + \ln n(\zeta)] \quad (5.57)$$

where the explicit form equation (5.27) of the first order solution has been inserted. By taking again into account that 1-norm of x is constant, one finally obtains

$$\frac{dS_Q(\zeta)}{d\zeta} = k_B \zeta \sum_k E_k \frac{dx_k(\zeta)}{d\zeta} = k_B \zeta \frac{dU_Q(\zeta)}{d\zeta} \quad (5.58)$$

that is the proportionality between the ζ derivative of the entropy and of the internal energy, which leads to the following identification of the quantum temperature on the basis of the thermal parameter ζ

$$\frac{1}{k_B T_Q} = \zeta \quad (5.59)$$

We emphasize that this is an exact result when the first order solution equation (5.27) for coefficients x can be safely employed, that is in the limit of a very large effective dimensionality $n(\zeta)$, for instance with macroscopic systems. It should also be mentioned that such a result was anticipated in part paragraph 3.6.3, but by invoking an approximation to quantum entropy which was motivated by the maximum entropy methodology of Jaynes [1].

The precise identification of the quantum temperature allows the definition other relevant thermodynamic functions, like the Helmholtz free energy

$$A_Q := U_Q - T_Q S_Q \quad (5.60)$$

$$= \sum_k x_k [E_k + k_B T_Q \ln x_k + k_B T_Q (1 - \gamma)] \quad (5.61)$$

$$= E_1 - k_B T_Q \ln n(\zeta) + k_B T_Q (1 - \gamma) \quad (5.62)$$

By taking into account that for a large $n(\zeta)$ the last term at the r.h.s. is negligible, and by considering an energy scale with the ground state as the origin, one recovers the standard relation of statistical mechanics

$$A_Q = -k_B T_Q \ln n(\zeta) \quad (5.63)$$

which allows the interpretation of the effective dimensionality $n(\zeta)$ as the corresponding partition function.

The quite simple evaluation of ensemble averages, performed on the asymptotic limit of RPSE statistics, suggests that also typicality of internal energy and entropy could be analytically investigated, by following the same strategy described by Fresch and Moro in [50]. However we report here only a numerical simulation that verifies as the distributions of internal energy and entropy narrow in the increasing of the density of states for fixed energy interval and thermal state.

In Figure 5.2 the distributions of internal energy U_Q (top-panel) and en-

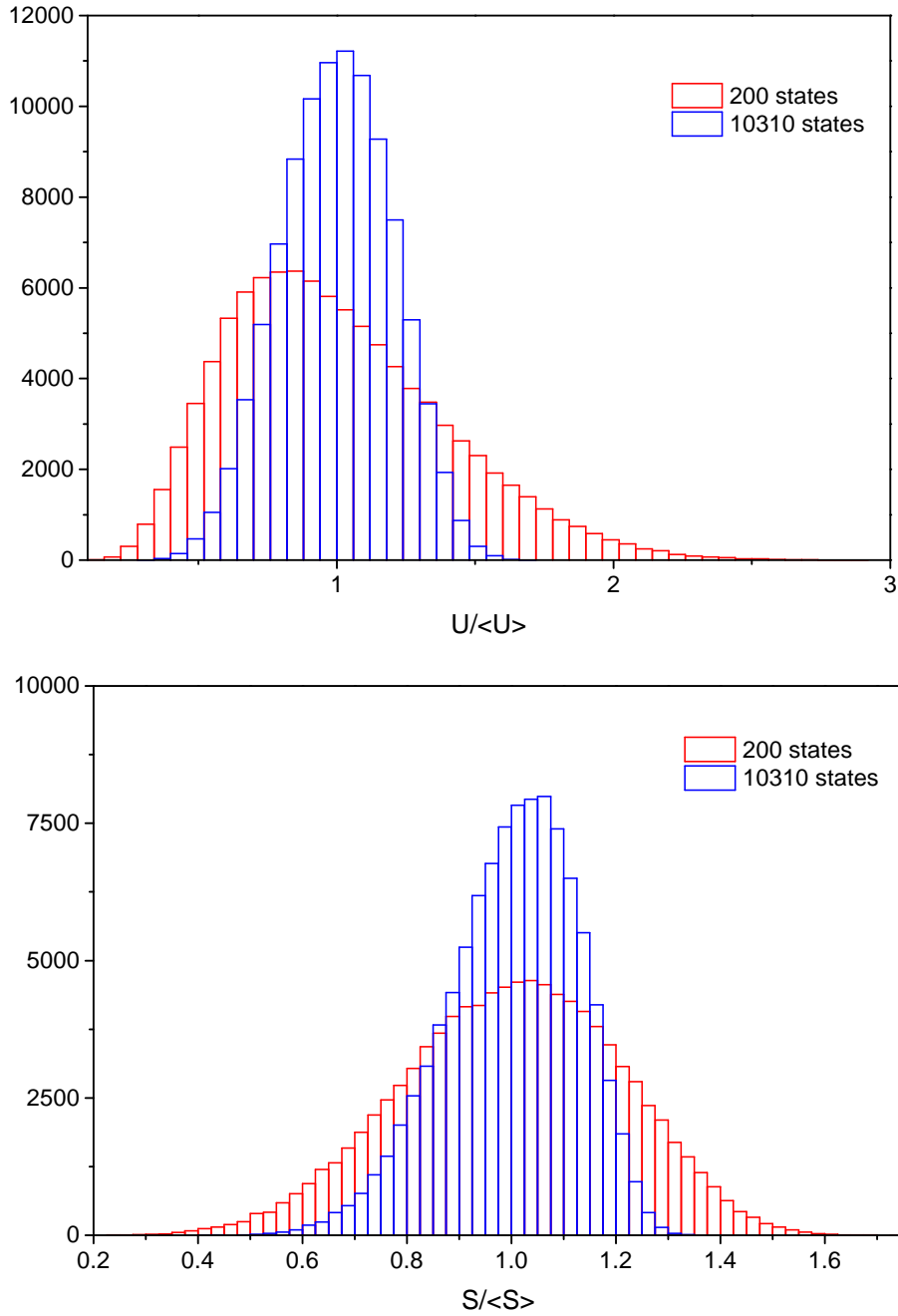


Figure 5.2: Distributions of internal energy U_Q (top-panel) and entropy S_Q (bottom panel) from a sample of 10^6 sets of TRE populations are reported for two different quantum systems. TRE populations have been obtained by the scaling algorithm explained in the main text, with a truncation term $m = 4$ and a fixed thermal parameter ζ . The typicality behaviour is clear by observing the two systems that differ for the number of eigenstates whose eigenvalues belong to a fixed energy interval, in order to mimic the increasing on the system size toward the macroscopic limit.

trophy S_Q (bottom-panel) are reported for two different density of states that correspond to an increasing number of energy eigenstates within a fixed energy interval. The same thermal parameter ζ has been considered. It can be noticed that when the Hilbert space dimension increase, the distribution of the properties with a thermodynamic correspondent narrows, this suggest the presence the typicality conditions enforcing the thermodynamic analysis.

5.A Asymptotic RPSE averages

In order to evaluate the asymptotic average described by equation (5.20) for a given function $f(\hat{Q})$ of scaled parameters (5.18) for RPSE populations, we consider initially its K -truncated form depending only the first K variables

$$f^{(K)}(\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_K) := f(\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_K, 0, 0, 0, \dots) \quad (5.64)$$

According to the analysis of Section III of ref. [50], its RPSE average for a N -dimensional active space with $N > K$ can be specified as an integral on the arguments of $f^{(K)}$ only:

$$\begin{aligned} \langle f^{(K)}(\hat{Q}) \rangle_{RPSE}^{(N)} &= \left(\prod_{k=1}^K \int_0^{b_{k,N}} dQ_k \right) f^{(K)}\left(\frac{Q_1}{N}, \frac{Q_2}{N}, \dots, \frac{Q_K}{N}\right) \times \\ &\quad \times \frac{(N-1)!}{(N-K-1)!} b_{K,N}(Q_1, Q_2, \dots, Q_K)^{N-K-1} \end{aligned} \quad (5.65)$$

where the constraints on RPSE populations due to the normalization has been taken into account by introducing the upper bounds $b_{k,N}$ to the integrals

$$b_{k,N}(Q) := 1 - \sum_{j=1}^k Q_j \quad (5.66)$$

Then by performing the change of integration variables to the scaled parameters \hat{Q}_k , we get the relation

$$\begin{aligned} \langle f^{(K)}(\hat{Q}) \rangle_{RPSE}^{(N)} &= \left(\prod_{k=1}^K \int_0^{Nb_{k,N}} d\hat{Q}_k \right) f^{(K)}(\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_K) \left[\prod_{k=1}^K \left(1 - \frac{k}{N}\right) \right] \times \\ &\quad \times b_{K,N}\left(\frac{\hat{Q}_1}{N}, \frac{\hat{Q}_2}{N}, \dots, \frac{\hat{Q}_K}{N}\right)^{N-K-1} \end{aligned} \quad (5.67)$$

that allows a straightforward evaluation of the asymptotic limit $N \rightarrow \infty$. The upper limits of integration can be extended to infinity because

$$b_{k,N}(\hat{Q}_1/N, \hat{Q}_2/N, \dots, \hat{Q}_k/N) = 1 + \mathcal{O}(1/N) \quad \text{for } N \rightarrow \infty \quad (5.68)$$

In the same limit the square bracket term in equation (5.67) can be replaced by the unity while the last term is conveniently evaluated in exponential form since

$$\begin{aligned} (N - K - 1) \ln b_{K,N}\left(\frac{\hat{Q}_1}{N}, \frac{\hat{Q}_2}{N}, \dots, \frac{\hat{Q}_K}{N}\right) &= (N - K - 1) \ln \left(1 - \sum_{k=1}^K \hat{Q}_k/N\right) = \\ &= (N - K - 1) \left(-\sum_{k=1}^K \hat{Q}_k/N + \mathcal{O}(1/N)\right) = -\sum_{k=1}^K \hat{Q}_k + \mathcal{O}(1/N) \end{aligned} \quad (5.69)$$

In this way the asymptotic average of the K -truncated function is specified as

$$\begin{aligned} \langle f^{(K)}(\hat{Q}) \rangle &= \lim_{N \rightarrow \infty} \langle f^{(K)}(\hat{Q}) \rangle_{RPSE}^{(N)} = \\ &= \left(\prod_{k=1}^K \int_0^\infty d\hat{Q}_k \right) \exp \left\{ -\sum_{k=1}^K \hat{Q}_k \right\} f^{(K)}(\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_K) \end{aligned} \quad (5.70)$$

Finally, by applying the limit $K \rightarrow \infty$ to the truncation of the function

$$\langle f(\hat{Q}) \rangle = \lim_{K \rightarrow \infty} \langle f^{(K)}(\hat{Q}) \rangle \quad (5.71)$$

we find equation (5.20) for the asymptotic average of the given function $f(\hat{Q})$.

5.B Evaluation of functions $g_k(x)$

For the evaluation of Eq. (5.40), the term $\Delta F(x, \hat{Q})$ is conveniently specified as

$$\Delta F(x, \hat{Q}) = \sum_{k=1}^{\infty} x_k \hat{Q}_k - 1 = \sum_{k=1}^{\infty} x_k \hat{Q}_k - \sum_{k=1}^{\infty} x_k = \sum_{k=1}^{\infty} x_k (\hat{Q}_k - 1) = \sum_{k=1}^{\infty} x_k \Delta \hat{Q}_k \quad (5.72)$$

where $\Delta\hat{Q}_k = \hat{Q}_k - 1 = \hat{Q}_k - \langle\hat{Q}_k\rangle$ is the deviation of a unnormalized population from its average. Then each contribution (5.40) can be specified as

$$g_k^{(m)}(x) := (-1)^{m-1} x_k \sum_{k_1} x_{k_1} \sum_{k_2} x_{k_2} \cdots \sum_{k_m} x_{k_m} \langle \hat{Q}_k \Delta\hat{Q}_{k_1} \Delta\hat{Q}_{k_2} \cdots \Delta\hat{Q}_{k_m} \rangle \quad (5.73)$$

Each term in the multiple summation is easily evaluated on the basis of the moments of an exponentially distributed variable:

$$\langle \hat{Q}_k^n \rangle = \int_0^\infty d\hat{Q}_k e^{-\hat{Q}_k} \hat{Q}_k^n = n! \quad (5.74)$$

Furthermore, the vanishing of the average of $\Delta\hat{Q}_k$ when it is alone, reduces considerably the number of non vanishing contributions to the multiple summation. Still the direct calculation becomes very involved by increasing the order m , that is the number of independent summations in Eq. (5.73). We report the result just for the first few of them:

$$\begin{aligned} G_k^{(1)}(x) &= -x_k^2 \\ G_k^{(2)}(x) &= 2x_k^3 + x_k ||x||_2 \\ G_k^{(3)}(x) &= -6x_k^4 - 3x_k^2 ||x||_2 - 2x_k ||x||_3 \\ G_k^{(4)}(x) &= 24x_k^5 + 12x_k^3 ||x||_2 + 8x_k^2 ||x||_3 + 3x_k (2||x||_4 + ||x||_2^2) \end{aligned} \quad (5.75)$$

Each function $G_k^{(j)}(x)$ is then specified as a linear combination of the powers of coefficient x_k multiplied by n -norms of x coefficients or their products. As a matter of fact, few simple rules are required to calculate iteratively the coefficients (integer numbers) of these linear combinations, rules which can be translated into a computer program which allows one to specify functions $G_k^{(j)}(x)$ up to large values of index j .

CHAPTER 6

Thermalization Dynamics

The so called *thermalization experiment* is one of the most interesting process to be studied at molecular lever. As a matter of fact, all the situations where different systems are brought in contact belong to this class of experiments, with the only requirement that the interaction is weak enough to preserve the physical properties of the systems. In the overwhelming majority of the situations, the previous condition is satisfied and represents a very mild assumption. Furthermore, since the quantum mechanical theory is believed to be more appropriate in the description of the behaviour at molecular level, the development of new strategies to follows the system dynamics from a purely quantum perspective is a very interesting task.

The tools developed in the previous chapters represent a little but important step towards the development of quantum mechanical analogue of Molecular Dynamic simulations by allowing the selection of an initial wave function for the system dynamics within a self consistent theoretical framework. Indeed the correspondence between microscopic thermal parameter and macroscopic temperature has been demonstrated as well as the emergence of equilibrium thermodynamics in the limit of large systems. Above all, unlike the more common statistical ensemble of pure states nowadays available, TRE ensemble is able to describe the thermalization experiment due to its inherent invariance and can be used both to characterize the systems before the switching-on of

the interaction and after the realization of equilibrium condition.

In this chapter I study some generic realizations of the thermalization experiment and instead of using a particular energy level structure, such as oscillators or spin systems that can have peculiar properties, I will consider a discrete energy spectrum derived from a density of states through a computational procedure developed by Enrico Nale [76] in his Ph.D. research. Since the energy eigenstate has a partial random character the results I am going to obtain are quite general and does not depend from the specific symmetries or other features of the problem of interest.

Whenever the considered situation is enough simple, an analytic insight is provided to the understanding of the inherent phenomena.

We will see as only in relative simple cases a thermodynamic equilibration is obtained by guaranteeing the equidistribution of internal energy between the systems that are brought in interaction. Whenever more complex situation are considered, such a definition of equilibrium is not applicable since an identical energy for the subsystems will never be attained. The equilibrium defined by the thermodynamics cannot be applied to the quantum mechanical description and an equivalent definition with a statistical meaning should be identified. This is a very important result of our analysis that is able to rationalize the situations characterized by an apparent absence of thermalization. In fact only by the use of statistical ensemble for wave functions a coherent picture of equilibrium can be obtained in different realizations of quantum systems.

In conclusion, the study of quantum dynamics from the wave function point of view can develop new interesting insights in the description of interactions between systems at the molecular level, which in perspective could be useful in the description of quantum phenomena like, for example, vibrational or electronic coherence transfer.

6.1 Description of isolated quantum system

In paragraph 2.1 I have introduced the basic quantum mechanical description of molecular systems in order to deal with dynamical processes fully at the quantum level. Here I intend to recall some of those definitions and complete them in order to describe the thermalization experiments we are going to consider.

Every time an isolated system is taken into account, it can be described equivalently by the wave function $\Psi(t)$

$$|\Psi(t)\rangle = \sum_k \sqrt{P_k} \exp(-i\alpha_k(t)) |E_k\rangle \quad (6.1)$$

that is the state vector of the system in the Hilbert space, and by the density matrix $\hat{\rho}(t)$ that expressed in the eigenvector basis is

$$\hat{\rho}(t) = |\Psi(t)\rangle \langle\Psi(t)| = \sum_{k,k'} \sqrt{P_k P_{k'}} \exp(-i\alpha_k(t) + i\alpha_{k'}(t)) |E_k\rangle \langle E_{k'}| \quad (6.2)$$

and represents the instantaneous projection operator, on the wave function direction. Furthermore the diagonal elements of the density matrix can be easily recognized to be the populations of the system

$$P_k = \langle E_k | \hat{\rho}(t) | E_k \rangle \quad (6.3)$$

Any expectation value $a(t)$ of an observable A can be equivalently computed using the wave function or density matrix description as

$$a(t) = \langle\Psi(t)| \hat{A} |\Psi(t)\rangle \quad (6.4)$$

$$a(t) = \text{Tr}\{\hat{A}\hat{\rho}(t)\} \quad (6.5)$$

where a particular role can be assigned to the expectation value of the Hamiltonian \hat{H}

$$E = \langle\Psi(t)| \hat{H} |\Psi(t)\rangle = \text{Tr}\{\hat{H}\hat{\rho}(t)\} = \sum_k P_k E_k \quad (6.6)$$

that describes the energy of the system. Such a description refers to the whole isolated system that includes the system of interest as well as its environment. As a matter of fact, whenever a system interact with its environment we should consider it as a subsystem in contact with the surrounding since the wave function can be introduced for isolated systems only. The same reasoning should be applied in the situation when afterwards we separate the two systems, essentially switching off the interaction among them. In fact we cannot consider them as completely isolated so to assign to each of them a wave function because of the entanglement that is generated whenever an interaction has taken place [77]. In these cases, the property of the system of interest S alone can

be described only through the reduced density matrix $\hat{\sigma}^S(t)$ of the subsystem

$$\hat{\sigma}^S(t) = \text{Tr}_E\{\hat{\rho}(t)\} \quad (6.7)$$

by tracing out the environment degrees of freedom. According to the reduced density matrix the expectation values for any observable A^s pertinent to the subsystem s can be specified

$$a(t) = \text{Tr}((\hat{A} \otimes \hat{\mathbb{1}}_E)\hat{\rho}(t)) = \text{Tr}_S(\hat{A}\text{Tr}_E\hat{\rho}(t)) = \text{Tr}_S(A\hat{\sigma}(t)) \quad (6.8)$$

In particular the diagonal elements of the reduced density matrix plays an important role in the description of the subsystem since, in analogy with equation (6.3), we can define them as *reduced populations* of the subsystem

$$P_{ks}^S(t) = \langle e_{ks}^S | \hat{\sigma}^S(t) | e_{ks}^S \rangle \quad (6.9)$$

where $|e_k^S\rangle$ are eigenvectors of the reduced density matrix $\hat{\sigma}_S$. It is important to notice as reduced populations have different properties in comparison with populations of the overall isolated system. First of all they are not constant of motion and secondly, whichever the global population statistics is, they are likely to be of canonical form when the system is small enough with respect to the environment [21, 22, 25].

A slightly different perspective has to be considered when the two initially isolated systems A and B that have never interacted before and at a certain instant one introduces a coupling term that allows them to exchange energy. We set this time instant as $t = 0$. Then, for $t < 0$ it is possible to assign a wave function, $|\Psi^A(t)\rangle \in \mathcal{H}^A$ and $|\Psi^B(t)\rangle \in \mathcal{H}^B$, to each isolated systems

$$t < 0 \quad |\Psi^A(t)\rangle = \sum_{k^A} \sqrt{P_{k^A}^A} \exp(-i\alpha_{k^A}^A(t)) |E_{k^A}^A\rangle \quad (6.10)$$

$$t < 0 \quad |\Psi^B(t)\rangle = \sum_{k^B} \sqrt{P_{k^B}^B} \exp(-i\alpha_{k^B}^B(t)) |E_{k^B}^B\rangle \quad (6.11)$$

where $|E_{k^A}^A\rangle$ and $|E_{k^B}^B\rangle$ are the eigenvectors of the corresponding Hamiltonian

\hat{H}^A and \hat{H}^B

$$\hat{H}^A |E_{k^A}^A\rangle = E_{k^A}^A |E_{k^A}^A\rangle \quad (6.12)$$

$$\hat{H}^B |E_{k^B}^B\rangle = E_{k^B}^B |E_{k^B}^B\rangle \quad (6.13)$$

At the same time, if we want to consider the overall system composed by both A and B , one must consider the Hilbert product space

$$\mathcal{H}^{A+B} = \mathcal{H}^A \otimes \mathcal{H}^B \quad (6.14)$$

either in presence or absence of interaction between A and B . In particular, for $t < 0$, when no interaction takes place, it is possible to define the Hamiltonian of the overall system, usually called *zero-order* Hamiltonian, as

$$\hat{H}_{t<0}^{A+B} = \hat{H}^A \otimes \hat{1}^B + \hat{1}^A \otimes \hat{H}^B \quad (6.15)$$

where the subscript $t < 0$ implies the absence of interaction. The eigenvalues problem associated to this Hamiltonian is

$$\hat{H}_{t<0}^{A+B} |E_{k^A}^A\rangle \otimes |E_{k^B}^B\rangle = (E_{k^A}^A + E_{k^B}^B) |E_{k^A}^A\rangle \otimes |E_{k^B}^B\rangle \quad (6.16)$$

where as basis for the Hilbert space \mathcal{H}^{A+B} we have selected the product basis of the separated systems. Moreover a generic state for this non interactive system is simply the product of the wavefunctions $|\Psi^A(t)\rangle$ and $|\Psi^B(t)\rangle$ of the separated systems

$$|\Psi(t)\rangle = |\Psi^A(t)\rangle \otimes |\Psi^B(t)\rangle \quad (6.17)$$

In order to simulate a thermalization experiment, we need to couple the two systems by allowing them to exchange their energy because of the presence of an interaction Hamiltonian \hat{H}^{int} . The introduction of the coupling term represents a singular point for the evolution of the system and for $t > 0$ the overall Hamiltonian includes also the interaction Hamiltonian \hat{H}^{int}

$$\hat{H}_{t>0}^{A+B} = \hat{H}^A \otimes \hat{1}^B + \hat{1}^A \otimes \hat{H}^B + \lambda_{int} \hat{H}^{int} \quad (6.18)$$

where λ_{int} is a constant that described the weight of the coupling contribution or, in other words, the interaction strength. Such an interaction, by modifying

the overall Hamiltonian, produces a rotation of their eigenvectors with respect to the situation at $t < 0$ and they are specified by

$$\hat{H}_{t>0}^{A+B} |E_j^{A+B}\rangle = E_j^{A+B} |E_j^{A+B}\rangle \quad (6.19)$$

where E_j^{A+B} are the energies eigenvalues for $t > 0$. Thus, the principal directions in the total Hilbert space cannot be described anymore as simple products of the decoupled basis set $|E_{k^A}^A\rangle |E_{k^B}^B\rangle$.

For $t < 0$, the evaluation of the properties of a subsystem, equivalently for A or B , is a trivial operation. For example we can consider the energy of the subsystem A

$$E_{<}^A = \langle \Psi(t) | \hat{H}^A \otimes \hat{1}^B | \Psi(t) \rangle = \langle \Psi^A(t) | \hat{H}^A | \Psi^A(t) \rangle \quad (6.20)$$

$$= \sum_{k^A} P_{k^A}^A E_{k^A}^A \quad (6.21)$$

that is equivalent to equation (6.6). At the same time, once the probability distribution on populations is provided, it is possible to compute its ensemble average

$$\langle E_{<}^A \rangle = \sum_{k^A} \langle P_{k^A}^A \rangle E_{k^A}^A \quad (6.22)$$

as well as its variance as

$$\sigma_{E_{<}^A}^2 = \langle (E_{<}^A - \langle E_{<}^A \rangle)^2 \rangle = \langle (E_{<}^A)^2 \rangle - \langle E_{<}^A \rangle^2 \quad (6.23)$$

Once the interaction is switched on, for $t > 0$, the wave function can be expressed as linear combination of the new basis of eigenvectors of the overall Hamiltonian $\hat{H}_{t>0}^{A+B}$

$$|\Psi^{A+B}(t)\rangle = \sum_j \sqrt{P_j^{A+B}} \exp(-i\alpha_j^{A+B}(t)) |E_j^{A+B}\rangle \quad (6.24)$$

where linear phases with the time, $\alpha_j^{A+B}(t) = \alpha(0) + E_j t / \hbar$. A question about how to connect the populations of the system after that the interaction has taken place with the parameters of the initially isolated wave function naturally arises. The answer can be provided from the condition of continuity on the

wave function at $t = 0$,

$$|\Psi^{A+B}(0)\rangle = |\Psi^A(0)\rangle |\Psi^B(0)\rangle \quad (6.25)$$

that allows to write the equivalence

$$P_j^{A+B} = |\langle E_j^{A+B} | \Psi(0) \rangle|^2 \quad (6.26)$$

$$= |\langle E_j^{A+B} | \Psi^A(0) \rangle \langle \Psi^B(0) | E_j^{A+B} \rangle|^2 \quad (6.27)$$

$$= \left| \sum_{k^A} \sum_{k^B} \langle E_j^{A+B} | (|E_{k^A}^A\rangle |E_{k^B}^B\rangle) \sqrt{P_{k^A}^A P_{k^B}^B} \exp(-i\alpha_{k^A}^A(0) - i\alpha_{k^B}^B(0)) \right|^2 \quad (6.28)$$

where $\langle E_j^{A+B} | (|E_{k^A}^A(t)\rangle |E_{k^B}^B(t)\rangle)$ is an element of the transformation matrix from the basis where $\hat{H}_{t<0}^{A+B}$ is diagonal to the one where $\hat{H}_{t>0}^{A+B}$ is diagonal. If we denote this element as

$$T_j^{k^A, k^B} = \langle E_j^{A+B} | (|E_{k^A}^A\rangle |E_{k^B}^B\rangle)^* \quad (6.29)$$

the previous equation can be written in a more compact form as

$$P_j^{A+B} = \left| \sum_{k^A} \sum_{k^B} (T_j^{k^A, k^B})^* \sqrt{P_{k^A}^A P_{k^B}^B} \exp(-i\alpha_{k^A}^A(0) - i\alpha_{k^B}^B(0)) \right|^2 \quad (6.30)$$

that results to be very useful in the following.

After the introduction of the interaction it is still possible to follow the properties of the subsystem and their variations. Particular relevance has to be given to subsystem energies, for instance of the system A ,

$$E_{>}^A(t) = \langle \Psi^{A+B}(t) | \hat{H}^A \otimes \hat{\mathbb{1}}^B | \Psi^{A+B}(t) \rangle \quad (6.31)$$

that is no longer constant in time. As a matter of fact the interaction allows the bodies to exchange their energy, leading to a subsystem energy with an explicit time dependence. In the following we will see as the subsystem with an initially higher temperature tends to realise energy to the colder system in order to equilibrate and then the energy of both systems starts to fluctuate around the equilibrium value. From the definition of population P_j^{A+B} of

equation (6.30) for the system after the interaction, it is possible to evaluate this equilibrium value of the subsystem energy, accounted by infinite time average according to (2.32)

$$\overline{E}_>^A = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt E_>^A(t) = \sum_j P_j^{A+B} \langle E_j^{A+B} | \hat{H}^A \otimes \hat{\mathbb{1}}^B | E_j^{A+B} \rangle \quad (6.32)$$

by using the appropriate change of basis set

$$\langle E_j^{A+B} | \hat{H}^A \otimes \hat{\mathbb{1}}^B | E_j^{A+B} \rangle = \sum_{k^A} \sum_{k^B} \langle E_j^{A+B} | (|E_{k^A}^A\rangle |E_{k^B}^B\rangle) E_k^A (\langle E_{k'^A}^A | \langle E_{k'^B}^B |) | E_j^{A+B} \rangle \quad (6.33)$$

where the matrix element of operator $\hat{H}^A \otimes \hat{\mathbb{1}}^B$ is evaluated on the basis of non interacting systems.

Once the initial wave function for both initially isolated systems is selected, it is possible to follow the dynamics of a single realization of the overall quantum system. However an other important piece of information concern the variability between different possible realizations of the system state within the same statistical ensemble. In order to statistically characterize the ensemble it is important to describe the ensemble average of properties depending on the populations that allows the calculation of their mean values as well as their variance. From equation (6.30) we can write

$$\begin{aligned} \langle P_j^{A+B} \rangle &= \sum_{k^A k'^A} \sum_{k^B k'^B} \langle E_j^{A+B} | (|E_{k^A}^A\rangle |E_{k^B}^B\rangle) (\langle E_{k'^A}^A | \langle E_{k'^B}^B |) | E_j^{A+B} \rangle \times \\ &\quad \langle \sqrt{P_{k^A}^A P_{k'^A}^A P_{k^B}^B P_{k'^B}^B} \exp(i\alpha_{k'^A}^A(0) - i\alpha_{k^A}^A(0) + i\alpha_{k'^B}^B(0) - i\alpha_{k^B}^B(0)) \rangle \end{aligned} \quad (6.34)$$

where the $\langle \cdot \rangle$ means the average according to the probability densities for the statistical ensembles of both initially isolated systems. Since phases and populations are statistically independent it is possible to calculate separately their averages. Moreover, phases are homogeneously distributed in their domain and therefore, in the summation of the previous equation only the terms with the same indexes where $k^A = k'^A$ and $k^B = k'^B$ survive. The resulting average

population reads

$$\langle P_j^{A+B} \rangle = \sum_{k^A} \sum_{k^B} |\langle E_j^{A+B} | (|E_{k^A}^A\rangle |E_{k^B}^B\rangle) |^2 \langle P_{k^A}^A \rangle \langle P_{k^B}^B \rangle \quad (6.35)$$

$$= \sum_{k^A} \sum_{k^B} (T_j^{k^A, k^B})^* \langle P_{k^A}^A \rangle \langle P_{k^B}^B \rangle \quad (6.36)$$

It is now straightforward to compute the ensemble average of subsystem energy of equation (6.32)

$$\langle \bar{E}_>^A \rangle = \sum_j \langle P_j^A \rangle \langle E_j^{A+B} | \hat{H}^A \otimes \hat{1}^B | E_j^{A+B} \rangle \quad (6.37)$$

as well as its variance

$$\sigma_{E^A}^2 = \langle (\bar{E}_>^A - \langle \bar{E}_>^A \rangle) \rangle \quad (6.38)$$

Analogously it is possible to obtain the properties of subsystem B with the appropriate change of the corresponding operators.

In conclusion, the dynamical simulation of the thermalization between two quantum systems can be computed once the following ingredients are provided:

- the energy spectrum of the single systems ($|E_{k^A}^A\rangle$ and $|E_{k^B}^B\rangle$ for all k^A, k^B) that defines the physical property of the systems;
- the interaction Hamiltonian \hat{H}^{int} that describes how the two systems interact and it allows them to exchange their energy;
- the initial states of the dynamics $|\Psi^A\rangle(0)$ and $|\Psi^B(0)\rangle$ of the two separated systems which is required to evaluate the evolution of the overall system state $|\Psi^{A+B}(t)\rangle$ under the effect of the interaction.

6.2 The model system

In order to consider a general model for a complex system with many degrees of freedom, I employ a computational algorithm developed by Enrico Nale [76] that provides energy spectrum with a partial random character on the basis of a given density of states. In the following I will briefly present the main features of his strategy as well as the main feature of the model which shall be employed.

Material systems are always characterized by a complex structure, often highlighted by the lack of symmetry elements. The precise description of these systems might be rather far from the standard Hamiltonian models such oscillators, rotators etc. and it results to be unnecessary if we are interested in the properties of only a subsystem, describe as an open system. As a matter of fact, as long as we couple a small quantum system with a thermal bath, we are not interested in reproducing a particular realization of the bath beyond its capability to exchange energy at constant temperature. Since the thermodynamics properties depends only on the energy eigenvalues regardless of the precise Hamiltonian operator expression, instead of focusing on the specification of an Hamiltonian for the system Nale has focused the attention only on the energy eigenvalues, that formally can be represented by the density of states

$$g(E) = \sum_{k=0}^{\infty} \delta(E - E_k) \quad (6.39)$$

where $\delta(\cdot)$ is the Dirac delta function.

At the same time statistical mechanics provides us typical models for the density of states which are characterized by a power law dependence on the energy

$$g(E) = \frac{C}{E_s} \left(\frac{E}{E_s} \right)^M \quad (6.40)$$

where C and M are positive and real parameters while E_s is the scaling unit of the energy. In particular if we consider ideal gases, the M exponent is proportional to the number of molecules N according to the relation $M = 3N/2$. This means that the energy levels become denser in increasing the energy.

By comparing equation (6.39) with (6.40), we realise that they are not strictly compatible since the delta Dirac is not an ordinary function. However the introduction of statistical tools describing the separation between consecutive energy levels fills the gap and provides the proper framework to connect density of states of equation (6.39) with the models of density of states eq. (6.40).

The separation between contiguous energy levels on quantum systems has been studied by Wigner [78], in the framework of complex systems without intrinsic symmetry elements. In particular he has verified, on a general ground, as the energy difference x between two consecutive levels, considered as a

stochastic variable, is characterized by the probability distribution

$$p_D(x) = \frac{\pi x}{2D^2} e^{-\frac{\pi x^2}{4D^2}} \quad (6.41)$$

where $D = \bar{x}$ is the mean value of the stochastic variable, whose variance is given as $\overline{(x - \bar{x})^2} = \frac{4-\pi}{\pi} D^2$. By introducing the difference $\Delta E_k = E_k - E_{k-1}$ between consecutive levels, it is possible to specify each allowed energy according to the previous energy

$$E_k = \sum_{m=1}^{m=k} \Delta E_m \quad (6.42)$$

Then we assume that each increment ΔE_m behaves as a stochastic variable according to the Wigner distribution (6.41) and a finite spectrum, with n levels, can be described by a joint probability density of all increments as

$$p_D^{(n)}(\delta E) = \prod_{m=1}^{m=n} p_{D_m}(\delta E) \quad (6.43)$$

where $\Delta E = (\Delta E_1, \Delta E_2, \dots, \Delta E_n)$ is the set of stochastic variables, while $D = (D_1, D_2, \dots, D_n)$ is the set of D_m parameters which determine all the Wigner distributions. The probability density on equation (6.43) allows the calculation of the mean value of any function $f(\Delta E)$ of ΔE variables

$$\overline{f^{(n)}}(\Delta E) = \int d\Delta E P_D^n(\delta E) f(\Delta E) \quad (6.44)$$

for example the mean value of E_k is given as

$$\overline{E_k} = \sum_{m=1}^{m=k} \overline{\Delta E_m} = \sum_{m=1}^{m=k} D_m \quad (6.45)$$

If we now take the mean value of the density of states of equation (6.39) with respect to the distribution (6.43), we obtain

$$\overline{g^{(n)}}(E) = \sum_k^{k=n} \overline{\delta(E - E_k)} = \sum_{k=1}^n \overline{g_k(E)} \quad (6.46)$$

where $g_k(E)$ represents the k -th contribution to the density of states

$$g_k(E) = \delta(E - E_k) \quad (6.47)$$

The mean density of states just introduced is a continuous function of energy and now it can be directly compared with the models for the density of states of material systems. The second required step is the choice of D coefficients in order to obtain an energy level sequence whose mean density of states approximates the model density of states. If the mean density of states were analytically accessible for every set of D , the optimized set of D coefficients could be in principle derived. But this is not the case and only approximate solutions are accessible by introducing appropriate constraints.

Since energy levels tend to thicken by increasing the energy, we realise that the D_m should be a decreasing function of m since it represents the mean separation between energy levels. At the same time, in order to deal with unbounded spectra it is reasonable to assume as

$$\sum_{m=1}^{\infty} D_m = \infty \quad (6.48)$$

From this assumptions, Enrico Nale [76] deduced a reasonable and quite general choice for the set D as

$$\frac{D_m}{E_s} = B \frac{1}{m^\alpha} \quad (6.49)$$

where B and α are real parameters. In particular if $0 < \alpha < 1$ the asymptotic property of equation (6.48) is satisfied. With a detailed analysis and by the proper use of a generalised form of the central limit theorem applied to each marginal distribution $p_k(E_k)$ of the energy variable E_k defined by (6.42), Enrico Nale has been able to demonstrate that these assumptions produce a mean density of states approximately described as

$$\overline{g_\alpha^n(E)} \simeq \frac{(1 - \alpha)^{\frac{\alpha}{1-\alpha}}}{B^{\frac{1}{1-\alpha}}} E^{\frac{\alpha}{1-\alpha}} \quad (6.50)$$

With a thorough comparison with equation (6.40) it is possible to relate the exponent M with $\frac{\alpha}{1-\alpha}$ while the coefficient C is inversely proportional to $B^{\frac{1}{1-\alpha}}$. Thus, the reasonable model of equation (6.49) for D_m parameters allows for the identification of α and B parameters that give rise to the desired density

of states. In particular in the following we will use $B = 1$ and $\alpha = 0.6$. This allows the sampling of Wigner distribution in order to obtain the energy spectra for our simulations.

6.3 Simple Interaction Hamiltonian

The next important information in order to perform a quantum dynamical experiment of thermalization concerns the form of interaction Hamiltonian \hat{H}^{int} . We are going to consider separately two different kinds of operators. Both are characterized by a partially random character in order to maintain as general as possible the results we are going to obtain. As a matter of fact the equilibration due to thermal exchange happens in a large set of physical situations and it is independent of the detailed form of the interaction.

In general the interaction between quantum systems is characterized by the presence of non-zero off-diagonal matrix elements whose contributions on the interaction increases with the interaction strength, controlled by the parameter λ_{int} . The general feature of the interaction is that of mixing all the states of the overall system deriving from the product of the energy states of initially isolated systems. If we consider common and reasonable situations, the mixing is likely to be proportional to the energy difference between two states such that a larger mixing is obtained when their energies are closer. Thus, we can analyse the limit case of the interaction with vanishing strength which results to be effective only between first neighbours and, in the particular cases when a two fold degeneracy is present, as in our model system, the interaction has the only role of removing the degeneracy on the overall system. Such an Hamiltonian can be specified in the form

$$\begin{aligned} \hat{H}^{int} = \widehat{W} = \sum_k \sum_{k' > k} & \left[(|E_k^A\rangle |E_{k'}^B\rangle) w_{kk'} (\langle E_{k'}^A| \langle E_k^B|) + \right. \\ & \left. + (|E_{k'}^A\rangle |E_k^B\rangle) w_{kk'}^* (\langle E_k^A| \langle E_{k'}^B|) \right] \end{aligned} \quad (6.51)$$

where $w_{kk'}$ is a generic complex element of the interaction matrix

$$w_{kk'} = \langle E_k^A | \langle E_{k'}^B | \hat{H}^{int} | E_{k'}^A \rangle | E_k^B \rangle \quad (6.52)$$

and where the diagonal elements $k = k'$ are set to zero in order to avoid a shift

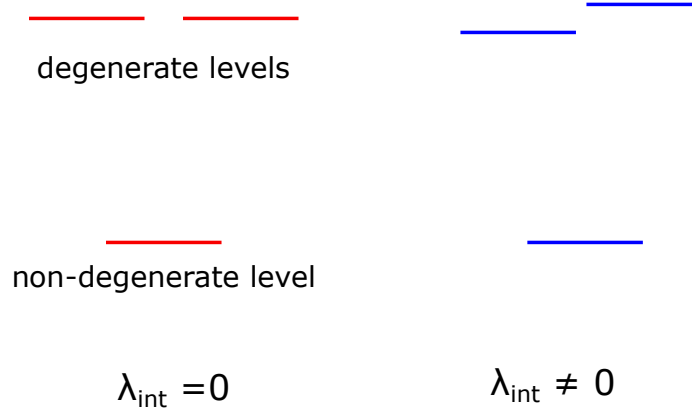


Figure 6.1: schematic representation of the interaction effect acting only on degenerate energy levels. The removal of degeneracy is provided whatever is the interaction strength λ_{int} .

on the energy scale for the global system. The resulting global Hamiltonian matrix $\hat{H}_{t>0}^{A+B}$ is a block-diagonal matrix and its diagonalization can be performed on each (2×2) -blocks specified by a pair of indexes $k < k'$ and written as

$$\begin{pmatrix} E_k^A + E_{k'}^B & w_{kk'} \\ w_{k'k}^* & E_{k'}^A + E_k^B \end{pmatrix} \quad (6.53)$$

leading to new the eigenvalues

$$E_j^{A+B} = E_k^A + E_{k'}^B - |w_{k,k'}| \quad (6.54)$$

$$E_{j'}^{A+B} = E_k^A + E_{k'}^B + |w_{k,k'}| \quad (6.55)$$

where we have introduced the cumulative indexes $j := (k, k')$ and $j' := (k', k)$. Then the new eigenvalues are obtained from the unperturbed ones by including an opposite shift determined by the strength of the interaction. Correspondingly the new eigenvectors are

$$|E_j^{A+B}\rangle = \frac{1}{\sqrt{2}} \left(|E_k^A\rangle |E_{k'}^B\rangle - \frac{w_{k,k'}}{|w_{k,k'}|} |E_{k'}^A\rangle |E_k^B\rangle \right) \quad (6.56)$$

$$|E_{j'}^{A+B}\rangle = \frac{1}{\sqrt{2}} \left(|E_k^A\rangle |E_{k'}^B\rangle + \frac{w_{k,k'}}{|w_{k,k'}|} |E_{k'}^A\rangle |E_k^B\rangle \right) \quad (6.57)$$

From this eigenvectors it is possible to notice as an increasing interaction strength does not produce a change of the eigenvectors directions but only of their eigenvalues. As a matter of fact the multiplicative factor λ_{int} would

modify the modulus of $w_{kk'}$ that, in turn, influences only the eigenvalue without having effects on the resulting eigenvectors.

We recall that the interaction Hamiltonian (6.51) does not modify the non-degenerate eigenvectors which are denoted as

$$|E_j\rangle = |E_k^A\rangle |E_k^B\rangle \quad (6.58)$$

with the cumulative index $j := (k, k)$. From the eigenvectors and the eigenvalues of the total Hamiltonian $\hat{H}_{>}^{A+B}$ after the interaction, it is possible to describe both the dynamical properties and the equilibrium ones of the overall system as well as the dynamical and equilibrium properties of its subsystems. In the following an analytical investigation will demonstrate as the equilibrium value for the subsystem energy coincides with the arithmetic mean energy of the systems before they are brought into contact, independently of the strength of the interaction Hamiltonian.

6.3.1 Subsystem equilibrium properties: an analytical investigation

The particular form of the interaction Hamiltonian allows the analytical calculation of the new eigenvectors and eigenvalues of the problem. Once the new principal directions are provided, it is possible to compute all the system properties as well as the properties of each subsystem. As already discussed, one of the most interesting property in order to follow the thermalization experiment is the energy of each subsystem, which can be associated with the energy flux. Before describing its dynamical evolution, we are interested in to its equilibrium value after that the interaction has taken place. In the following, by the use of the population definition (6.30) and by using the results of the previous paragraph, I will shows as the interaction, independently of its strength, produces an equilibrium where the two subsystems have exactly the same energy. This section is rather technical but demonstrates as the previous definitions can be practically used in a simple case.

I start by using the definition of subsystem equilibrium energy of equation

(6.32) as

$$\overline{E}_>^A = \sum_{k,k'} P_{k,k'}^{A+B} \langle E_{k,k'}^{A+B} | \hat{H}^A \otimes \mathbb{1}^B | E_{k,k'}^{A+B} \rangle \quad (6.59)$$

$$\begin{aligned} &= \sum_k P_{k,k} \langle E_{k,k}^{A+B} | \hat{H}^A \otimes \mathbb{1}^B | E_{k,k}^{A+B} \rangle + \\ &+ \sum_k \sum_{k'>k} \left[P_{k,k'}^{A+B} \langle E_{k,k'}^{A+B} | \hat{H}^A \otimes \mathbb{1}^B | E_{k,k'}^{A+B} \rangle + \right. \\ &\quad \left. + P_{k',k}^{A+B} \langle E_{k',k}^{A+B} | \hat{H}^A \otimes \mathbb{1}^B | E_{k',k}^{A+B} \rangle \right] \end{aligned} \quad (6.60)$$

where in the last equality we have separated the contributions of the non-degenerate energy levels, those which are not influenced by the interaction, from the contributions deriving from the two-fold initially degenerate levels. If we now combine equation (6.60) with the explicit expression of eigenvectors of equations (6.56) and (6.57), we obtain

$$\overline{E}_>^A = \sum_k P_{k,k}^{A+B} E_k^A + \frac{1}{2} \sum_k \sum_{k'>k} (P_{k,k'}^{A+B} + P_{k',k}^{A+B}) (E_k^A + E_{k'}^A) \quad (6.61)$$

that can be equivalently expressed as

$$\overline{E}_>^A = \sum_k P_{kk}^{A+B} E_k^A + \frac{1}{4} \sum_k \sum_{k' \neq k} (P_{kk'}^{A+B} + P_{k',k}^{A+B}) (E_k^A + E_{k'}^A) \quad (6.62)$$

by changing the domains of the summations indexes. The subsystem energy is expressed in function of the global populations P_j^{A+B} of the system in the bases of $|E_j^{A+B}\rangle$ eigenvectors and in function of the eigenvalues E_k^A of the subsystem A at $t < 0$.

The evaluation of the P_j^{A+B} populations allows us to easily compute the equilibrium value for the subsystem energy after the thermalization process. From the definition (6.26) and by the use of equations (6.56), (6.57) and (6.58) we obtain

$$P_{k,k}^{A+B} = \left| \langle \langle E_k^A | \langle E_k^B | \rangle | \Psi^A(0) \rangle | \Psi^B(0) \rangle \right|^2 = P_k^A P_k^B \quad (6.63)$$

$$P_{k,k'}^{A+B} = \left| \langle \langle E_k^A | \langle E_{k'}^B | - \frac{w_{kk'}}{|w_{kk'}|} \langle E_{k'}^A | \langle E_k^B | \rangle | \Psi^A(0) \rangle | \Psi^B(0) \rangle \right|^2 \quad (6.64)$$

$$P_{k',k}^{A+B} = \left| \langle \langle E_k^A | \langle E_{k'}^B | + \frac{w_{kk'}}{|w_{kk'}|} \langle E_{k'}^A | \langle E_k^B | \rangle | \Psi^A(0) \rangle | \Psi^B(0) \rangle \right|^2 \quad (6.65)$$

and then

$$P_{k,k'}^{A+B} + P_{k',k}^{A+B} = \left| \langle \langle E_k^A | \langle E_{k'}^B | \rangle | \Psi^A(0) \rangle | \Psi^B(0) \rangle \right|^2 + \left| \langle \langle E_{k'}^A | \langle E_k^B | \rangle | \Psi^A(0) \rangle | \Psi^B(0) \rangle \right|^2 \quad (6.66)$$

$$= P_k^A P_{k'}^B + P_{k'}^A P_k^B \quad (6.67)$$

and finally the equilibrium value $\bar{E}_>^A$ of the energy of the subsystem A can be computed as

$$\bar{E}_>^A = \sum_k P_k^A P_k^B E_k^A + \frac{1}{4} \sum_k \sum_{k' \neq k} (P_k^A P_{k'}^B + P_{k'}^B P_k^A) (E_k^A + E_{k'}^A) \quad (6.68)$$

$$= \frac{1}{4} \sum_k \sum_{k'} (P_k^A P_{k'}^B + P_{k'}^B P_k^A) (E_k^A + E_{k'}^A) \quad (6.69)$$

$$= \frac{1}{2} \sum_k P_k^A E_k^A + \frac{1}{2} \sum_k P_k^B E_k^B = \frac{E_{<}^A + E_{<}^B}{2} \quad (6.70)$$

The equilibrium energy of a subsystem is the mean value of the energies at $t < 0$. The energy flux from the hotter body to the colder one produces, on the average, the same value for the energy on both subsystems.

$$\bar{E}_>^A = \bar{E}_>^B = \frac{E_{<}^A + E_{<}^B}{2} \quad (6.71)$$

This represents a very important result. As a matter of fact, in the presence of an interaction Hamiltonian, whose effect is that of eliminating the two-fold degeneracy, any single realization of the quantum system produces the thermal equilibrium where the two subsystems equilibrate their energy exactly to the same value, obtaining an equipartition on the energy. It is important to stress that this result holds whatever the interaction strength is, provided that it has the only effect of eliminating the degeneration.

6.3.2 The thermalization experiment

The analytic investigation has been integrated by computer simulations. The first issue that arises in these simulations is about the dimension of the systems that are manageable in the available computer, taking into account both the accessible memory and the requirements of computational time. I have considered 80 eigenstates for each isolated system, that means a total Hilbert

space $\mathcal{H}^{A+B} = \mathcal{H}^A \otimes \mathcal{H}^B$ with a dimension of 6400, with operators in general represented by matrices with 6400×6400 elements. This dimension is not far from the maximum dimension computable in the workstation available for this work with 8 GB of RAM. Even if it is a moderate dimension, it is equally able to show the most important features of the thermalization experiment and it enables us to have a first insight on this very interesting phenomenon. As already discussed at the end of paragraph 6.1, we need to specify the energy spectrum of the isolated system, the interaction Hamiltonian and the initial state for the time evolution in order to perform the simulations of the thermalization experiment.

The spectrum of the model systems is obtained by means of the algorithm developed by Enrico Nale [76] and described in paragraph 6.2, that allows to sample the energy spectrum of a system from a given density of states. In our particular case the two systems have an identical energy spectrum and only one sampling has to be performed. The simulation reported here represents a typical case where the model parameters are $B = 1$ and $\alpha = 0.6$. It produces a spectrum (shown in Figure 6.2) that tightens with the increasing of energy as expected for real molecular systems. The overall spectrum for $t < 0$ is described by the eigenvalues of the product of the eigenstates $|E_k^A\rangle |E_k^B\rangle$ with a two-fold degeneration if $k \neq k'$.

The interaction Hamiltonian removes the degeneration with a strength factor of $\lambda_{int} = 10^{-2}$ to guarantee that the interaction is perturbative. In particular, the perturbativity \mathcal{P}_{int} has been quantified as

$$\mathcal{P}_{int} = \frac{E^{A+B} - E^A - E^B}{E^A + E^B} = 2.22 \cdot 10^{-4} \quad (6.72)$$

Notice that the parameter \mathcal{P}_{int} is equal to zero if the perturbation has no effect and is equal to one when the interaction energy has the order of magnitude the energies of the two systems.

The dynamics of the wave function is then computed as solution of Schrödinger equation (2.3) with the use of two different Hamiltonians for the two time domains

$$\begin{array}{ll} \text{for } t \leq 0 & H_{t < 0}^{A+B} \\ \text{for } t > 0 & H_{t > 0}^{A+B} \end{array}$$

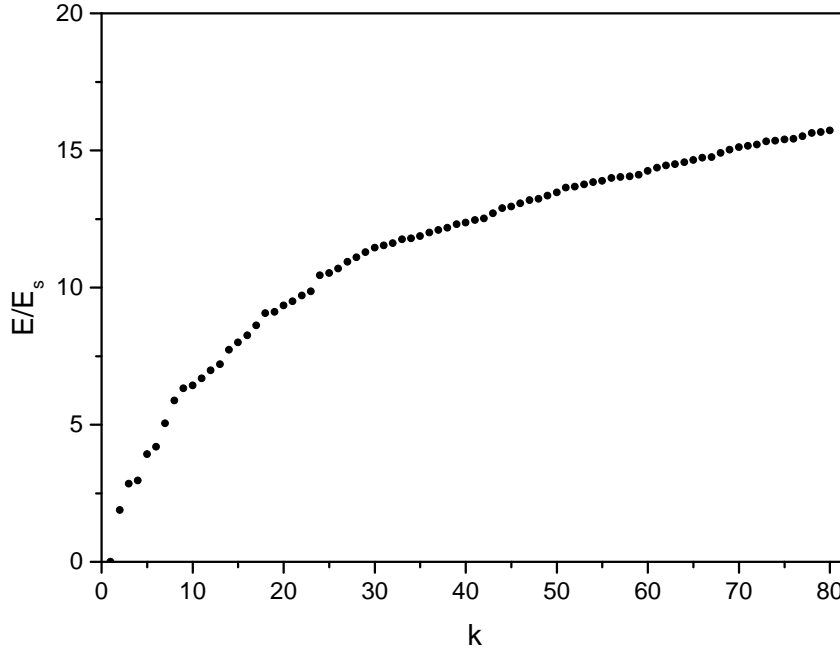


Figure 6.2: The energy spectrum for both systems A and B is shown. The abscissa axes counts the eigenstates with energy represented in the ordinata axes. The energy difference between first neighbours decreases as the energy increases, as expected for real systems.

where $H_{t<0}^{A+B}$ and $H_{t>0}^{A+B}$ are (6.15) and (6.18) respectively.

The initial wave function is chosen according to (6.17), that in turn derives from equations (6.10) and (6.11). The initial phases $\alpha_k^A(t)$ and $\alpha_k^B(t)$ are randomly sampled according to the uniform probability distribution $p(\alpha)$ (4.44), while populations are sampled from TRE statistics by the use of the algorithm described in the previous chapter. In particular, two different thermal parameters are introduced to characterize the two initial systems $\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$. I wish to point out that the selection of the inverse temperature is constrained by the number of states used in the simulation. Indeed the lowering of the thermal parameter implies an higher quantum temperature so that the population is spread out on eigenvectors with higher energy. Since the finiteness of the system is only a practical need, we want to perform simulations where the excluded states do not influence the properties of the system we observe. In order to reach such an objective we use inverse temperature parameters such that the excluded states have negligible energy density. It corresponds to neglect eigenstates with such a lower population that does not

influence the overall properties of the system. The lower thermal parameter ζ^A has been selected on the bases of the Gaussian approximation of the energy density (3.43), the maximum energy eigenvalues $E_{k_{max}}$ is set to coincide with the maximum of the Gaussian profile incremented by three times the gaussian variance (see equation (3.44)), leading to a thermal parameter

$$\zeta_{lim} = \frac{M + 3\sqrt{M}}{E_{k_{max}}} \quad (6.73)$$

All the simulations have been performed with $\zeta^A, \zeta^B > \zeta_{lim}$.

As an alternative procedure one could have performed simulations for the identical physical state by increasing the system dimensions. Then, if the properties are not influenced by this operation we can state that the leading contribution for the population is already included in the lower dimensional Hilbert space.

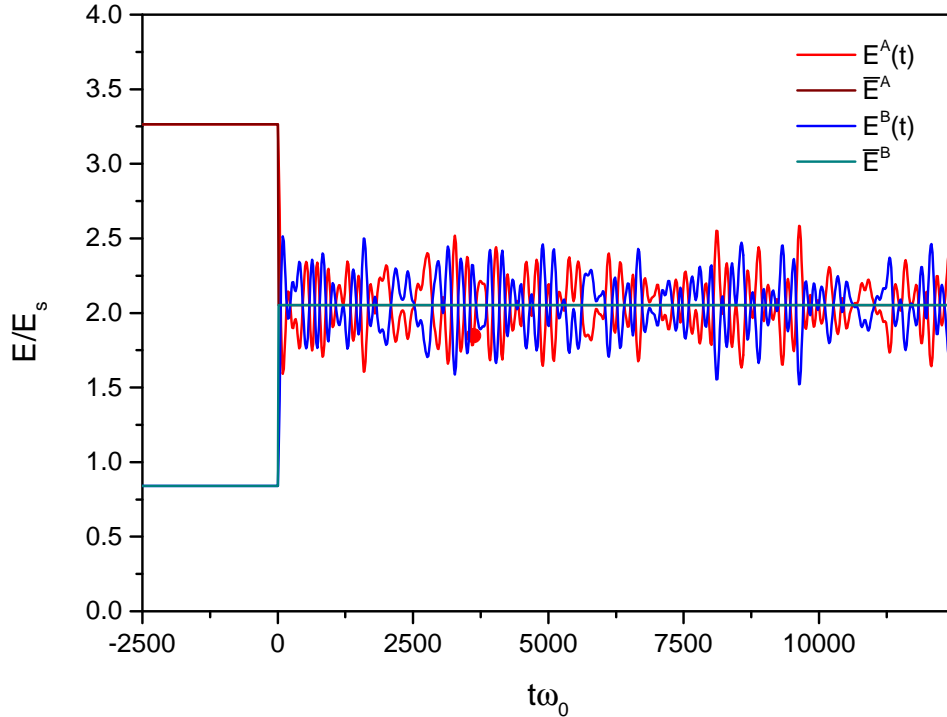


Figure 6.3: The subsystems energy $E^A(t)$ (red line) and $E^B(t)$ (blue line) are shown in function of time, different thermal parameters for the systems are selected, $\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$ respectively. Both energies fluctuate around the same equilibrium value. The equilibrium energy \bar{E}^A and \bar{E}^B are presented as well.

At the beginning of the simulation, no energy exchange is detectable until

the interaction brings the two systems in contact so that they are no longer isolated. The evolution due the thermalization is depicted in Figure 6.3 where it is possible to observe as the subsystem energies, $E^A(t)$ and $E^B(t)$, are constant in the absence of interaction and then, for $t > 0$, the subsystems exchange their energies and equilibrate to an average value, around which they start to fluctuate. Figure 6.3 shows also the equilibrium values for the energy of the subsystems \bar{E}^A and \bar{E}^B , computed as infinite time average. It can be noticed as the equilibrium values of the energies are equal for both subsystems, as the analytic investigation has demonstrated. The hotter body releases energy to the colder one until they reach, on average, the same energy. The relaxation dynamics can be better observed at shorter time scales as reported in Figure 6.4.

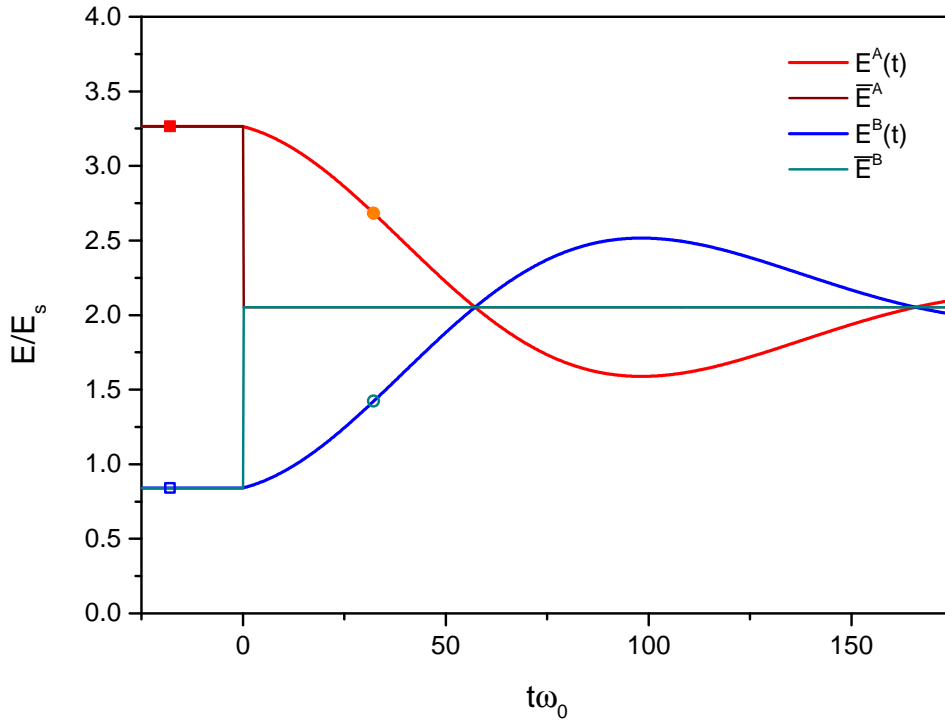


Figure 6.4: The dynamics of relaxation is shown as a zoom of Figure 6.3. In red is reported the energy $E^A(t)$ of the subsystem A, while the blue line represents the energy $E^B(t)$ of the subsystem B. The markers (square and circles) refers to the two times employed in Figure 6.5a.

The energy changes are determined by a redistribution of the reduced populations on both systems. The reduced populations are no longer constant

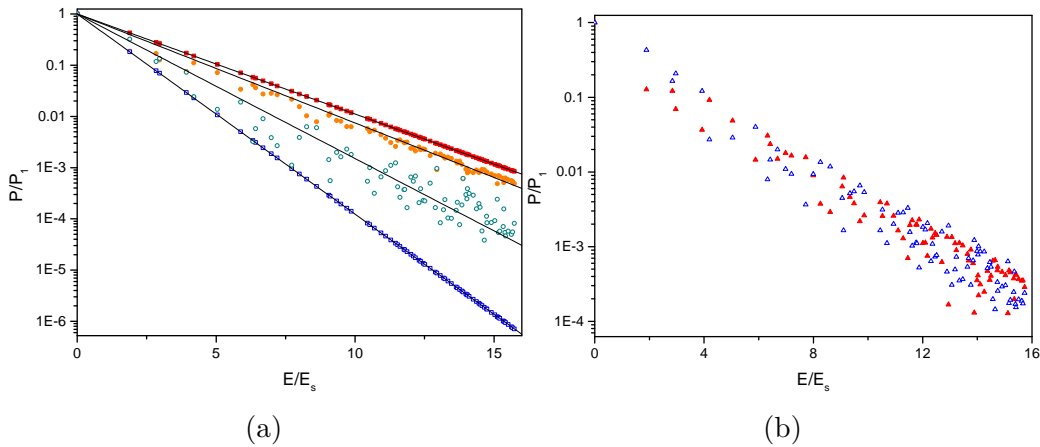


Figure 6.5: the reduced populations are reported for different times. (a) The time instants are marked by the corresponding symbols in Figure 6.4. The black lines are reported only to guide the eye. The two times correspond to situations before the interaction has been considered and during the relaxation time respectively; (b) a generic time after the relaxation is reported, system A is in red and B in blue

of motion and they show an explicit time dependence. As one see from Figure 6.5a, where reduced populations are plotted against energy levels at two different times, the reduced populations varies in function of time until they reach the equilibrium state (Figure 6.5b).

In order to simplify the visualization I have selected the typical case when the starting populations are exactly at their average values. This can be noticed in Figure 6.5a where the initial populations, denoted by red and blue squares for systems A and B respectively, lie on a line forming a scissor-type graph (notice the log scale of ordinate axes). During the relaxation period the populations redistribute and the scissor starts to close. At the end of the equilibration, the populations are gathered around a value that can be referred to the average thermal state.

The time dependence of the reduced populations determines the fluctuations of the energy of the subsystems. The equilibration is driven by the equipartition of energy [63] reached when the two systems are in the same thermal state.

The same type of results are obtained for any interaction strength λ_{int} due to the specific form of the interaction Hamiltonian \hat{H}^{int} . The major effect of the coupling strength (not reported here) is that of modifying the quantum dynamics such that a faster relaxation is recovered when stronger interaction

is considered.

Let us now analyse in detail the equilibrium state. As we have already discussed, the equilibrium value for the energy is the same for the two subsystems. However this does not provide us any information about their energy distribution. In order to characterize the equilibrium values of the reduced population within the thermalization resilient ensemble, I have compared their ensemble average with the populations that we expect from the TRE statistical ensemble, by supposing that the equilibrium is characterized by an average thermal parameter ζ^{A+B} defined as

$$T_Q^{A+B} = \frac{T_Q^A + T_Q^B}{2} = \frac{1}{2\zeta^A} + \frac{1}{2\zeta^B} = \frac{1}{\zeta^{A+B}} \quad (6.74)$$

Such a comparison is obtained by defining a distance parameter as

$$\mathcal{D}_{TRE} = \sum_k |\langle P_k \rangle_{\zeta^{A+B}} - \langle \bar{P}_k^A \rangle| \quad (6.75)$$

where $\langle P_k \rangle_{\zeta^{A+B}}$ is the average of the k -th population of TRE ensemble with a thermal state ζ^{A+B} and $\langle \bar{P}_k^A \rangle$ is the ensemble average of the equilibrium reduced population computed on a sample of $5 \cdot 10^3$ points. Once the Hamiltonian is provided, from any initial state I have computed the equilibrium values of each population, as infinite time average, and then I have calculated its mean in the sample. Different thermal parameters have been considered and the results are summarised in Figure 6.6, where the values of \mathcal{D}_{TRE} are reported for different rates ζ_B/ζ_A is shown, for fixed value $\zeta^A = 0.45/E_s$.

The distance between the TRE ensemble averages for the populations and their equilibrium value after the thermalization experiment increases for higher ratios of the thermal parameters. This is expected for the thermalization resilient ensemble since it is not strictly invariant with respect the interaction but only robust enough. The result is perfectly in agreement with that of Figure 3.10, with the important difference that here we are considering a realistic representation of a quantum system with a discrete energy. In conclusion, the TRE ensemble has shown once again its robustness with respect the interaction between systems with very large differences in their thermal states, so demonstrating as it can be a valid ensemble in the description of quantum pure states.

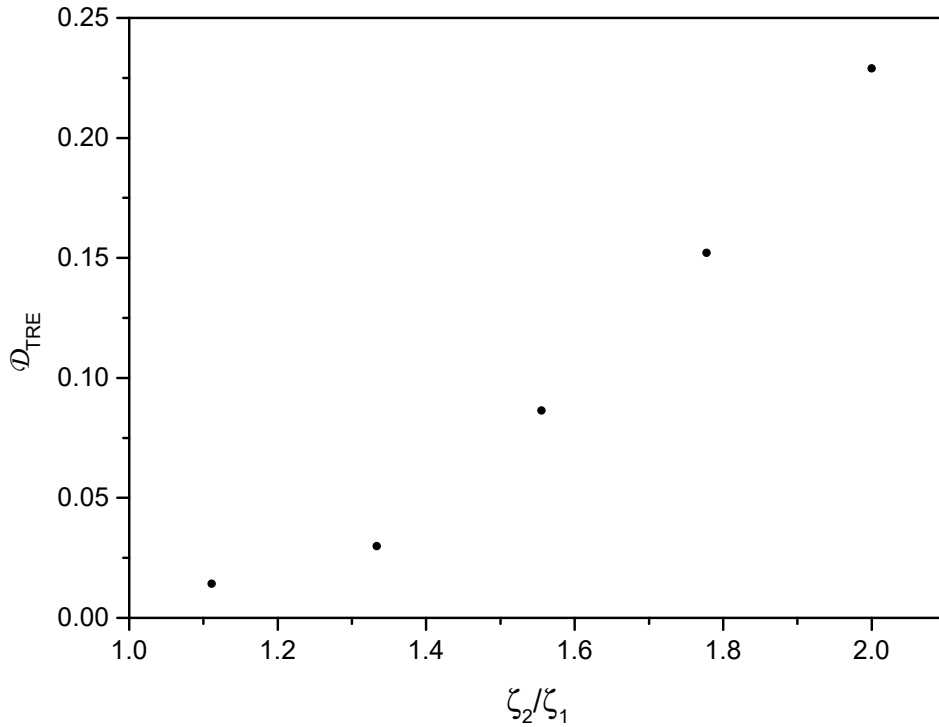


Figure 6.6: The distance between ensemble average of equilibrium reduced populations and the canonical populations (equation (6.75)) is reported, for different ratios of inverse temperatures ζ^B/ζ^A and fixed $\zeta^A = 0.45/E_s$. The canonical populations are computed at the mean temperature $T^{A+B} = \frac{1}{\zeta^{A+B}} = \frac{1}{2} \left(\frac{1}{\zeta^A} + \frac{1}{\zeta^B} \right)$

This simple model for the interaction Hamiltonian has been also very useful in order to demonstrate the feasibility of a full quantum dynamical simulation of model systems. It has also shown the robustness of TRE ensemble in a large domain of thermal states. However more general laws of the interaction Hamiltonian need to be considered for a realistic simulation. As a matter of fact the interaction that only removes the degeneracy is a limit situation that can not exhaustively describe molecular systems.

6.4 A more general interaction: Random Matrix

The previous sections have been focused on the analysis of a simple realization of the interaction between two identical systems, that allows energy exchange between degenerate energy levels and guarantees the same equilibrium energy for both subsystems. We are going now to consider a more general interaction beyond the simple removal of the degeneration by allowing the energy exchange between more than two eigenstates. Such an objective can be achieved by the use of a random matrix where elements mix all the energy eigenstates. We assume that the interaction Hamiltonian is lacking of the self interaction contributions

$$\begin{aligned} (\langle E_{k'A}^A | \langle E_{k'B}^B | \hat{H}^{int} (|E_{k''A}^A \rangle |E_{k'B}^B \rangle) &= 0 \\ (\langle E_{k'A}^A | \langle E_{k'B}^B | \hat{H}^{int} (|E_{k'A}^A \rangle |E_{k''B}^B \rangle) &= 0 \end{aligned} \quad \forall k, k', k''$$

In fact we wanted to consider only those contributions that produce a mixing of different states by avoiding contributions due to self interactions that have no physical meaning. In addition, since the two systems are identical, it is natural to assume in the interaction Hamiltonian the same type of symmetry

$$\langle E_{k'A}^A | \langle E_{k'B}^B | \hat{H}^{int} |E_{k''A}^A \rangle |E_{k'''B}^B \rangle = \langle E_{k'A}^A | \langle E_{k'B}^B | \hat{H}^{int} |E_{k''A}^A \rangle |E_{k'''B}^B \rangle \quad (6.76)$$

This would not be guaranteed if a generic interaction matrix with a random character is employed. The use of a random matrix excludes analytical investigation and only simulations through an exact diagonalization can be performed in order to study the thermalization experiment on a general ground.

The simulations we are going to discuss, as in the previous paragraph, are about two finite systems (80 eigenstates) with identical energy spectrum that at $t = 0$ are brought into contact. Different Hamiltonian strengths will be considered in the following, parametrized by λ_{int} coupling constant. The first interesting difference with respect to the previous simple Hamiltonian can be noticed in Figure 6.7 for a typical wave function, where the dynamics of the subsystem energies equilibration, $E^A(t)$ and $E^B(t)$ (fluctuating profiles), as well as their equilibrium values (straight lines), are shown in four different coupling strength conditions. The equilibrium of a single realization does not

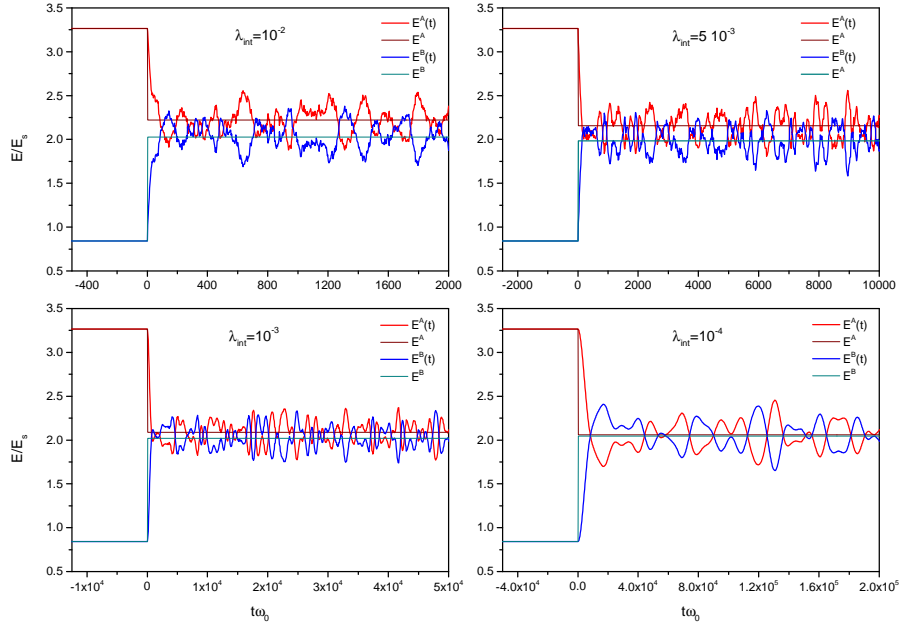


Figure 6.7: Typical equilibration of the subsystems energies for different strengths of interaction Hamiltonian, $\lambda = 10^{-2}$ left-top panel, $\lambda_{int} = 5 \cdot 10^{-3}$ right-top, $\lambda_{int} = 10^{-3}$ bottom-left and $\lambda_{int} = 10^{-4}$ bottom-right. In each graph the equilibrium value of subsystem energies are reported as well. The thermal parameter for the statistical sampling is $\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$.

guarantees the equidistribution of the subsystems energies to an equal value for both subsystems. In particular, by going from the strongest interaction (top-left panel) to the weaker one (bottom-right panel), we can notice that, as long as the λ_{int} parameter decreases, the equilibrium values for the subsystem energy (straight lines) tend to get closer. The proximity can be quantified by a mean distance parameter $D_{E_m, (\bar{E}^A, \bar{E}^B)}$ between average energy ($E_m = \frac{E_{t<0}^A + E_{t<0}^B}{2}$) and both subsystem equilibrium energies \bar{E}^A and \bar{E}^B of the two subsystems which is defined as

$$D_{E_m, (\bar{E}^A, \bar{E}^B)} = \frac{|E_m - \bar{E}^A| + |E_m - \bar{E}^B|}{2} \quad (6.77)$$

This parameter, is reported in Figure 6.8 for different interaction strengths.

It can be noticed that as long as the interaction decreases, the distance $D_{E_m, (\bar{E}^A, \bar{E}^B)}$ approaches to zero. As a matter of fact, we get closer to the limit situation where the interaction is effective only between eigenvectors with the same energy, the case we have analysed in the previous section.

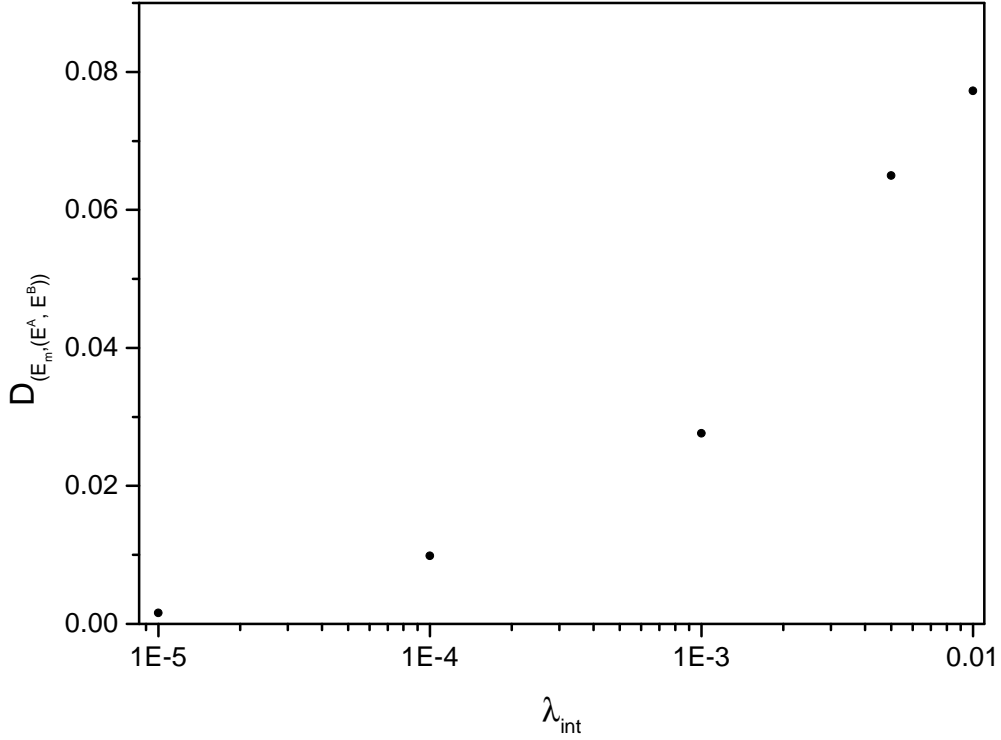


Figure 6.8: The distance $D_{E_m,(\bar{E}^A, \bar{E}^B)}$, defined in the main text, is reported for different interaction strengths λ_{int} .

If we look carefully to panel *a* of figure 6.7, in particular to the mean of equilibrium energies, we can understand as that interaction cannot be considered as perturbative since one can clearly detect a variation with respect to the same mean before the interaction. However this does not modify our considerations on the thermalization experiment with this general Hamiltonian model and it can be considered as an example where the weak coupling limit hypothesis is no more fully satisfied. For the sake of completeness and in order to quantify the strength of the interaction I report here the perturbativity \mathcal{P}_{int} (equation (6.72)) for all the considered cases.

	$\lambda_{int} = 10^{-2}$	$\lambda_{int} = 5 \cdot 10^{-3}$	$\lambda_{int} = 2 \cdot 10^{-3}$	$\lambda_{int} = 10^{-3}$	$\lambda_{int} = 10^{-4}$
\mathcal{P}_{int}	$2.2 \cdot 10^{-3}$	$3.65 \cdot 10^{-4}$	$3.15 \cdot 10^{-4}$	$2.43 \cdot 10^{-5}$	$4.81 \cdot 10^{-6}$

The macroscopic interpretation of this experiment would lead naturally to an equilibrium characterized by the same energy for both subsystems. If we bring two identical macroscopic bodies at different temperatures to interact

afterwards we separate them, according to the classical thermodynamics we expect the same internal energy for both of them. However no a priori law guarantees that microscopic complex systems behaves exactly as the macroscopic ones. As a matter of fact, the emergence of thermodynamic behaviour of the TRE ensemble has been demonstrated only in the macroscopic limit of the quantum system through the analysis of distributions within the ensemble such that, once a property manifests typicality, it can be considered as representative for every realization.

A property is said to be typical when different realizations of the quantum systems behaves similarly as far as the property is concerned. However our system is not in this condition as shown in Figure 6.9 where the ensemble average of subsystems equilibrium energies, from a sample of 5000 cases, is reported together with some of these realizations, for two different interaction strengths, $\lambda_{int} = 10^{-2}$ (top panel) and $\lambda_{int} = 10^{-3}$ (bottom panel).

The presence of large fluctuations between different realizations it is immediately evident and it is reasonably caused by the limited dimensions of the Hilbert spaces for the two initially isolated systems. Further analyses on larger systems are needed in order to validate this conclusion.

Contrary to what expected from a macroscopic description of material systems that follows the laws of thermodynamics, single realizations of microscopic quantum systems, even if described with many eigenstates, do not equilibrate exactly to the same energy for both subsystem, but this does not mean that equilibrium condition is not reached for the property energy. We suggest that equilibrium condition should not be examined on the ground of the single realizations but it should be defined in a statistical sense within the intrinsic variability of the ensemble of wave functions (pure states). Two systems, after that the interaction allows them to exchange energy, equilibrate if the equilibrium energies are within the ensemble variance, in order to guarantee the equilibration also in the random matrix interaction models. The possibility to define a statistical equilibrium has its origin on explicit definition of a statistical ensemble for the wave function and it represents one of the novelty elements of the present approach. Without the knowledge of the behaviour of different realizations of a quantum systems, the equilibrium can be studied clearly from the comparison between subsystems energies and from the distance from the canonical subsystem density matrix. As we have shown here,

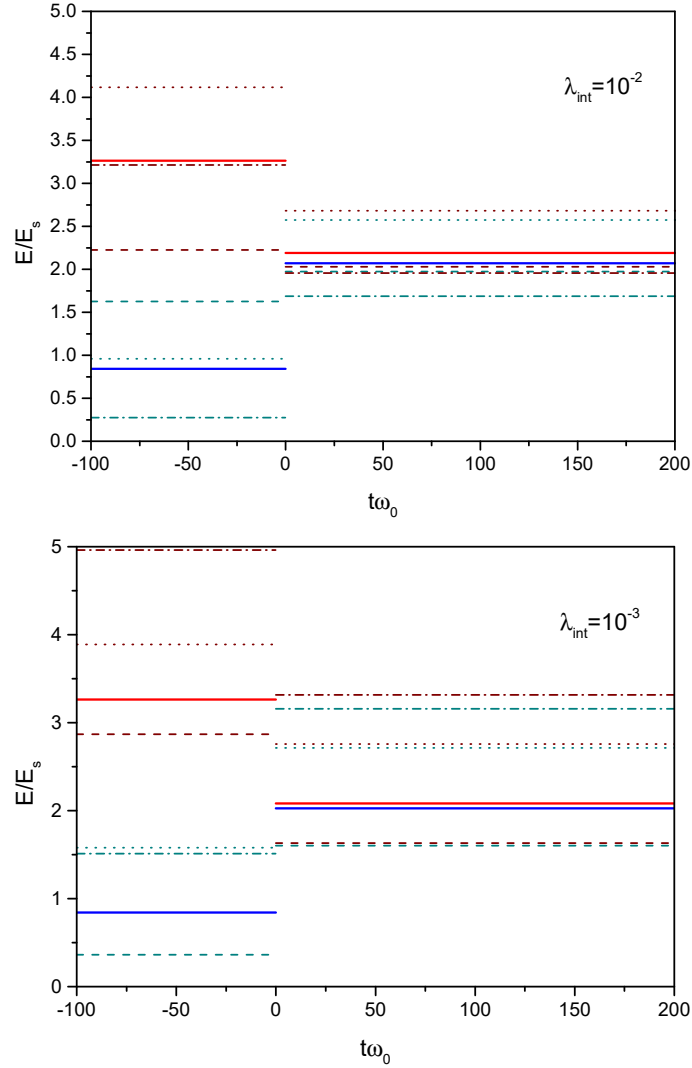


Figure 6.9: ensemble average of equilibrium subsystem energies ($\langle E^A \rangle$ red lines and $\langle E^B \rangle$ blue lines), before and after the introduction of the interaction term ($t = 0$), are shown in two different realizations of the interaction Hamiltonian, $\lambda_{int} = 10^{-2}$ and $\lambda_{int} = 10^{-3}$ on the top and bottom panel, respectively. The ensemble average is computed on a sample of $5 \cdot 10^3$ point. The additional dashed lines refers to energies related to examples of single realizations of the quantum systems. The thermal parameters for the two systems are $\zeta^A = 0.45/E_s$ and $\zeta_B = 0.9/E_s$.

the equilibrium definition on the basis of the subsystem energies can be misleading since only the most simple structure of interaction Hamiltonian can lead to the same type of equilibrium of macroscopic thermodynamics. This new perspective on quantum equilibration is rather intriguing to me and it can provide new insights to the experiment on energy exchange, very common at

the molecular level.

Within this model it is also possible to investigate the role of the interaction strength λ_{int} on the dynamics of the equilibration. For instance, Figure 6.10

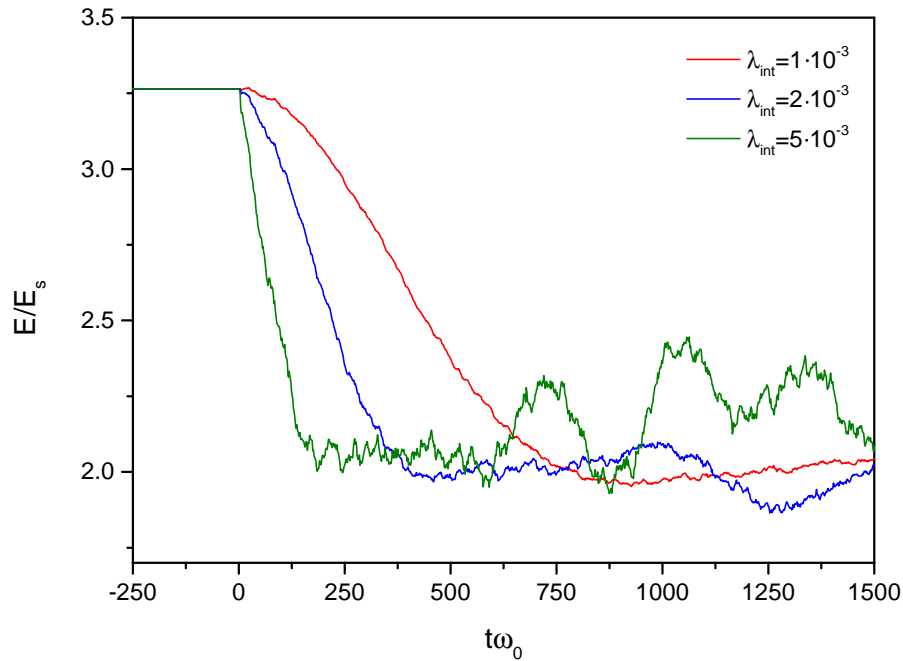


Figure 6.10: The effect of different interaction strengths is shown on the equilibration of the subsystem energy $E^A(t)$, for a single typical realization of a quantum state where $\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$

shows how the dynamics of the subsystem energy $E^A(t)$, deriving from the same sampled wave function ($\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$), in different conditions of interaction strength. It can be noticed that the relaxation toward the equilibrium values is faster by increasing the strength of the interaction.

6.5 From Schrödinger evolution to entropy production

In the so called *thermalization* experiment we bring in interaction two different bodies, initially characterized by different temperatures. Our realization of this kind of experiment considers two identical quantum systems, representing our bodies, which initial wave function is sampled within the Thermalization Resilient Ensemble, fully specified by the thermal parameter ζ , the quantum analogue of the inverse of macroscopic temperature. This quantum experiment, as well as its thermodynamic correspondent, generates a energy flux from the hottest system to the colder one. Thermodynamic theory describes such a process as an irreversible process of an isolated system with a correspondingly increase of the entropy. We can observe the same behaviour from

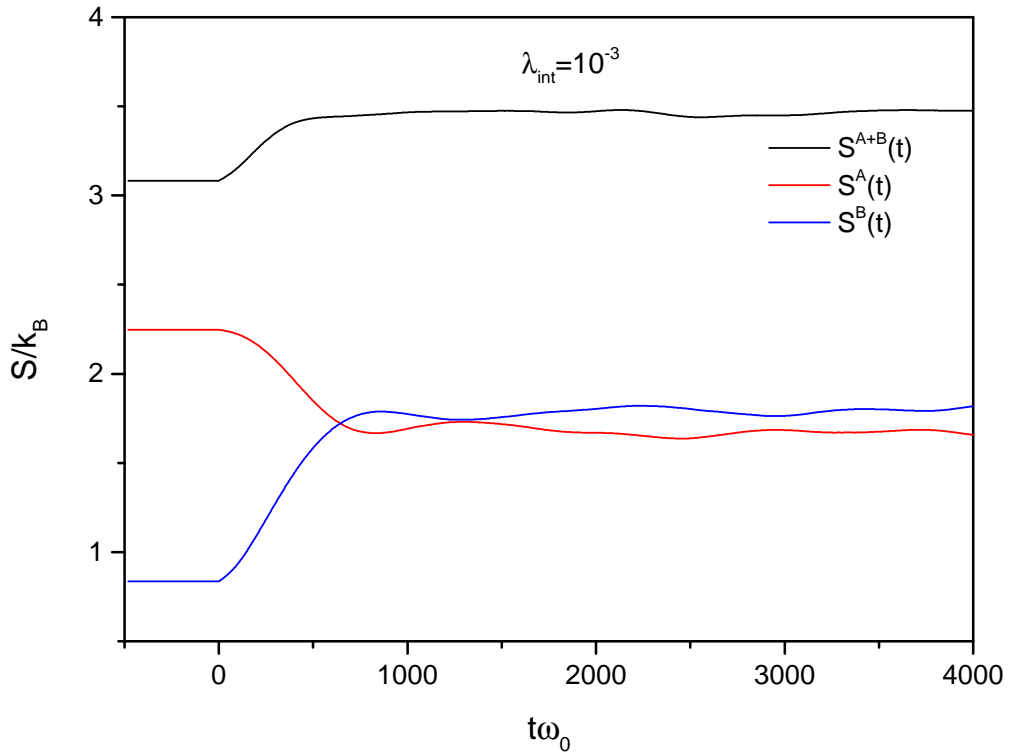


Figure 6.11: ensemble averages of subsystem entropies $S^A(t)$ and $S^B(t)$ are reported during a thermalization experiment. The ensemble average is computed on a sample of $5 \cdot 10^3$ wave functions from distributions characterised by $\zeta^A = 0.45/E_s$ and $\zeta^B = 0.9/E_s$. The interaction strength is $\lambda_{int} = 10^{-3}$.

the quantum dynamics by leading to the microscopic entropy defined on the basis of ensemble average of Shannon entropy on populations

$$S^A(t) = -k_B \sum_k \langle P_k^A(t) \ln P_k^A(t) \rangle \quad (6.78)$$

where the ensemble average can be obtained with a Montecarlo sampling. A similar relation can be written for the subsystem B . In Figure 6.11 I have reported the entropy evolution for the two subsystems as well as the entropy of the overall system $S^{A+B}(t)$ accounted by the summation of the two separated entropies

$$S^{A+B}(t) = S^A(t) + S^B(t) \quad (6.79)$$

One can clearly see that the equilibration produces an increase of the overall entropy as expected from thermodynamics. Thus we can state that the thermalization experiment is characterized by an increasing on the total entropy also at the quantum level. It represent a very interesting result that shows how entropy production can be considered as a driving force also at the quantum level.

CHAPTER 7

Conclusions

The dynamics of relaxation processes is a very important issue for the comprehension of the behavior of molecular systems at quantum level. Moreover, the possibility to solve the Schrödinger equation and to follow the time evolution of expectation values of some molecular observables has opened new issues on the meaning of equilibrium properties on thermalized systems. In this framework it is of primary importance of being able to characterize the molecular system we want to simulate in terms of a well determined thermal state that account for its thermodynamic behavior. In my opinion, it can be accomplished only through a statistical description. With this thesis I want to give my contribution on the development of a self consistent theoretical framework for the statistical description of quantum pure states.

The privileged statistical ensembles of pure states, characterized by a uniform distribution within an active space, clearly manifest their major shortcoming when a thermalization experiment is considered. Once two initially isolated systems, characterized by different temperatures, are brought in contact, the resulting equilibrium properties can not be any more described by the uniform distribution. This is, in my opinion a severe drawback as long as isolated quantum systems can be always considered as deriving from the interaction between previously isolated systems.

Starting from the just mentioned weakness I have derived a new statistical

ensemble aimed to overcome it, by imposing the condition of the invariance of the average populations in the thermalization experiment. It has allowed the identification of a precise energy dependence of the average populations and, above all, the identification of thermodynamic properties directly from the quantum description. A well defined thermal parameter, accounted as a quantum temperature, naturally emerges and it can be used to describe different thermal states also in very small quantum systems, even two level systems, a task which cannot be accomplished with uniform statistical ensembles. Furthermore the robustness has been demonstrated for the Thermalisation Resilient Ensemble, since it tends to preserve its structure in the range of most probable energies.

However, the knowledge of the average population alone is not sufficient in order to perform a dynamical simulation when one must consider different realizations of the same thermal state. With this objective I have developed a statistical sampling strategy that allows for the control of random choices of the initial quantum state in a self-consistent way. In particular it allows the description of the thermalization experiment fully at a quantum level through the solution of the Schrödinger equation.

Some dynamical experiments have been performed for different interaction Hamiltonians with the statistics providing a clear definition of the thermal states.

The new quantum statistical ensemble might be an useful tool in the road to Quantum Dynamical Simulations playing the same role of classical statistical ensemble in the Molecular Dynamics Simulations.

Bibliography

- [1] E. T. Jaynes. Information theory and statistical mechanics. *Phys. Rev.*, 106(4):620–630, May 1957.
- [2] J. R. Mayer. Bemerkungen über die kräfte der unbelebten natur. *Ann. Chimie. und Pharmacie*, page 233, 1842.
- [3] Albert Einstein. *Autbiographical Notes*. Open Court Publishing Company, 1979. p.31.
- [4] J. C. Maxwell. On the final state of a system of molecules in motion subject to forces of any kind. *Nature*, 8(208):537, October 1873.
- [5] J. W. Gibbs. *Elementary principles in statistical mechanics*. Charles Scribner’s Sons, 1902.
- [6] George D. Birkhoff. Proof of the ergodic theorem. *Proceedings of the National Academy of Sciences*, 17(12):656–660, 1931.
- [7] A. Y. Khinchin. *Mathematical Foudations of Statistical Mechanics*. Dover, New York, 1949.
- [8] Richard Tolman. *The Principles of Statistical Mechanics*. Dover Publications, 1979.
- [9] Kerson Huang. *Statistical Mechanics*. John Wiley & Sons, 1987.

- [10] Jochen Gemmer, M. Michel, and Günter Mahler. *Quantum Thermodynamics: emergence of Thermodynamic Behaviour within composite quantum system*. Number 784 in Lecture Notes in Physics. Springer-Verlag Berlin Heidelberg, 2009.
- [11] Seth Lloyd. *Black Holes, Demons and the Loss of Coherence: How complex systems get information, and what they do with it*. PhD thesis, Theoretical Physics, The Rockefeller University, 1988.
- [12] Seth Lloyd. Pure state quantum statistical mechanics and black holes. *arXiv:1307.0378v1*, 2013.
- [13] Christian Gogolin. *Equilibration and thermalization in quantum systems*. PhD thesis, Fachbereich Physik der Freien Universität Berlin, 2014.
- [14] J. M. Deutsch. Quantum statistical mechanics in a closed system. *Phys. Rev. A*, 43:2046–2049, Feb 1991.
- [15] Mark Srednicki. Chaos and quantum thermalization. *Phys. Rev. E*, 50:888–901, Aug 1994.
- [16] M. Rigol, V. Dunjko, and M. Olshanii. Thermalization and its mechanism for generic isolated quantum systems. *Nature*, 452(7189):854–858, 2008.
- [17] Anatoli Polkovnikov, Krishnendu Sengupta, Alessandro Silva, and Mukund Vengalattore. *Colloquium* : Nonequilibrium dynamics of closed interacting quantum systems. *Rev. Mod. Phys.*, 83:863–883, Aug 2011.
- [18] W. Beugeling, R. Moessner, and Masudul Haque. Finite-size scaling of eigenstate thermalization. *Phys. Rev. E*, 89:042112, Apr 2014.
- [19] Marcos Rigol. Breakdown of thermalization in finite one-dimensional systems. *Phys. Rev. Lett.*, 103:100403, Sep 2009.
- [20] M. Rigol and M. Srednicki. Alternative to eigenstate thermalization. *Phys. Rev. Lett.*, 108(11):1–5, 2012.
- [21] Sheldon Goldstein, Joel L. Lebowitz, Roderich Tumulka, and Nino Zanghì. Canonical typicality. *Phys. Rev. Lett.*, 96:050403, Feb 2006.

- [22] S. Popescu, A. J. Short, and A. Winter. Entanglement and the foundation of statistical mechanics. *Nat. Phys.*, 2:754, 2006.
- [23] W. H. Zurek. Environment-induced superselection rules. *Phys. Rev. D*, 26:1862–1880, Oct 1982.
- [24] W. H. Zurek. Decoherence, einselection, and the quantum origins of the classical. *Rev. Mod. Phys.*, 75:715, 2003.
- [25] N. Linden, S. Popescu, A. J. Short, and A. Winter. Quantum mechanical evolution towards thermal equilibrium. *Phys. Rev. E*, 2009.
- [26] E. Schroedinger. An undulatory theory of the mechanics of atoms and molecules. *Phys. Rev.*, 28(6):1049–1070, 1926.
- [27] J. Von Neumann. Beweis des ergodensatzes und des h-theorems in der neuen mechanik. *Zeitschrift für Physik A*, 57:1–2, 30–70, 1929. translated by Tumulka.
- [28] C. Jarzynski. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.*, 78:2690–2693, 1997.
- [29] G.E. Crooks. Nonequilibrium measurements of free energy differences for microscopically reversible markovian systems. *J. Stat. Phys.*, 90:1481–1487, 1998.
- [30] Eli Barkai & YounJoon Jung & Robert Silbey. Theory of single-molecule spectroscopy: Beyond the ensemble average. *Annual Review of Physical Chemistry*, 55:457–507, 2004.
- [31] S. Goldstein, J. L. Lebowitz, C. Matrodonato, R. Tumulka, and N. Zanghi. Approach to thermal equilibrium of macroscopic quantum systems. *Phys. Rev. E*, 81(011109):1–9, 2010.
- [32] Arnau Riera, Christian Gogolin, and Jens Eisert. Thermalization in nature and on a quantum computer. *Phys. Rev. Lett.*, 108:080402, Feb 2012.
- [33] V.I. Yukalov. Equilibration and thermalization in finite quantum systems. *Laser Physics Letters*, 8(7):485–507, 2011.

- [34] J. Eisert, M. Friesdorf, and C. Gogolin. Quantum many-body systems out of equilibrium. *Nat Phys*, 11(2):124–130, February 2015.
- [35] P. Reimann. Canonical thermalization. *New J. Phys.*, 12(055027), 2010.
- [36] Franz Schwabl and William Brewer. *Statistical Mechanics*. Springer Berlin Heidelberg, 2002.
- [37] Hal Tasaki. From quantum dynamics to the canonical distribution: General picture and a rigorous example. *Phys. Rev. Lett.*, 80:1373–1376, Feb 1998.
- [38] Elena Canovi, Davide Rossini, Rosario Fazio, Giuseppe E. Santoro, and Alessandro Silva. Quantum quenches, thermalization, and many-body localization. *Phys. Rev. B*, 83:094431, Mar 2011.
- [39] Christian Gogolin and Jens Eisert. Equilibration, thermalization, and the emergence of statistical mechanics in closed quantum systems. *arXiv:1503.07538v1*, pages 1–105, 2015.
- [40] Peter Mazur and Elliott Montroll. Poincaré cycles, ergodicity, and irreversibility in assemblies of coupled harmonic oscillators. *Journal of Mathematical Physics*, 1(1):70–84, 1960.
- [41] O Penrose. Foundations of statistical mechanics. *Reports on Progress in Physics*, 42(12):1937, 1979.
- [42] S. Goldstein, J. L. Lebowitz, R. Tumulka, and N. Zanghì. Long-time behavior of macroscopic quantum systems. *The European Physical Journal H*, 35(2):173–200, 2010.
- [43] B. Fresch and G. J. Moro. Emergence of equilibrium thermodynamic properties in quantum pure states. i. theory. *J. Chem. Phys.*, 133(034509):1–12, 2010.
- [44] P. Reimann. Typicality for generalized microcanonical ensembles. *Phys. Rev. Lett.*, 99(16):4, 2007.
- [45] P. Reimann. Foundation of statistical mechanics under experimentally realistic condition. *Phys. Rev. Lett.*, 101(19):4, 2008.

- [46] Christian Bartsch and Jochen Gemmer. Dynamical typicality of quantum expectation values. *Phys. Rev. Lett.*, 102:110403, Mar 2009.
- [47] Edwin T. Jaynes. Foundations of probability theory and statistical mechanics. In Mario Bunge, editor, *Delaware Seminar in the Foundations of Physics*, volume 1 of *Studies in the Foundations Methodology and Philosophy of Science*, pages 77–101. Springer Berlin Heidelberg, 1967.
- [48] J. L. Lebowitz and O Penrose. Modern ergodic theory. *Physics Today*, 26:23, Feb 1973.
- [49] B. Fresch and G. J. Moro. Typicality in ensembles of quantum states: Monte carlo sampling versus analytical approximations. *J. Phys. Chem. A*, 113:14502–14513, 2009.
- [50] B. Fresch and G. J. Moro. Beyond quantum microcanonical statistics. *J. Chem. Phys.*, 134(054510):1–16, 2011.
- [51] E. Schroedinger, E. dinger. Energieaustausch nach der wellenmechanik. *Annalen der Physik*, 388(15):956–968, 1927.
- [52] Erwin Schroedinger. *Statistical Thermodynamics*. Dover Publications, 1989.
- [53] Bloch F Walecka J D. *Fundamentals of Statistical Mechanics: M: Manuscript and Notes of Felix Bloch*. World Scientific Publishing Company, 2 edition, 2000.
- [54] J. Naudts and E. Van der Straeten. A generalized quantum microcanonical ensemble. *J. Stat. Mech.: Theory and Experiments*, page P06015, 2006.
- [55] Carl M Bender, Dorje C Brody, and Daniel W Hook. Solvable model of quantum microcanonical states. *Journal of Physics A: Mathematical and General*, 38(38):L607, 2005.
- [56] Dorje C Brody, Daniel W Hook, and Lane P Hughston. Unitarity, ergodicity and quantum thermodynamics. *Journal of Physics A: Mathematical and Theoretical*, 40(26):F503, 2007.

- [57] Boris V. Fine. Typical state of an isolated quantum system with fixed energy and unrestricted participation of eigenstates. *Phys. Rev. E*, 80(5):19, 2009.
- [58] B. Fresch and G. J. Moro. Emergence of equilibrium thermodynamic properties in quantum pure states. ii. analysis of a spin model system. *J. Chem. Phys.*, 133(034510):1–13, 2010.
- [59] J. L. Alonso, A. Castro, J. Clemente-Gallardo, J. C. Cuchí, P. Echenique, J. G. Esteve, and F. Falceto. Nonextensive thermodynamic functions in the schrödinger-gibbs ensemble. *Phys. Rev. E*, 91:022137, Feb 2015.
- [60] Guido Gentile Giovanni Gallavotti, Federico Bonetto. *Aspects of Ergodic, Qualitative and Statistical Theory of Motion*. Texts and Monographs in Physics. Springer Berlin Heidelberg, 2004.
- [61] B. Fresch and G. J. Moro. Typical response of quantum pure states. *Eur. Phys. J. B*, 86:233, 2013.
- [62] E. Çinlar. *Probability and Stochastics*. Graduate Texts in Mathematics. Springer New York, 2011.
- [63] A. V. Ponomarev, S. Denisov, P. Hänggi, and J. Gemmer. Quantum thermal equilibration from equipartition. *Europhys. Lett.*, 98(40011):1–6, May 2012.
- [64] P.M. Mors and M. Feshbach. *Methods for Theoretical Physics*, volume 1. 1953.
- [65] P. Reimann. Typicality of pure states randomly sampled according to the gaussian adjusted projected measure. *J. Stat. Phys.*, 2008.
- [66] E. T. Jaynes. Information theory and statistical mechanics. *Phys. Rev.*, 108(102):171–190, October 1957.
- [67] W. K. Wootters. Random quantum states. *Found. Phys.*, 20(11):1365–1378, 1990.
- [68] M. Abramowitz and I. Stegun. *Handbook of Mathematical Functions, With Formulas, Graphs, and Mathematical Tables*. Dover Publications, New York, 1965.

- [69] B.A. Dubrovin, A.T. Fomenko, and S.P. Novikov. *Modern Geometry-Methods and Applications*. Springer-Verlag, 1985.
- [70] David A. Harville. *Matrix Algebra From a Statistician's Perspective*. Springer-Verlag New York, 1997.
- [71] Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller, and Edward Teller. Equation of state calculations by fast computing machines. *The Journal of Chemical Physics*, 21(6):1087–1092, 1953.
- [72] W. K. Hastings. Monte carlo sampling methods using markov chains and their applications. *Biometrika*, 57(1):97–109, 1970.
- [73] K. Zyczkowski and H.J. Sommers. Induced measures in the space of mixed quantum states. *J. Phys. A: Math. Gen.*, 34:7111–7125, 2001.
- [74] K. Zyczkowski. Volume of the set of separable states. ii. *Phys. Rev A*, 60(5):3496–3507, 1999.
- [75] B. Fresch. *Typicality, Fluctuations and Quantum Dynamics: Statistical Mechanics of Quantum systems*. PhD thesis, Molecular Sciences, University of Padua, 2008/2009.
- [76] Enrico Nale. Wigner's system generator. Technical report, University of Padua, 2015.
- [77] J. Gemmer and G. Mahler. Entanglement and the factorization-approximation. *The European Physical Journal D - Atomic, Molecular, Optical and Plasma Physics*, 17(3):385–393, 2001.
- [78] Eugene P. Wigner. Random matrices in physics. *SIAM Review*, 9(1):1–23, 1967.