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Typicality, Fluctuations and Quantum Dynamics: Statistical Mechanics of Quantum systems

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Typicality, Fluctuations and Quantum Dynamics:

Statistical Mechanics of Quantum systems

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TIPICALITA`, FLUTTUAZIONI E DINAMICA QUANTISTICA : MECCANICA STATISTICA DI SISTEMI QUANTISTICI

SOMMARIO

Nuove tecnologie hanno reso possibile lo studio spettroscopico di proprietà di singola molecola e di singolo spin, inoltre, gli avanzamenti nel campo delle nanotecnologie, mettono costantemente alla prova la nostra comprensione dei meccanismi che governano la dinamica a livello quantistico. Questi recenti sviluppi stanno rinnovando l'interesse intorno a questioni fondamentali non pienamente comprese e risolte; una di queste questioni riguarda i fondamenti della meccanica statistica quantistica. Lo scopo della presente tesi è quello di dare un contributo in questo affascinante campo, alla luce degli importanti cambiamenti avvenuti negli ultimi vent' anni nella nostra comprensione della meccanica quantistica. In particolare gli studi condotti nell'ambito della teoria dell'informazione hanno profondamente modificato la nostra percezione dell' *entanglement* quantistico. Questo è stato per lungo tempo considerato una proprietà quasi paradossale della materia su scala atomica mentre oggi è ritenuto un fenomeno essenziale e onnipresente importante per comprendere l'emergere del mondo macroscopico così come lo conosciamo. Inoltre, la formulazione e lo sviluppo del cosiddetto "*decoherence program"* ha introdotto un nuovo paradigma nella descrizione dell'evoluzione temporale dei sistemi quantistici riconoscendo il ruolo fondamentale dell'interazione con l'ambiente nel determinare aspetti essenziali della dinamica. Assumendo una prospettiva in linea con questi progressi, in questa tesi si parte dall'idea che la correlazione quantistica, l'entanglement, non possa essere ignorata nel derivare una descrizione statistica coerente dei sistemi complessi tradizionalmente considerati in meccanica statistica. La logica conseguenza di questo punto di vista è che la meccanica statistica quantistica non possa essere basata sull'idea dell'esistenza di insiemi di sistemi quantistici fra loro indipendenti, ma al contrario debba emergere dalla descrizione in termini di una singola funzione d'onda (stato puro) che descrive il sistema nella sua globalità, i.e. il sottosistema di interesse insieme con il suo ambiente ("*environment*").

Allo scopo di costruire tale descrizione, in questa tesi si considera in primo luogo la distribuzione di probabilità che descrive lo stato di equilibrio di un sistema quantistico isolato.

Essa è definita, in analogia con la teoria ergodica classica, sulla base dell'evoluzione temporale del sistema. Per studiare l'emergere delle proprietà termodinamiche si introducono poi distribuzioni di probabilità su insiemi di stati puri ("*Ensemble Distributions"*). Tali distribuzioni sono derivate sulla base della geometria dello spazio di Hilbert che descrive il sistema nella sua interezza. Inoltre si sono sviluppati gli strumenti teorici che permettono la caratterizzazione di tali distribuzioni di probabilità: essi consistono da un lato nell'implementazione di metodi numerici di tipo Monte Carlo che permettono il campionamento statistico diretto delle distribuzioni, d'altro canto sono state sviluppate approssimazioni analitiche delle distribuzioni sulla base del principio di massima entropia.

I risultati fondamentali che emergono dal quadro teorico sviluppato sono illustrati mediante lo studio della statistica in sistemi di spin: il messaggio fondamentale è che le funzioni termodinamiche, come l'entropia del sistema globale e lo stato di equilibrio di un sottosistema, sono caratterizzate da distribuzioni sull' *ensemble* che risultano molto concentrate intorno ad un valore tipico. Dall'analisi condotta si deduce quindi che ognuno dei singoli stati puri considerati nell'insieme è caratterizzato dallo stesso valore delle funzioni termodinamiche studiate. Questa è una chiara evidenza della proprietà di tipicalità, ("*typicality*"), di queste funzioni. L'essenza di questo risultato è che la nostra incapacità di conoscere i dettagli dello stato quantistico del sistema non è così importante dal momento che la grande maggioranza dei possibili stati che appartengono all'insieme considerato sono caratterizzati dallo stesso valore delle proprietà termodinamiche alle quali siamo interessati. In virtù di tale proprietà risulta sensato studiare gli andamenti dei valori tipici delle proprietà termodinamiche. Sotto certe condizioni si ritrovano i risultati della meccanica statistica standard: in particolare lo stato di equilibrio di un sottosistema risulta essere in media lo stato canonico di Boltzmann alla temperatura definita dall'usuale relazione termodinamica $dS = \beta dU$.

Nella seconda parte della tesi, invece, si illustra la dinamica associata allo stato di equilibrio di un sistema in interazione con il suo ambiente. Le caratteristiche delle fluttuazioni intorno ai valori medi di equilibrio dipendono sia dall'entanglement tra il sistema e l'ambiente che dal tipo di interazione considerato. Per finire si considera la connessione fra la dinamica delle fluttuazioni all'equilibrio e i processi di rilassamento da uno stato iniziale di non equilibrio.

Il lavoro presentato in questa tesi è stato in parte motivato da un analisi critica dei metodi stocastici utilizzati nella modellizzazione teorica delle spettroscopie magnetiche. Durante il primo anno di dottorato tali metodologie sono state impiegate per l'interpretazione di alcune osservabili in esperimenti di risonanza magnetica elettronica bidimensionale. [Fresch B., Frezzato D., Moro G. J., Kothe G., Freed J. H.; J. Phys. Chem. B., 110, 24238, (2006)].

TYPICALITY, FLUCTUATIONS AND QUANTUM DYNAMICS: STATISTICAL MECHANICS OF QUANTUM SYSTEM

ABSTRACT

Recently, the possibility of investigating single molecule, or single spin observables, as well as the necessity of a better understanding of the mechanisms underlying quantum dynamics in order to obtain nanoscale devices and nanostructered materials suitable for quantum computing tasks, have revived the interest in foundational aspects of quantum statistical mechanics. This thesis aims to give a contribution to this field by re-considering the statistical characterization of a quantum system at the light of some paradigmatic changes in our understanding of quantum theory which have taken place in the last two decades. In particular the impressive development of quantum information theory has changed the perceptions of quantum entanglement: for a long time it has been considered a somewhat paradoxical property of the matter at the atomic scale, but now it is regarded as an essential and ubiquitous phenomenon whose consequences are affecting the very macroscopic world that we experience. Still the decoherence program has brought out the importance of considering a quantum system together with its environment in order to clarify some key aspects of quantum dynamics. Thus, we start from the idea that quantum correlations are ubiquitous and somewhat uncontrollable in systems with many degrees of freedom which are typically considered in statistical mechanics. As a consequence we assume the standpoint that quantum statistical mechanics has not to be based on the underlying idea of a collection of many, independent quantum systems but rather it has to emerge at the level of a global wavefunction (pure state) which describes the system as well as its environment as a whole.

In order to investigate the consequences of these assumptions we study the equilibrium distribution of an isolated quantum system. This is defined, in analogy with the ergodic foundations of classical statistical mechanics, on the basis of the time evolution of the quantum state. Then, we study the emergence of thermodynamic properties in a quantum system by studying the probability distribution of some function of interests, as the entropy and the equilibrium state of a subsystem, on Ensembles of Pure States. Such a probability distribution is derived from the geometry of the Hilbert space, and the theoretical tools suitable for its characterization are developed. On the one hand we perform a numerical sampling of the

ensemble distributions by employing Monte Carlo techniques, on the other hand simpler analytical approximation of the geometrical distributions are derived by means of a maximum entropy principle.

Model systems composed of an ensemble of spins are chosen to illustrate the salient features which emerge from the developed theoretical framework: the main point is that the Ensemble Distributions of “thermodynamic observables” (entropy or equilibrium state of a subsystem) are sharply peaked around a typical value. From the analysis it emerges that *each* of the overwhelming majority of the wavefunctions which has appreciable weight in the considered ensemble, is characterized by the same value of the “macroscopic” functions. This is a striking evidence of the “typicality” of these properties. In the essence, our impossibility to know the state of the system in detail does not matter, just for the remarkable fact that almost all quantum states behave essentially in the same way. By virtue of this typicality the study of the behaviour of the typical values of the thermodynamic function become meaningful. Notably, under certain conditions, one recovers the results of standard statistical mechanics, that is, the equilibrium average of the state of a subsystem can be cast in the Boltzmann canonical form at the temperature given by the usual thermodynamical relation $dS = \beta dU$.

In the second part of the thesis we consider the dynamical aspects of the equilibrium state of a subsystem interacting with its environment. The fluctuations around the equilibrium average critically depends on the entanglement between the system and the environment and on the form of the interaction Hamiltonian. The connection between the dynamics of the fluctuations of an observable at the equilibrium and the relaxation toward the equilibrium from a “non typical” initial value is also investigated with the aid of simple model systems.

The study presented in this thesis was partly motivated by a critical analysis of the statistical methods available for the theoretical modelling of magnetic resonance experiments. One of these, the Stochastic Liouville Equation, has been employed in a work completed during the first year of my Ph.D. program in order to interpret some feature of a two dimensional electron spin resonance experiment, [Fresch B., Frezzato D., Moro G. J., Kothe G., Freed J. H.; J. Phys. Chem. B., 110, 24238, (2006)].

LIST OF ACRONYMS

PSD: Pure State Distribution

ED: Ensemble Distribution

RPSE: Random Pure State Ensemble

FEEE: Fixed Expectation energy Ensemble

RDM: Reduced Density Matrix

DM: density matrix

CLT: Central Limit Theorem

CHAPTER 1

INTRODUCTION

1.1. STATISTICAL MECHANICS

Through the rational thought which characterizes the scientific knowledge, many different theories have been developed in order to describe and interpret the rules which govern the physical phenomena. The main ingredients of these theories, as well as the nature of the logical connections between them, sensibly depend on the complexity of the object under study. Still, the description of complex phenomena can be approached from different perspective which leads to physical theories of completely different characters. A striking example of this is the duality, for a given physical system, between its thermodynamical characterization and the pure mechanical description. Thermodynamics has been initially formulated as a pure phenomenological science describing the behaviour of macroscopic systems. Indeed, it has been developed at a time when the atomistic nature of the matter was not well understood; nonetheless it is a fully self consistent physical theory whose validity is beyond any doubt today. At the end of the nineteenth century the increasing popularity of the atomic theory of matter stimulated the research of a microscopic foundation of thermodynamics, i.e. a connection between a pure mechanical description of a system and its thermodynamic properties. The natural tools to look for such a connection are of statistical nature. The birth of statistical mechanics due to the innovative work of Maxwell[1], Boltzmann[2] and Gibbs[3] among others, was

---

[1] Maxwell J. C., *On the Dynamical Theory of Gases*, Philosophical Transactions of the Royal Society of London, 157, pp. 49-88, (1867).

[2] Boltzmann L, *On the relation between the second law of the mechanical theory of heat and the probability calculus with respect to the theorems on thermal equilibrium*, Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe 76, 373–435, (1877).

[3] Gibbs J. W.: *Elementary Principles in Statistical Mechanics. Developed with Especial Reference to the Foundation of Thermodynamics.* Yale Univ. Press (1902).

an enormous step toward a more organic comprehension of the mechanisms which underlie physical phenomena.

The peculiarity of statistical mechanics is that it deals with probability distributions: on the one hand this is the reason of its success in connecting the microscopic mechanical description with other theories which account for macroscopic phenomena, on the other hand this is also the root of the difficulties one encounters when trying to rigorously justify its principles. Despite these difficulties, or perhaps right for the necessity to face these difficulties, the work on the foundations of statistical mechanics has lead to insight into many crucial issues as the role of chaos in classical dynamic and the emergence of macroscopic irreversibility from the microscopic, time reversible, equations of motion.

There is, however, a curious fact in this story: the underlying microscopic theory which is often assumed in order to discuss foundations of statistical physics is classical mechanics. Meanwhile quantum theory has produced a paradigmatic change so to become the theory of the microscopic world which is believed to be more fundamental than classical mechanics. However, the basic structure of modern statistical mechanics is still close to that formulated by Gibbs.

This fact invites a critical re-examination of the foundations of quantum statistical mechanics.

Equilibrium statistical mechanics finds its conceptual justification in the ergodic theory, [Khinchin, (1949)]: the trajectory of the representative point of the system in the phase space is supposed to fill up the hyper surface of constant energy uniformly, spending an equal amount of time in equal volumes of the phase space. From the assumption of ergodicity, the microcanonical distribution for an isolated classical system can be derived and, under certain assumptions about the energy density, this leads to the Boltzmann canonical distribution for a subsystem.

It is interesting to note that, while the justification of the microcanonical ensemble in equilibrium classical mechanics has been the object of lively debates for almost one century, in quantum mechanics the microcanonical ensemble is simply assumed, see e.g. ref. [Huang, (1987), Tolman (1980)], and the only justification remains a hand-waving analogy with classical ergodicity and the agreement with experiments. Indeed, the notion of ergodicity leads to statistical mechanics only at the classical mechanics level. Attempts to extend the notion of ergodicity to the quantum domain have not been successful in leading to a similar conclusion. The problem of quantum ergodicity was discussed for the first time in a famous paper by Von

Neumann[4]. In this paper Von Neumann established an inequality which he thought gave a dynamical foundation to quantum ergodic theory. Several subsequent contributions [Haar (1955); Farquhar (1957); Bocchieri (1958), (1959)] strongly criticized the results of Von Neumann and, in conclusion, the problem was left open.

Recently, basic questions of quantum statistical physics have gained renewed interest, [Popescu, (2006), Goldstein, (2006), Reimann, (2007), (2008)]. In addition questions of relaxation and thermalization for non equilibrium system are again receiving attention from foundational perspective, [Rigol, (2008)] This is partly triggered by intuitions from quantum information theory which have shed light on a fundamental feature of quantum theory such as the existence of non local correlation among quantum systems, i.e. the quantum entanglement [Wootters, (1998)]. Entanglement is, currently, one of the most studied phenomena in physics. This because, besides being an issue of fundamental interest, it is considered as the crucial resource for quantum information processing [Nielsen, (2000)]. The transformation of the point of view about entanglement has been remarkable. In less than a century, from being considered a somewhat paradoxical property of the matter at the atomic scale we arrive to regard it as an essential and ubiquitous phenomenon whose consequences are affecting the very macroscopic world that we experience, [Vedral, (2008)]. Still its role in the foundations of statistical physics has been only recently recognized, [Popescu, (2006)].

There is a second very important change in perspective that has took place in the last two decades in quantum theory, and it is related to a better understanding of the measurement process as well as the transition from quantum to classical world. A quantum state is identified with a wavefunction, $\psi\left(t\right)$, which is, in general, a superposition of many different eigenstates of an observable. However, the superposition principle, which is one of the most revolutionary elements introduced by quantum mechanics, is not easily reconcilable either with the appearance of a well defined outcome in a measurement process, nor with our usual perception of the physical world. The so called “measurement problem” in quantum theory concerns the breaking of the unitary evolutions of a generic wavefunction to give a single measured outcome which corresponds to just one state among those which contributes to the definition of the quantum state before the measurement. Von Neumann, [Von Neumann, (1996)], being a mathematician, postulated that an observation reduces the wavefunction, or “probability amplitude”, to a probability distribution. However we think that, from a physical

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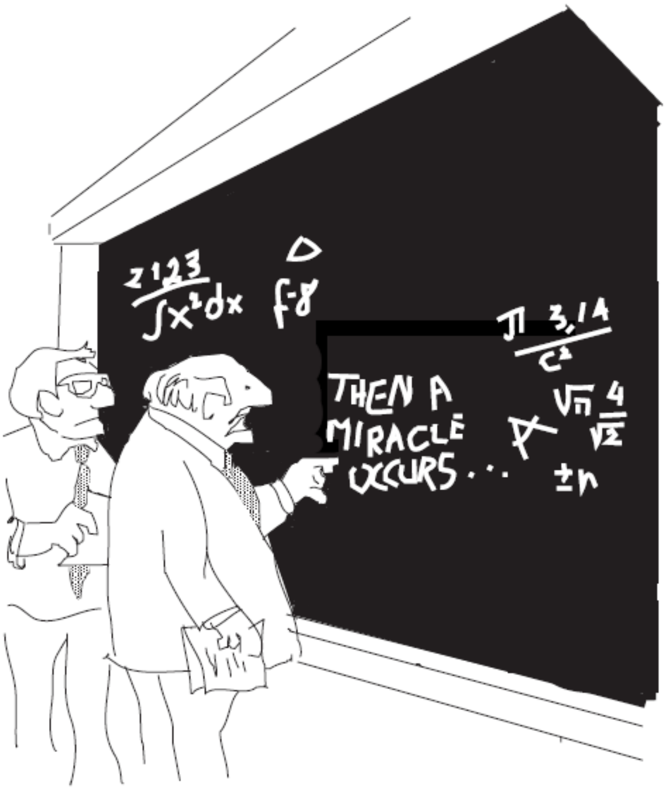
[4] Von Neumann J., *Beweis des Ergodensatzes und des H-Theorems in der neuen Mechanik*, Z. Phys. 57 30, (1929)

point of view, a postulate does not lead to new knowledge and the postulated reduction of the wavefunction risks to have the role of the “miracle” of the cartoon (Figure 1-1). The “wavefunction collapse” postulate has deeply influenced also the foundation of quantum statistical mechanics because one is tempted to not distinguish the statistical characterization of a time evolving quantum system from the statistics associated with an eventual measurement outcome. However the *decoherence program* initiated by Zurek [Zurek, (1982), (2003)], has moved the attention back again to the unitary evolution of the total wavefunction by demonstrating how the entangling interactions between a quantum system and its environment can destroy coherence between the states of the quantum system. While the question whether decoherence provides or at least suggests a solution to the measurement problem is still object of debate and active research, [Schlosshauer, (2004)], it is sure that decoherence bring out the importance of considering a quantum system together with its surrounding in order to clarify some key aspects of the quantum theory.

The aim and the goal of the present thesis are to re-consider the statistical characterization of quantum systems from a point of view which is close in spirit to that of decoherence. In particular we share the idea that quantum correlations are ubiquitous and somewhat uncontrollable in system with many degrees of freedom which are typically considered in statistical mechanics. As a consequence we assume the standpoint that quantum statistical mechanics has not to be based on the underlying idea of a collection of many, independent quantum systems but rather it has to emerge at the level of a global wavefunction (pure state) which describes the system as well as its environment as a whole.



I think you should be more explicit here in step two...

Figure 1- 1: S. Harris Cartoon

1.2 DIFFERENT LEVELS OF DESCRIPTION IN CLASSICAL AND QUANTUM MECHANICS

Within the framework of classical mechanics, self-consistent and efficient methods have been developed for the stochastic modelling of a system interacting with the environment playing the role of thermal bath. The basic formalisms are provided in a complementary way by stochastic differential equations (i.e., Langevin equations) for the trajectories or by Fokker-Planck equations for the probability density. A comparably well recognized methodology is not available for quantum systems. In such a case, even the basic tools of a stochastic model have not a clear definition, and alternative (and conflicting as well) choices have been proposed in the literature, see e.g. [Gardiner, (1988); van Kampen, (1996), (2005); Strunz (2001)]

We now briefly analyze the problem from a methodological point of view, in order to recognize what should be the ideal structure to be used in the stochastic modelling of open quantum systems.

First, let us recall the standard methods employed to model classical systems interacting with a thermal bath in order to point out the salient features of a statistical description in comparison with the full, exact, mechanical description. The system of interest (which could be also a molecule, or even a subset of its degrees of freedom) is described by the set $x=(Q,P)$ of coordinates and momenta, while the set $x_B \equiv (q_B, p_B)$ will be employed for the (thermal) bath. The overall system described by the set $x^{tot} \equiv (x, x_B)$ of coordinates and momenta is supposed to be isolated. In the following, the main methodological ingredients are characterized as separate items:

1. *__Evolution of the overall system__*: It is fully characterized through the trajectory $x^{tot}(t)$ in the phase space Γ pertinent to the overall system. The time evolution of the overall system is specified by an ordinary differential equation

$$\frac{d}{dt} x_j^{tot}(t) = X_j(x^{tot}) \tag{1.2.1}$$

with the vector field $X(x^{tot})$ provided by classical mechanics. It should be emphasized in this framework that these trajectories are made available (at some level of approximation) by using Molecular Dynamics (MD) simulations.

2. *__Evolution of the system of interest__*. The trajectories $x(t)$ fully characterize the system but, because of the interactions with the bath, they cannot be obtained as solutions of an autonomous equation like (1.2.1). On the other hand, Molecular Dynamics simulation can provide statistical information on both static (equilibrium) and dynamic properties of the system.

3. *__Stochastic modeling__*. This can be done at two levels: by describing the time evolution of the state of system through i) Langevin type of equations (stochastic differential equations)

$$\frac{d}{dt} x_j(t) = a_j(x) + b_{jk}(x)\eta_k(t) \tag{1.2.2}$$

where $a_j(x)$ are the deterministic components of the field while $\eta_k(t)$ are independent white-noise components, or through ii) a Fokker-Planck equation for the probability density $p(x,t)$

$$\frac{\partial}{\partial t} p(x,t) = -A_j(x)\frac{\partial p(x,t)}{\partial x_j} + \frac{B_{jk}(x)}{2}\frac{\partial^2 p(x,t)}{\partial x_j \partial x_k} \tag{1.2.3}$$

These two levels have a complementary nature since, given a Langevin form, one can derive the corresponding Fokker-Planck equation, and the other way around. It should be stressed that in order to properly represent the open system according to an autonomous differential equation, the fluctuating contribution in eq. (1.2.2) is essential. Indeed, in the absence of such a term, the equilibrium condition, instead of being represented by a distribution on x, would be determined by one or a finite set of x values in correspondence of the stationary solutions of the deterministic counterpart of eq. (1.2.2).

We emphasize that a given system specified according to items 1) and 2), does not find an exact correspondence with the stochastic model 3), in the meaning that differences would arise in the time dependent properties evaluated with the two procedures. The stochastic methods can only provide approximations to the “true” dynamics of the system, even if through a self-consistent procedure. The equilibrium distribution $p_{eq}(x)$, that is the stationary solution of eq. (1.2.3) has to be considered separately. As long as $p_{eq}(x)$ can be considered as an independent ingredient in modelling the Fokker-Planck equation (1.2.3), one can choose it to represent exactly the equilibrium distribution of the system (to be obtained, for instance, by a proper sampling of MD trajectories). On the other hand, such a distribution can be evaluated by describing the system of interest according to the Statistical Thermodynamics for the canonical ensemble.

In the quantum case the three level of description mentioned above have not a clear counterparts. We know that an isolated quantum system is characterized by a wave function $\psi(t)$ whose time evolution is governed by the Schrödinger equation. A completely equivalent description is obtained by means of the pure state density matrix $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$. If the corresponding eigenvalue problem can be solved to some level of approximation, one can think of Quantum Dynamics (QD) simulations providing the time evolution of the overall system. On the other hand if one is interested in the dynamics of a quantum subsystem the density matrix formalism became convenient. The Reduced Density Matrix of the subsystem is obtained by taking the partial trace over the environment degree of freedom

$$\mu(t) = \mathrm{Tr}_E\left(\rho(t)\right) \tag{1.2.4}$$

and it provides a complete representation for the system of interest since it allows the calculation of any observable for the subsystem. It should be emphasized that in this framework, the wave function of the system is not defined, and only the description through the reduced density matrix $\mu(t)$ is meaningful. On the other hand, such a density matrix is lacking of an autonomous equation because of the interaction with the bath, and its exact evolution can be derived only from the time dependence of the overall density matrix by performing suitable QD simulations. Like for classical systems, one might develop a model for its evolution by including both a deterministic component associated to the dynamics for the isolated system, and a fluctuating component arising from the stochastic interactions with the bath, that is

$$i\hbar\frac{\partial}{\partial t}\mu(t) = a\mu(t) + b(\mu,t) \tag{1.2.5}$$

where a is the superoperator describing the deterministic dynamics, while $b(\mu,t)$ accounts for the noise contributions. A complementary level of description should be represented by the probability density $p(\mu,t)$ for the reduced density matrix. Once a suitable set of variables has been introduced to parameterize the density matrix, one can conceive a Fokker-Planck equation describing the evolution of such a probability density, in strict relation with Langevin-type of equation (1.2.5).

The conclusion of such an analysis is that, for a complete analysis of open quantum systems, one should employ or stochastic differential equations for the reduced density matrix, or time dependent probability distributions on it. The idea of probability distribution on reduced density matrix is not present in quantum statistical mechanics because the density matrix itself has always been considered as the quantum analogue of the classical probability distribution. This is due on the one hand to the *ensemble* view which characterizes the standard quantum statistical mechanics, [Tolman, (1980)], in which the density matrix is essentially thought to represent the probability that the system is in one or in another pure state described by a well defined wavefunction. On the other hand, as already mentioned, this is also due to the statistical character of the quantum measurement process. In this sense the density matrix is associated to the probability to obtain one or another definite outcome in an idealised set up in which we can perform the same measure on an ensemble of identically prepared quantum system, [Fano, (1957)].

In this thesis we shall leave the above mentioned standpoints and start from the only assumption that since a quantum system which interacts with its environment can not be described by a pure state than it has to be described by its instantaneous reduced density matrix, $\mu(t)$.

Still, it is well know that the dynamical description of an open system has to account for the relaxation toward an equilibrium state, [Kohen, (1997)]. Thus, while the density matrix of an isolated system evolves unitarily according to the Von Neumann equation, the time evolution of the reduced density matrix of a system in contact with a heat bath has to include dissipation. In the framework of non equilibrium statistical mechanics the standard way to "introduce" irreversible relaxation is the treatment of open systems by means of a master equation for the statistical reduced density matrix, [Davies, (1976); Breuer, (2002)].

Any differential equation for a density matrix must preserve its unit trace, its hermiticity and positive definiteness. The most general form of such an equation has been derived by Kossakowsky and by Lindblad, [Lindblad (1976); Gorini (1976)], by means of an axiomatic approach, that is, by *assuming* a linear differential equation for the time evolution of the density matrix

$$\frac{d\rho_S(t)}{dt} = \mathcal{L}\rho_S(t) \tag{1.2.6}$$

The generator $\mathcal{L}$ represents a superoperator which is given explicitly in its diagonal form by

$$\mathcal{L}\rho_S = -i\left[H, \rho_S\right] + \sum_{k=1}^{N^2-1} \gamma_k \left(A_k \rho_S A_k^\dagger - \frac{1}{2}\left\{ A_k^\dagger A_k, \rho_S \right\} \right) \tag{1.2.7}$$

The first term of the generator represents the unitary part of the dynamics generated by the Hamiltonian H. The operators A_k, introduced above as linear combinations of the basis operators F_i in Liouville space, are usually referred to as Lindblad operators and the corresponding density matrix equation is called the Lindblad equation. As one can see the time evolution of the reduced density matrix includes the dissipation but exhibit no stochastic features.

It is interesting to note that in order to provide a microscopic derivation of eq. (1.2.6) from the underlying complete mechanical description, one has to pass through a number of assumption and approximation. The starting point is usually to take the partial trace over the environment on both sides of the Liouville Von Neumann equation for the total system

$$\frac{d\mu(t)}{dt} = -iTr_B\left[H(t), \rho(t)\right] \tag{1.2.8}$$

Notice that in the r.h.s of eq. (1.2.8) we still have the total density matrix and thus one would have in principle to specify the initial state of the whole system. The initial value problem is dismissed by assuming that initially the bath is in equilibrium, described by a canonical density matrix, and uncorrelated with the system

$$\rho(0) = \rho_S(0) \otimes \rho_{eq}^B \tag{1.2.9}$$

Notice that already at this stage the density matrix in eq. (1.2.9) is not a pure state density matrix, i.e. it does not correspond to a wavefunction. It is for this reason we have used a different symbol for the density matrix of the system, i.e. $\rho_S(0)$, by reserving the notation μ for the density matrix obtained by applying the partial trace operation to the pure state density matrix of the overall system as in eq. (1.2.4). One then proceeds by assuming the weak coupling condition in order to perform a perturbative expansion in the interaction strength of eq. (1.2.8). Given $\rho_S(0)$ one thus explicitly calculate the reduced density matrix after a small time Δt which reads

$$\rho_S(\Delta t) = \rho_S(0) - i\left[H_S, \rho_S(0)\right]\Delta t + \Delta t \mathcal{K} \rho_S(0) \tag{1.2.10}$$

where $\mathcal{K}$ is a superoperator acting on the Liouville space of the system. At this point further two assumptions have to be introduced in order to recover an equation which can be cast in the Lindblad form, (1.2.7). One of this concerns the dynamic of the bath which has to be fast compared to the relaxation time of the system; the other is the so called rotating wave approximation, (also known as secular approximation in magnetic spectroscopy language). For a complete derivation we refer the interested reader to the excellent exposition in ref. [Breuer, (2002)]. For our purposes, it is worthy to focus on the assumption about the initial condition, eq. (1.2.9). This is of course an artificial assumption since the system and its environment are never fully uncorrelated as they are constantly interacting. Furthermore, as point out by van Kampen, [van Kampen, (2004)], it is not sufficient to assume the absence of correlation between the system and its environment at some initial time $t = 0$. Indeed, in order to pass from eq. (1.2.10) to a differential equation like eq. (1.2.6), one must to assume that the unavoidable correlation, which is built between the system and its environment in a time step Δt, does not affect the results at each new time step Δt. This is of course an assumption which has deep implications and it is conceptually unsatisfactory especially after the lesson of decoherence and the recognition of the important role of quantum entanglement even in macroscopic phenomena, [Brukner, (2006)]. The words of van Kampen are particularly effective:

“There is no valid reason for this condition [eq. (1.2.9)]*: nobody believes that it is necessary for understanding Brownian motion to assume that at some time in the past the Brownian particle was uncorrelated with the surrounding fluid.* [...] *Brownian motion, rather then starting at one initial moment, is a fluctuating phenomenon taking place while the total system is in equilibrium.”*

[van Kampen, (2005)]

The standard set up of quantum statistical mechanics implies that the equilibrium state, i.e. the stationary solution of the time evolution equation (1.2.6), is described by a specific density matrix, say ρ_{eq}. On the contrary, with our approach the equilibrium state would be described by the stationary distribution $p_{eq}(\mu)$ on the reduced density matrix. From this perspective, also the Statistical Thermodynamics of quantum systems appears to be lacking, as long as it provide information not on $p_{eq}(\mu)$, but on the average of ρ_{eq}. On the other hand, if QD simulations can be performed, one can think of characterizing such a distribution $p_{eq}(\mu)$ by performing a suitable statistical sampling.

1.4 OVERVIEW OF THE THESIS

As it emerges from the arguments discussed above, statistical quantum mechanics is far from being a well founded and completely understood field, despite its unquestionable success in accounting for many experimental evidences, such as the interpretation of the results from a wide range of spectroscopic techniques. However also the recent developments in this field, as the possibility of investigating single molecule, or single spin observables, refs. [Suter, (2008); Neumann, (2008); Berezovsky, (2008)], as well as the necessity of a better understanding of the mechanisms underlying quantum dynamic in order to obtain nanoscale devices and nanostructered materials suitable for quantum computing tasks, have revived the interest in foundational aspects of quantum statistical mechanics. This thesis aims to give a contribution on this fascinating field from a perspective which is in line with the recent developments presented in refs. [Goldstein, (2006); Popescu, (2006); Reimann, (2007)]. One of the key ingredients of this new perspective consists of shifting the focus from the traditional statistical equilibrium ensemble back to the role and predictability of one single experimental realization of a system and its environment described theoretically by a quantum mechanical pure state.

The first part of the thesis deals with the statistical characterization of quantum systems at the equilibrium and with the connection between equilibrium statistic and thermodynamic properties.

In particular in Chapter 2 we recall the quantum mechanical description of an isolated quantum system and then define the equilibrium distribution of any observables on the base of its time evolution. There is a strong analogy with the ergodic foundation of classical statistical mechanics. On the one hand one finds an equilibrium distribution function which is strictly valid only for the considered quantum state, on the other hand, from the standard quantum statistical mechanics, one has the intuition that at least some state functions, such as the thermodynamic functions, e.g. the entropy, should not depend on the detail of the quantum state but only on other thermodynamic properties such as the energy. We thus want to answer the following questions:

Is the equilibrium average of some functions of interest independent on the initial state of the system $\psi\left(0\right)$?

If so, is it equal to an appropriate thermal average with respect to some properly defined equilibrium probability distribution?

To analyse these points we study in Chapter 3 the probability distribution on Ensembles of pure state. In this framework by *ensemble* we always mean an abstract construction for the statistical sampling of the possible pure states of an isolated quantum system and should not be confused with real ensemble of systems or of wavefunctions. The Ensemble Distributions are derived by considering the geometry of the Hilbert space and the constraints used to specify the ensemble. In particular we shall consider the ensemble of all the wavefunctions which lie in the Hilbert space (Random Pure State Ensemble) and the ensemble of all the wavefunctions characterized by a given value of the expectation energy, (Fixed Expectation Energy Ensemble). The distributions for these ensembles are high dimensional functions defined in non trivial domains.

In Chapter 4, the tools for the study of the ensemble probability distributions are developed: on the one hand we perform a numerical sampling of the ensemble distributions by employing Monte Carlo techniques, on the other hand simpler analytical approximation of the geometrical distributions are derived by means of a maximum entropy principle.

By using these tools, in Chapter 5 we study the properties of the Ensemble Distribution of the entropy and of the equilibrium average of the Reduced Density Matrix of a subsystem for a system composed of n spins $1/2$. The major point which emerges from such an analysis is that Ensemble Distributions are sharply peaked around a typical value. Generally the variance of the ensemble distribution diminishes as the number of spins and thus the dimension of the Hilbert space increases. Evidently the sharp distribution on the "thermodynamic observable" (entropy or equilibrium state of the subsystem) can emerge only if it is true that for *each* of the overwhelming majority of the microscopic state (wavefunctions) which has appreciable weight in the considered ensemble, we would obtain the same behaviour of the "macroscopic" functions. This is a striking evidence of the "typicality", [Goldstein, (2006)] of some properties among the wavefunctions which could describe our system. In other world, for many properties of interest, it does not matter our impossibility to know the state of the system in detail just for the remarkable fact that almost all quantum states behave essentially in the same way.

By virtue of such a typicality property, it is meaningful to study the behaviour of the typical values of a given function. In Chapter 6 we consider the dependence of the typical entropy and of the typical value of the reduced density matrix of a subsystem as a function of the internal energy. It is shown that the behaviour of this quantity depends on the definitions of the ensemble. Notably for the Random Pure State Ensemble, one recovers the results of standard statistical mechanics, that is, the equilibrium average of the state of a subsystem has the Boltzmann canonical form at the temperature given by the usual thermodynamical relation $dS = \beta dU$. Instead, different behaviours emerge for the typical values in the Fixed Expectation Energy Ensemble.

In Chapter 7 we briefly comment the obtained results. The main message is that we can understand the emergence of thermodynamic properties within a single pure quantum state and leave behind the idea of ensemble of pure states which is inconsistent with basic concept of quantum mechanic as the superposition principle.

In the second part of the thesis we consider the dynamical aspects of the equilibrium state of a subsystem. Once we have established that for a typical wavefunction which describes the total isolated system, i.e. subsystem of interest plus its environment, the equilibrium average of the reduced density matrix of the subsystem is canonical, we pass to consider the equilibrium fluctuations about this average value. This implies to study a single, time evolving, pure quantum state. The connection between the dynamics of the equilibrium fluctuations of an observable and the relaxation toward the equilibrium from a "non typical" initial value is also investigated with the aid of simple model systems.

In Chapter 8 the equilibrium fluctuations of the reduced density matrix of the system of interest is first analyzed from a general point of view, and a relation between the amplitude of such fluctuations and the entanglement of the system with its surrounding is found. Furthermore, by considering a simple system made up of spins interacting through a pure dephasing term, we point out the relation between the dynamics of the equilibrium fluctuations and the decoherence process.

With the aim of introducing a model system as general as possible, in Chapter 9 we study the equilibrium fluctuations of a two level system which interacts with its environment through a interaction Hamiltonian modelled by means of a Gaussian Orthogonal Random Matrix. The fluctuations amplitude are calculated as a function of the interaction strength and analyzed with the aid of perturbation theory. Furthermore, in order to investigate the relation between the equilibrium dynamic and the relaxation from a non equilibrium state we simulate a Free Induction Decay experiment. A first theoretical interpretation of these results is given and finally the interesting points which require further investigation are discussed.

The study presented in this thesis was partly motivated by a critical analysis of the statistical methods available for the theoretical modelling of magnetic resonance experiments. In a work completed during the first year of my Ph.D. program we developed an analysis of the effects of the collective fluctuations in ordered fluids (such as liquid crystal or membranes), on certain observables in a two dimensional electron-electron double resonance spectroscopy (2D-ELDOR). For the sake of logical consistency, I do not report about this work here, however it can be found at the following reference:

Fresch B., Frezzato D., Moro G. J., Kothe G., Freed J. H.; *Collective fluctuations in ordered fluids investigated by two-dimensional electron-electron double resonance spectroscopy*; J. Phys. Chem. B., 110, 24238, (2006).

PART I:

EQUILIBRIUM AND STATISICAL THERMODYNAMICS OF ISOLATED QUANTUM SYSTEMS

CHAPTER 2

DYNAMICS OF ISOLATED QUANTUM SYSTEMS AND THE PURE STATE DISTRIBUTION

2.1 INTRODUCTION

In this chapter we will deal with the statistical characterization of a quantum system which can be described by a wavefunction. Thus we assume that the system is isolated, in the meaning that energy interactions with the surrounding are missing, but also we require that our system is not entangled with other quantum systems. Only when both conditions are satisfied one can define the wavefunction of the system independently of the environment.

Under these conditions, the time evolution of the system is unitary and completely determined by the Hamiltonian operator. We will assume that our system is bounded and, therefore, with a discrete Hamiltonian spectrum.

In the same spirit of the ergodic foundation of classical statistical mechanics we shall define the equilibrium probability distribution function on the basis of the region of the Hilbert space which is explored by the system during its time evolution.

2.2 QUANTUM MECHANICAL DESCRIPTION OF THE TIME EVOLUTION:

The state of an isolated quantum system is completely specified by its wavefunction $\psi(t)$, in which case we say that the system is in a pure state, whatever is the wavefunction. Formally the wavefunction is an element of the complex Hilbert space $\mathcal{H}$ of dimension N. Here a finite dimensional Hilbert space is considered, and one has to evaluate the limit $N \to \infty$ when the generalization to the infinite dimensional case is required.

The normalization condition reads

$$\langle \psi(t) | \psi(t) \rangle = 1 \tag{2.2.1}$$

where the bra-ket notation denotes as usual the scalar product between two elements of the Hilbert space.

Let us introduce an arbitrary orthonormal basis set for the Hilbert space

$$\langle u_i | u_j \rangle = \delta_{ij} \tag{2.2.2}$$

with the basis vectors determined within a phase factor. Thus the wave vector can be expanded on such a basis

$$\psi(t) = \sum_{i=1}^{N} c_i(t) u_i \tag{2.2.3}$$

where the coefficients of the expansion, $c_i(t) := \langle u_i | \psi(t) \rangle$, are nothing else but the coordinates which identify the state with respect to the selected basis and carry the parametric dependence on time.

The corresponding density operator reads

$$\rho(t) := |\psi(t)\rangle\langle\psi(t)| = \sum_{i,j}^{N} c_i(t) c_j^*(t) |u_i\rangle\langle u_j| \tag{2.2.4}$$

and the density matrix specifies the representation of such an operator in the chosen basis

$$\rho_{ij} = \mathrm{Tr}\left(\rho |u_j\rangle\langle u_i|\right) = \langle u_i | \rho | u_j \rangle = c_i(t) c_j^*(t) \tag{2.2.5}$$

The density matrix has the following properties

1. unit trace: $\mathrm{Tr}\left(\rho\left(t\right)\right)=1$

2. hermiticity: $\rho\left(t\right)=\rho\left(t\right)^{\dagger}$

3. positive definiteness: $\left\langle\phi\middle|\rho\middle|\phi\right\rangle\geq 0$ for every $\left|\phi\right\rangle\in H$

Notice that a density matrix which represents a pure state can be regarded as the projection operator onto the one dimensional subspace determined by $\psi\left(t\right)$, so that another property is

4. idem potency $\rho\left(t\right)^{2}=\rho\left(t\right)$

The evolution of the quantum state is ruled by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t)=H\psi\left(t\right) \tag{2.2.6}$$

which, written for the density operator, takes the form of the Liouville-Von Neumann equation

$$i\hbar\frac{\partial\rho\left(t\right)}{\partial t}=\left[H,\rho\left(t\right)\right] \tag{2.2.7}$$

where the square brackets denote the commutator: $\left[H,\rho\right]:=H\rho-\rho H$. A time independent Hamiltonian will be employed, as long as the system is isolated.

In the analysis of the time evolution of the quantum state, one finds that the Hilbert space has a privileged basis in correspondence to the eigenvectors of the Hamiltonian

$$He_n=E_ne_n \tag{2.2.8}$$

$$\left\langle e_i\middle|e_j\right\rangle=\delta_{ij} \tag{2.2.9}$$

since it allows the direct solution of the Schrödinger equation

$$\psi(t)=U\left(t\right)\psi(0)=\sum_{n}c_n\left(0\right)e^{-iE_nt/\hbar}e_n \tag{2.2.10}$$

where $U\left(t\right)$ is the unitary time evolution operator, while $c_n\left(0\right):=\left\langle e_n\middle|\psi\left(0\right)\right\rangle$ are the components of the initial state in the energy representation.

The density operator is then specified as

$$\rho(t):=\left|\psi(t)\right\rangle\left\langle\psi(t)\right|=\sum_{n,m}c_n(0)c_m^*(0)e^{-i(E_n-E_m)t/\hbar}\left|e_n\right\rangle\left\langle e_m\right| \tag{2.2.11}$$

In the following, unless otherwise explicitly stated, we shall employ the density matrix representation eq. (2.2.11) on the basis of the Hamiltonian eigenstates.

This is in the essence the mechanical description of an isolated quantum system: from the knowledge of the Hamiltonian and of the initial state $\psi(0)$ of the system one predicts, in the deterministic meaning, the state $\psi(t)$ of such a system at any time and in the full detail. The analysis we shall present is primarily based on the unitary time evolution governed by the Schrödinger equation [Schrödinger, (1926)] and thus no measurement-like process is considered. This is a quite natural assumption when the object of the study is the nature of the thermal equilibrium or the mechanisms which underlie the tendency to reach it in many body systems [Rigol, (2008); Srednicki (1999)]. This is due to the necessity of separating the problem of the statistical description of dynamical properties, i.e. the statistical mechanic of a quantum system, from the problem of quantum measurement.

The state of the system described by the time evolving density matrix uniquely determines the expectation value of any quantum mechanical operator A

$$a(t):=\left\langle\psi(t)\right|A\left|\psi(t)\right\rangle=\mathrm{Tr}\left\{A\rho(t)\right\}=\sum_{n,m}A_{m,n}c_n(0)c_m(0)^*e^{-i(E_n-E_m)t/\hbar} \tag{2.2.12}$$

where

$$A_{m,n}=\left\langle e_m\right|A\left|e_n\right\rangle \tag{2.2.13}$$

If A represents a physical observable, than A is hermitian and $a(t)$ is real. However, we will not restrict the analysis to this case only, by considering generic operators A. In particular the expectation value of non hermitian operators like

$$A=\left|e_n\right\rangle\left\langle e_m\right| \tag{2.2.14}$$

can be identified with elements of the density matrix

$$\rho_{nm}(t)=Tr\left(\left|e_m\right\rangle\left\langle e_n\right|\rho(t)\right)=c_n(0)c_m(0)^*e^{-i(E_n-E_m)t/\hbar} \tag{2.2.15}$$

Notice that operators which commute with the Hamiltonian H, $\left[A,H\right]=0$, are constant of motion, $\mathrm{Tr}\left(A\rho\left(t\right)\right)=\mathrm{cost}$, because they are diagonal in the same basis of H.

Furthermore, the energy E of the system, given as the expectation value of the Hamiltonian operator, is a conserved quantity

$$E=\left\langle\psi\left(t\right)\middle|H\middle|\psi\left(t\right)\right\rangle=\sum_n\left|c_n\left(t\right)\right|^2E_n=\sum_n\left|c_n\left(0\right)\right|^2E_n \tag{2.2.16}$$

2.3 STATISTICAL CHARACTERIZATION OF THE EQUILIBRIUM

The main objective of the statistical mechanics of classical isolated systems at equilibrium is the replacement of the mechanical description given by a trajectory, with a description in terms of probability density on the space which represents the possible states of the evolving system during its motion, i.e. the phase space Γ, [Khinchin, (1949)]. The ergodic approach to the foundation of statistical mechanics allows one to recognize the conditions of validity of such a replacement. Let us briefly recall them

1. There are subspaces of the phase space which always transforms into themselves during the natural motion, and they are called invariant parts of the phase space.

2. An invariant part V is called metrically indecomposable if it cannot be represented in the form
$$V=V_1+V_2$$
where V_1 and V_2 are in turn invariant parts with non vanishing measure.

3. Birkhoff's Theorem: let V be an invariant part of Γ with finite volume and $f\left(P\right)$ a phase function defined at all points $P\in V$, then the following limit

$$\hat{f}\left(P\right)=\lim_{T\to\infty}\frac{1}{T}\int_0^T f\left(P,t\right)dt \tag{2.3.1}$$

exists almost everywhere on V. Moreover if V is metrically indecomposable, then almost everywhere on V

$$\hat{f}(P) = \frac{1}{\mathcal{M}V} \int_V f(P) dV \tag{2.3.2}$$

where $\mathcal{M}V$ is the total measure of the set V.

The proofs of these results as well as a detailed discussion of their implication in classical statistical mechanic can be found in ref. [Khinchin, (1949)]. The Birkhoff's theorem is important for the foundations of statistical mechanic because it provides a rigorous proof of the equivalence between asymptotic time averages, which represent by definition the equilibrium "macroscopic" properties of the system, and phase space averages. The equivalence can be established if the time evolution of the system, i.e. the motion of its representative point in the phase space, covers all the region of phase space in which we want to perform the averaging procedure.

In the following we describe how the ergodic approach can be applied to isolated quantum systems.

2.3.1 TIME AVERAGE AND EQUILIBRIUM PROBABILITY DISTRIBUTIONS

The isolated quantum system, when considered for long enough time, can be taken as a representation of an equilibrium system. Thus the equilibrium average can be identified with the asymptotic time average. In particular the averaged density matrix is given as

$$\overline{\rho} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt\, \rho(t) \tag{2.3.3}$$

Let us first consider the simpler case of a system with a non degenerate energy spectrum

$$E_n - E_m \neq 0 \qquad \text{for} \qquad n \neq m \tag{2.3.4}$$

the generalization to degenerate energy spectra does not change substantially the conclusion, and it will be discuss in the Appendix 2.2. Under the condition eq. (2.3.4) the time average is readily performed

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, e^{-i(E_n-E_m)t/\hbar} = \delta_{n,m} \tag{2.3.5}$$

and the averaged density matrix can be specified as

$$\overline{\rho} = \sum_n \left|c_n(0)\right|^2 |e_n\rangle\langle e_n| = \sum_n P_n |e_n\rangle\langle e_n| \tag{2.3.6}$$

Where we have introduced the N conserved quantities $P_n := |c_n(0)|^2$ which we shall call "populations" associated to the n-th basis vector. They are the diagonal elements of the pure state density matrix

$$P_n = Tr\left(|e_n\rangle\langle e_n|\rho(t)\right) = \rho_{nn} \tag{2.3.7}$$

which do not depend on time since $\left[H, |e_n\rangle\langle e_n|\right] = 0$.

The time evolving quantum state can thus be parameterized in terms of constant populations and time dependent phases: by writing the initial coefficients of eq. (2.2.10) in polar form as

$$c_n(0) = \sqrt{P_n}e^{i\alpha_n} \tag{2.3.8}$$

the state vector at time t is specified as

$$\psi(t) = \sum_n c_n(t)e_n = \sum_n \sqrt{P_n}\exp\left(i\left(\alpha_n - E_n t/\hbar\right)\right)e_n \tag{2.3.9}$$

The set of populations fulfills the normalization requirement

$$\sum_{i=1}^N P_i = 1 \tag{2.3.10}$$

and determine the total energy of the system (2.2.16)

$$E = \langle\psi|H|\psi\rangle = \sum_n P_n E_n \tag{2.3.11}$$

In conclusion, for a given Hamiltonian, a pure state is uniquely identified through the set of populations $P = \{P_1, ..., P_N\}$ and the set of initial phases $\alpha = \{\alpha_1, ..., \alpha_N\}$ defined with respect to the Hamiltonian eigenfunctions.

One can introduce also the following entropic functions which depend only on populations and thus is characteristic of a certain pure state

$$S = -\sum_n P_n \log P_n \tag{2.3.12}$$

The entropy as defined in the above equation is not the Von Neumann entropy, $S_{VN} = -\mathrm{Tr}\{\rho \log \rho\}$ (which for a pure state is always zero). It actually corresponds to the entropy as defined by Shannon, which is usually interpreted as a measure of the lack of information about the outcome of a given measurement. In this context we are not interest in the measurement process so the function (2.3.12) is rather interpreted as a measure of the degree of disorder of a quantum pure state in relation to its decomposition onto the Hamiltonian eigenstates. In particular a vanishing entropy would be recovered only for a stationary eigenenergy state.

The time averaged density matrix eq. (2.3.6) determines the energy of the system and all the other conserved quantities, as well as the entropy as defined in (2.3.12). However $\overline{\rho}$, being a statistical density matrix, cannot be interpreted as the density matrix of a given wavefunction. Indeed it violates the condition of idem potency $\overline{\rho}^2 \neq \overline{\rho}$ unless just one state is populated, which corresponds to the system in a stationary eigenenergy state. Though the density matrix has been proposed for nearly 80 years, there are still confusions and sometime disputes on matter related to it. Some are caused by confusion in the terminology, but others are true disputes of the fundamental nature. It can be discussed, for example, if it can actually be associated to a single quantum system or has to be interpreted as describing only ensembles of systems, each described by a wavefunction, refs. [Aharonov, (1999); d'Espagnat, (1998); Long, (2006)]. Here by avoiding at all the problems related to the measurement process, we shall adopt the point of view that a density matrix actually describes a single quantum system.

Let $f(a)$ be any (real) function of the expected value (2.2.12) defined in a domain $U \in \mathbb{R}$, and then we *define* the equilibrium probability distribution $p(a)$ through the equality

$$\overline{f(a)} = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, f\left(a(t)\right) = \int_U da\, f(a)p(a) \tag{2.3.13}$$

provided the first limit exists.

It is worth to note explicitly that the average of a function $f(a)$ which is not linear in the observable a does not coincides with the function $f(\overline{a})$ evaluated at the average value $\overline{a}$ of the observable. Indeed the average density matrix allows the calculation of the average of the expectation value

$$\overline{a(t)} = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt a(t) = Tr\left\{A\overline{\rho(t)}\right\} = \sum_n A_{nn}P_n \tag{2.3.14}$$

but not the average of the n-power

$$\overline{a(t)^n} = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\left(a(t)\right)^n = \overline{\mathrm{Tr}\left\{\left[A\rho(t)\right]^n\right\}} \neq \left(\mathrm{Tr}\left\{A\overline{\rho}\right\}\right)^n \tag{2.3.15}$$

Let us now consider a generic observable $a(t)$ as given in (2.2.12) which is not a constant of the motion. Let us imagine to pick a statistical sample of its values along a given time trajectory. In this way one can obtain the probability distribution $p(a)$ of eq. (2.3.13). We shall now assume that no accidental degeneracy occurs in the frequency spectrum [Peres, (1984); Tasaki, (1998)], i.e.

$$E_n - E_{n'} = E_m - E_{m'} \quad \text{only if} \quad n = m \;\text{ and }\; n' = m', \;\text{ or }\; n = n' \;\text{ and }\; m = m' \tag{2.3.16}$$

Under this condition one can easily evaluate the variance σ^2 of the observable $a(t)$

$$\sigma_A^2 = \overline{a(t)a(t)^*} - \overline{a(t)}^2 = \sum_n \sum_{n'\neq n} P_n P_{n'} A_{nn'} A^*_{nn'} \tag{2.3.17}$$

Which is equivalent to the sum of the variances of the real and imaginary part of the expected value $a(t)$.

Eqs. (2.3.14), (2.3.17) show that average and variance of observables along a given trajectory depends on the matrix representation of the operator and on the populations but not on the initial phases α. As discussed in Appendix 2.1, this conclusion can be generalized to demonstrate the phase independence also of the distribution function $p(a)$, which then carries a parametric dependence on the set of populations only. This implies that the distribution function $p(a)$ and the average of any function $f(a)$ of the observable as well, are independent of the choice of the initial time for the sampling along the trajectory, since a shift of the time origin $t \to t+\Delta t$ is equivalent to a shift of the initial phases $\alpha_n \to \alpha_n - E_n t/\hbar$. Of course the independence on the initial time is a prerequisite for dealing with a distribution function describing a truly equilibrium system.

2.3.2 PURE STATE DISTRIBUTION (PSD)

In the previous section we have shown how to derive in the ergodic framework the distribution function $p(a)$ for a generic time dependent observable $a(t)$. Now we generalize such an approach in order to obtain the distribution function for the time dependent density matrix $\rho(t)$, which we shall denote as the Pure State Distribution (PSD). It represents the more general statistical description of the equilibrium state of an isolated quantum system. The basic procedure is the same: a statistic sample for the density matrix can be always obtained from a long enough trajectory of the system. However, one must take into account that the statistical observable is not a parameter but an operator which should satisfy the constraints 1-4 listed in Section 2.2 and, therefore, a suitable parameterization of the density matrix has to be introduced. Given the wavefunction specified in eq. (2.3.9), it is convenient to specify the density matrix as

$$\rho(t) = \sum_{n,m} \sqrt{P_n P_m}\, \exp[-i\alpha_{n,m}(t)] |e_n\rangle\langle e_m| \tag{2.3.18}$$

where we have introduced the time dependent relative phase $\alpha_{n,m}(t)$ between directions e_n and e_m according to the relation

$$\alpha_{n,m}(t) := \alpha_n - \alpha_m - \omega_{n,m} t \tag{2.3.19}$$

$\omega_{n,m} := (E_n - E_m)/\hbar$ being the (angular) transition frequency between the two eigenstates. Because of the sum rule

$$\alpha_{n,m}(t) + \alpha_{m,l}(t) = \alpha_{n,l}(t) \tag{2.3.20}$$

these relative phases are not independent. Only $(N-1)$ of them can be taken as independent, and a convenient choice for them is provided by the set of angles

$$\gamma = \{\gamma_1, \gamma_2, \cdots, \gamma_{N-1}\} \qquad \gamma_j(t) := \gamma_{j+1,1}(t) = \gamma_{j+1,1}(0) + \omega_{j+1,1} t \tag{2.3.21}$$

which allows one to specify the instantaneous value of any relative phase

$$\alpha_{n,m}(t) = \gamma_{n-1}(t) - \gamma_{m-1}(t) \tag{2.3.22}$$

The set $\gamma(t)$ of angles together with the set P of constant populations represent the set of stochastic variables

$$X(t) \equiv \left\{\underline{P}, \underline{\gamma}(t)\right\} \tag{2.3.23}$$

which determine the instantaneous value of the density matrix (and also the reverse condition holds, i.e., that for a given set X of parameters one can determine in a unique way the corresponding density matrix). In other words such parameters are the coordinates of the phase space, i.e. the space of the possible state of the system.

According to this identification of the stochastic variables, one can determine the probability distribution $p(P \mid \gamma)$ on angles for a given set P of populations, with normalization

$$\int d\gamma\, p(P \mid \gamma) = 1 \tag{2.3.24}$$

where

$$\int d\gamma := \int_0^{2\pi} d\gamma_1 \int_0^{2\pi} d\gamma_2 \cdots \int_0^{2\pi} d\gamma_{N-1} \tag{2.3.25}$$

having chosen the standard definition domain for each angle: $0 \le \gamma_j < 2\pi$. The distribution function should be identified by imposing the condition that, for any function $f(\gamma)$, the average on the angle space and the average along a trajectory should be equivalent:

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\ f(\gamma(t)) = \int d\gamma\, f(\gamma)\, p(P \mid \gamma) \tag{2.3.26}$$

In the case of a two-dimensional problem with one angle only, such a distribution is obviously homogeneous as long as the angle $\gamma_1(t)$ has a linear dependence on the time

$$N=2: \qquad p(P\,|\,\gamma)=1/2\pi \tag{2.3.27}$$

Because of the linear dependence of all these angles, one should expect that such a distribution is homogeneous also in systems with a larger dimensionality ($N>2$). However, this is not necessarily true and, to clearly show the origin of the problem, in Figure 2.1, we have represented in the (γ_1,γ_2) plane part of a trajectory for a $N=3$ systems. The upper panels represent the trajectory by attributing to the angles values in the infinite $\mathbb{R}^2$ domain, while in the lower panels the representations of the same trajectory but with the angles in their definition domain $0\le\gamma_1,\gamma_2<2\pi$, which represents their true phase space, are reported. On the right part referring to a case of incommensurate transition frequencies $\omega_{2,1}$ and $\omega_{3,1}$, the trajectory tends to cover all the phase space. On the contrary on the left side for the case of commensurate transition frequencies with the ratio $\omega_{3,1}/\omega_{2,1}=2$, the trajectory occupies a zero measure subset of the phase space corresponding to two segments. Evidently the homogenous angle distribution can be employed only in the case of incommensurate transition frequencies.

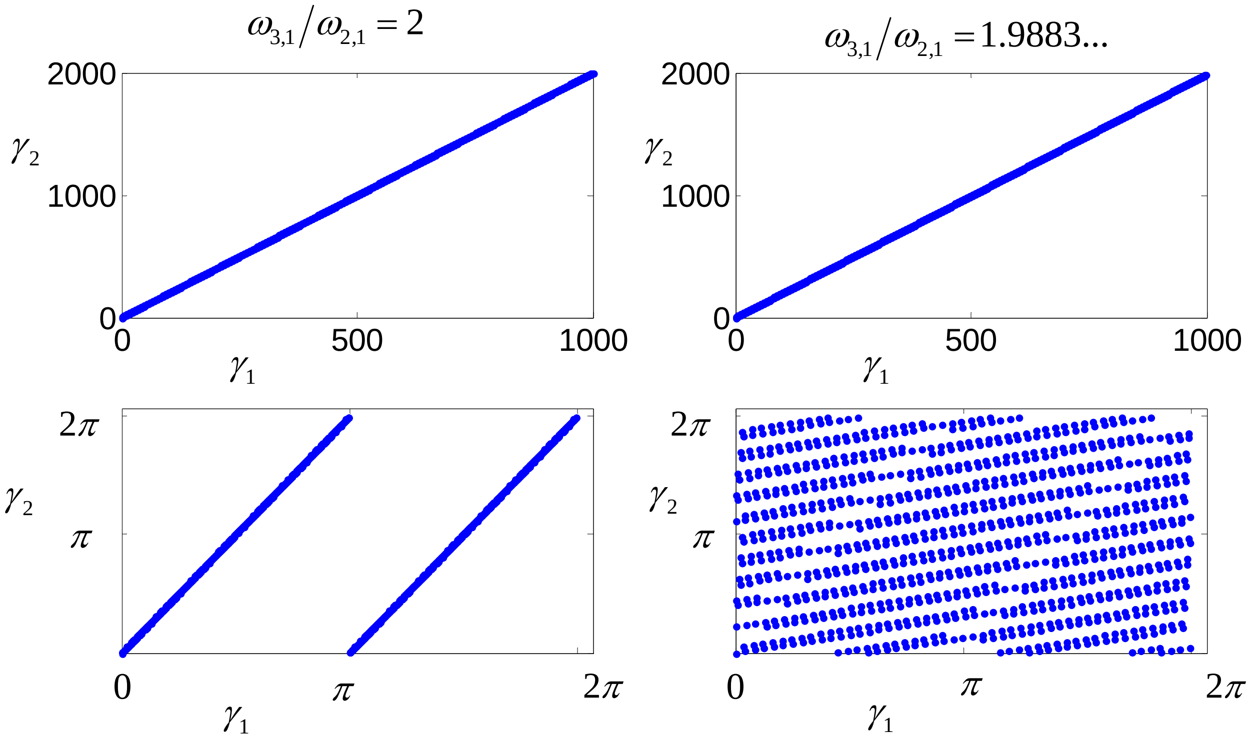


Figure 2- 1: Angles variables for the case $N=3$ in a portion of time evolution: in the real plane (upper panels) and in the domain $[0,2\pi)$ (lower panels). The left side depict the phase space trajectory in the case of commensurate frequency while on the right side the case of two incommensurate frequency is reported.

In order to provide a more formal analysis of the problem, let us introduce the Fourier transform of the distribution function

$$p(P|\gamma) = \sum_{n_1} \exp(in_1\gamma_1) \sum_{n_2} \exp(in_2\gamma_2) \cdots \sum_{n_{N-1}} \exp(in_{N-1}\gamma_{N-1}) p_{n_1,n_2,\ldots n_{N-1}}(P) \qquad (2.3.28)$$

with coefficients given as

$$p_{n_1,n_2,\ldots n_{N-1}}(P) = \frac{1}{(2\pi)^{N-1}} \int d\gamma \exp\left(-i\sum_{j=1}^{n-1} n_j\gamma_j\right) p(P|\gamma) \qquad (2.3.29)$$

For a given set of indices $(n_1, n_2, \ldots n_{N-1})$, let us select the function

$$f(\gamma) = \frac{1}{(2\pi)^{N-1}} \exp\left(-i\sum_{j=1}^{n-1} n_j\gamma_j\right) \qquad (2.3.30)$$

From its average on the phase space according to the series expansion eq. (2.3.28) of the distribution function, one derives that

$$\overline{f} = p_{n_1,n_2,\ldots n_{N-1}}(P) \tag{2.3.31}$$

On the other hand, by evaluating $\overline{f}$ as the average along the trajectory, the following relation is recovered

$$\begin{aligned}\overline{f} &= \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\,\frac{1}{(2\pi)^{N-1}}\exp\left(-i\sum_{j=1}^{N-1} n_j\gamma_j(t)\right) = \\ &= \frac{1}{(2\pi)^{N-1}}\exp\left(-i\sum_{j=1}^{N-1} n_j\gamma_j(0)\right)\lim_{T\to\infty}\frac{1}{T}\int_0^T dt\exp\left(-it\sum_{j=1}^{N-1} n_j\omega_{j+1,1}\right)\end{aligned} \tag{2.3.32}$$

which is not vanishing only if the following constraint is satisfied

$$\sum_{j=1}^{N-1} n_j\omega_{j+1,1} = 0 \tag{2.3.33}$$

In conclusion, by comparing the two average of f we derive that an expansion coefficient $p_{n_1,n_2,\ldots n_{N-1}}(P)$ is not vanishing only under the previous condition. An obvious case is that for vanishing values of all the indices, $n_1 = n_2 \ldots = n_{N-1} = 0$. But the important question to answer is whether this is the only case satisfying such a constraint. In all generality the answer is negative. For instance let us consider the case when two transition frequencies are commensurate, i.e. $\omega_{2,1}/\omega_{3,1} = e/k$ with e and k integer numbers. Then the constraint is satisfied also for the following non vanishing set of indices $n_1 = k,\; n_2 = -e,\; n_3 = n_4 \ldots = n_{N-1} = 0$. To exclude this type of peculiar cases, in the following we shall assume that all the transition frequency are incommensurate, in which case the expansion coefficients are given as

$$p_{n_1,n_2,\ldots n_{N-1}}(P) = \frac{\prod_{j=1}^{N-1}\delta_{n_j,0}}{(2\pi)^{N-1}} \tag{2.3.34}$$

which corresponds to a homogeneous distribution on the angles

$$p(P\,|\,\gamma) = \frac{1}{(2\pi)^{N-1}} \tag{2.3.35}$$

Such a conclusion, however, calls for a discussion about the issue of how reasonable is the assumption of incommensurability of transition frequency. In real systems, with different types of interactions, which of them with different possible magnitude according to interparticle distance, the energy eigenvalues, and correspondingly the transition frequency, are characterized by distributions with at least partially random character. This, for instance, is the underling point of view supporting the statistical analysis of the energy levels in complex quantum system like in the Wigner theory [Wigner, (1967), Casati (1996)], and which justify the employment of mathematical tools like the random matrix theory, [Guhr (1998), Esposito (2003), Lebowitz (2004)]. Thus, if the transition frequencies have to be selected with some level of randomness, it would result a vanishing probability that two of them are commensurate, since the ensemble of rational numbers is a subset of zero measure of the set of real number. On the other hand, often quantum systems are described with particular Hamiltonian models leading to commensurate transition frequencies. An obvious example is the triplet spin system $\left(N=3\right)$ with only two Zeeman interactions, in which case $\omega_{3,1}=2\omega_{2,1}$. In this case, one can think always there are others sort of interactions, that are neglected in the model, but which slightly modifies the energy spectrum so leading to incommensurate transition frequency. Moreover one can assume that these interactions are so weak that lead only infinitesimal modifications of the transition frequency predicted by the model, but sufficient to destroy them commensurability. Then, one is legitimate to adopt a homogeneous angles distribution for the PSD, still continuing to use simple models for the energy spectrum. The same kind of arguments support the application of the result of our analysis requiring the non degeneracy of the energy spectrum to model system lacking such a property, as illustrated in Appendix 2.2.

It should be emphasised the PSD distribution allows in principle the calculation of the average of any function of the observable. Since the population P and the angles $\gamma\left(t\right)$ determines the instantaneous density matrix $\rho\left(t\right)$, one can denote its functional dependence as

$$\rho\left(t\right)=\rho\left(P,\gamma\left(t\right)\right) \tag{2.3.36}$$

Thus the average of a function $f\left(a\left(t\right)\right)$ can in principle be determined through the angle averaging

$$\overline{f\left(a\left(t\right)\right)}=\int d\gamma\, f\left(\mathrm{Tr}\left[A\rho\left(P,\gamma\left(t\right)\right)\right]\right)p\left(P|\gamma\right) \tag{2.3.37}$$

Notice that with a suitable manipulation of the previous angle integral, one can in principle derive the distribution function $p(a)$ of the observable a.

One can assume the point of view that the Pure State Distribution is the distribution on the set of parameters which belong to the ergodic subspace, i.e. the indecomposable part, of the full phase space. The central point is that the equilibrium probability distribution, the PSD, is defined on the basis of the temporal evolution of the single system through eq. (2.3.26) and this is the same concept which lies on the base of the ergodic theory. Then, the linearity of the Schrödinger evolution makes the problem of identification of the ergodic region of the phase space very simple in principle for quantum mechanical systems. The PSD identifies the region of the Hilbert space, characterized by a fixed set of N populations, which is invariant as well as metrically indecomposable, to which then the Birkhoff's theorem can be applied.

This point of view is also used in ref. [Brody, (2007)] in order to define a statistical equilibrium density matrix $\bar{\rho}$ which assure that the average expected value of observables (2.3.14) is given as

$$\langle a \rangle_{eq} = Tr\left(\bar{\rho} A\right) \tag{2.3.38}$$

In this approach the specification of $(N-2)$ integral of the motion is required in order to perform the statistical average and in order to give a thermodynamical characterization of the equilibrium state. The diagonal elements of $\bar{\rho}$ are in fact written as functions of these conserved quantity in a form which resembles the grand canonical distribution function.

Also Rigol et al. in ref [Rigol, (2008)] recognizes the infinite time average (2.3.14) of an observable as its equilibrium value. Thus the authors introduce a "diagonal ensemble" which is seen as an ensemble formed by the Hamiltonian eigenvectors with a corresponding statistical weight determined by the set of populations, see eq. (2.3.6).

We do not follow this line and we prefer to avoid the identification of the equilibrium state with an ensemble of eigenstates. Instead we use the asymptotic time average in order to define the corresponding equilibrium average. Indeed the time averaged density matrix of eq. (2.3.6) represents the equilibrium average density matrix, which is exactly the density matrix averaged on the pure state distribution (2.3.35).

In conclusion, the isolated quantum system is fully characterized through the PSD distribution on the angles for the given set of populations, that is

$$p(P,\gamma)=\delta(P-P_0)\frac{1}{(2\pi)^{N-1}} \tag{2.3.39}$$

Then the issue of quantifying the populations of a given quantum system naturally arises. By excluding the exceptional case of a system prepared with a priori defined populations, it should be clear that complete information on the populations is not available, and that one can analyze only statistically the different possibilities for the given system. That is, one should consider ensembles of pure state distributions, corresponding to the system with different sets of populations, in order to derive the suitable statistical distribution for the set of populations. This will be the objective of the next Chapter.

Sill one can introduce particular pure state distributions by selecting the populations according to the standard procedure of equilibrium statistical mechanics. In this context the usual quantum microcanonical setup, refs. [Tolman, (1980); Huang (1987)] can be interpreted as a particular choice for the populations, that is

$$P_n=\begin{cases}\dfrac{1}{\Omega(E)\Delta E} & \text{if} \quad E-\Delta E\le E_n\le E\\ 0 & \text{otherwise}\end{cases} \tag{2.3.40}$$

Where $\Omega(E)$ is the density of energy levels and the parameter ΔE is fixed and small with respect to E. Notice that the corresponding entropy is given by the Boltzmann formula $S=k_B\ln N$, where $N=\Omega(E)\Delta E$ is the number of populated eigen energy. It should be emphasised that the particular PSD obtained by using the model for the populations given in eq. (2.3.40) is conceptually different from the conventional microcanonical distribution. Indeed this latter only concerns with the average density matrix, while the PSD is intended to describe the full distribution on the instantaneous density matrix, including its fluctuations. However, there is no compelling reason why an isolated system should be in an eigenstate of the Hamiltonian, or in a superposition of stationary states all with about the same energy. On the contrary, time-dependent states are generic and their time average determines the equilibrium condition. This point of view has been emphasized by Schrödinger who, in his preface of ref. [Schrödinger, (1952)], states *"To ascribe to every system always one of its sharp energy values is an indefensible attitude"*.

Recently a generalized microcanonical ensemble has been proposed in refs. [Brody, (2005), (2007); Bender, (2005)] in which the microcanonical energy is identified with the expectation value of the Hamiltonian. This framework defines an *Ensemble of pure state* because many different sets of populations can give the same expectation energy. However it is not clear how such an ensemble description can be related with the statistical characterization of a single quantum state. To circumvent this point Naudts et al. in [Naudts, (2006)] propose to apply the maximum entropy principle. Indeed one can maximize the Gibbs entropy, $S=-\sum_n^N P_n \log P_n$, under the constraints of normalization and constant expectation energy, $E=\langle H\rangle$. By imposing such a constraint by means of Lagrangian multipliers, one derive the canonical set of populations

$$P_n=\frac{e^{-\beta E_n}}{Q} \qquad Q:=\sum_n e^{-\beta E_n} \tag{2.3.41}$$

with parameter β given as implicit solution of the equation

$$E=\frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \tag{2.3.42}$$

and identified with $\beta=1/k_B T$ according to conventional statistical mechanics. In this way the populations are uniquely specified, and they coincide with the *canonical distribution* of statistical mechanics. It should be emphasized, however, that the coupling with a thermal bath has not to be invoked and thus we find a canonical statistic associated to microcanonical conditions.

2.4 SYSTEM PLUS ENVIRONMENT PARTITION OF THE ISOLATED SYSTEM

In order to describe a quantum system S which can interact with its surrounding E, we should consider it as a subsystem of the composed system $S+E$. Indeed a striking feature of quantum mechanics is that any interaction also produces entanglement, [Gemmer, (2001)]. As a consequence the description in terms of wavefunction can be rigorously applied only to isolated quantum system. Moreover, even in the ideal case of absence of any energetic interactions, the system S can always be entangled with another quantum system with which it interacted in the past [d'Espagnat, (1990)]. In this case it is impossible to assign two separate wavefunctions to the subsystems. For these reason we will always consider the total system $S+E$ to be in a pure state and thus described by a wavefunction $\psi(t)$.

The Hamiltonian of the total system can be generally partitioned as

$$H = H_S + H_E + H_{SE} \tag{2.4.1}$$

where H_S is the Hamiltonian of the subsystem of actual interest, H_E is the Hamiltonian of the rest of the overall system, i.e. the environment, and H_{SE} is the interaction Hamiltonian.

We choose the eigenvectors of the system and environment Hamiltonian as the basis set for the corresponding Hilbert spaces $\mathcal{H}_S$, of finite dimension N_S, and $\mathcal{H}_E$ of dimension N_E, that is

$$\mathcal{H}_S := span\left\{\left|s\right\rangle, s=1,\ldots N_S \left|H_S\left|s\right\rangle = E_s\left|s\right\rangle\right.\right\} \tag{2.4.2}$$

$$\mathcal{H}_E := span\left\{\left|b\right\rangle, b=1,\ldots N_E \left|H_E\left|b\right\rangle = E_b\left|b\right\rangle\right.\right\} \tag{2.4.3}$$

Where the energy is intended in frequency unit. The total pure state thus lies in the tensor product space $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_E$ spanned by the product basis $\left\{\left|sb\right\rangle = \left|s\right\rangle\left|b\right\rangle, sb=1,\ldots N_S N_E\right\}$.

Let us consider first the ideal case where no interaction between the system and the environment are present, $H_{SE}=0$. The eigenfunctions of the total Hamiltonian coincides with the product basis, $\left|n\right\rangle = \left|sb\right\rangle$ and the total wavefunction can be expanded in such a basis as usual

$$|\psi(t)\rangle = \sum_n \sqrt{P_n} e^{i(\alpha_n - E_n t)} |n\rangle \tag{2.4.4}$$

where $E_n = E_s + E_e$ and the index n specifies the state sb.

We stress that also in this case the system and the environment can be in an entangled state, that is, the total wavefunction could not be cast in a factorized form, $\psi \neq \psi_S \otimes \psi_E$. The state of the system S has to be specified through its Reduced Density Matrix (RDM), which is defined as the trace over the environmental degree of the total instantaneous density matrix eq. (2.2.11).

$$\mu(t) = \mathrm{Tr}_E \rho(t) \tag{2.4.5}$$

If the system S is to some extent entangled with the other system E then it is not possible to assign to it an autonomous wave function, as a consequence its Reduced Density Matrix is not idem potent, that is $\mu(t)^2 \neq \mu(t)$. In this case the state of the quantum system is said to be mixed. For a bipartition of a total pure state there exists a unique measure of the entanglement between the two parts [Popescu, (1997)]. This is the Von Neumann entropy which can be computed equivalently from the system or the environment Reduced Density Matrix

$$S(t) = -\mathrm{Tr}\left(\mu_S(t) \ln \mu_S(t)\right) = -\mathrm{Tr}\left(\mu_E(t) \ln \mu_E(t)\right) \tag{2.4.6}$$

Another quantity which is often used because it is simpler to compute is the purity $\mathcal{P}$, [Zurek, (1991)], defined as

$$\mathcal{P}(t) = \mathrm{Tr}\left(\mu(t)^2\right) \tag{2.4.7}$$

It provides the first nontrivial term in a Taylor series expansion of the Von Neumann Entropy about its maximum value. It assumes the maximum value of 1 fore pure states and it is bounded from below by $1/N_S$.

The RDM of the system specifies the expectation value of any observable pertinent to the system only, $A \in \mathcal{H}_S$, indeed

$$a(t) = \mathrm{Tr}\left(A\rho(t)\right) = \mathrm{Tr}_S\left(A\,\mathrm{Tr}_E\,\rho(t)\right) = \mathrm{Tr}_S\left(A\mu(t)\right) \tag{2.4.8}$$

In the case of no interaction, $H_{SE}=0$, despite of the non existence of an autonomous wavefunction for the system of interest one can still formulate an autonomous equation for the time evolution of its Reduced Density Matrix, eq. (2.4.5). Starting from the Liouville-Von Neumann equation for the pure state density matrix eq (2.2.7) and by applying the trace operator one has

$$i\hbar\frac{\partial\mu(t)}{\partial t}=\mathrm{Tr}_E\left[H_S+H_E,\rho(t)\right] \tag{2.4.9}$$

and by considering that

$$\mathrm{Tr}_E\left(\left[H_E,\rho\right]\right)=0 \tag{2.4.10}$$

one obtains

$$i\hbar\frac{\partial\mu(t)}{\partial t}=\left[H_S,\mu(t)\right] \tag{2.4.11}$$

This is not the case when one consider the presence of an interaction between the system and the environment, this case will be discuss in more detail in the Part II of the present study.

The solution of (2.4.11) is

$$\mu(t)=\sum_{ss'}^{N_S}\mu_{ss'}(0)e^{-i\left(E_s-E_{s'}\right)t}\left|s\right\rangle\left\langle s'\right| \tag{2.4.12}$$

Where the initial state $\mu(0)$ is determined from (2.4.5) for $t=0$ and is explicitly given by

$$\mu(0)=\sum_{ss'}\sum_{b}e^{i\left(\alpha_{sb}-\alpha_{s'b}\right)}\sqrt{P_{sb}P_{sb'}}\left|s\right\rangle\left\langle s'\right| \tag{2.4.13}$$

Notice that if no interaction are present the Von Neumann entropy eq. (2.4.6) and the purity, eq. (2.4.7), are conserved during the time evolution.

According to (2.3.13) the equilibrium average of the Reduced Density Matrix is

$$\bar{\mu}=\sum_{s}\sum_{b}P_{sb}\left|s\right\rangle\left\langle s\right| \tag{2.4.14}$$

APPENDIX 2.1: INITIAL PHASES INDEPENDENCE OF THE EQUILIBRIUM DISTRIBUTION OF AN OBSERVABLE

To demonstrate the independence of $p(a)$ of eq, (2.3.13) on the phases parameters α, let us consider the Fourier transform $\tilde{p}(q)$ of the equilibrium distribution

$$\tilde{p}(q) := \int_{-\infty}^{\infty} da\, e^{iqa}\, p(a) \tag{A2.1.1}$$

and its series expansion

$$\tilde{p}(q) = \sum_{n=0}^{\infty} \frac{(iq)^n}{n!} \int_{-\infty}^{\infty} da\, a^n\, p(a) = \sum_{n=0}^{\infty} \frac{(iq)^n}{n!} \overline{a^n} \tag{A2.1.2}$$

which is specified through the moments $\overline{a^n}$.

Let us evaluate the n-th power of $a(t)$ according to eq. (2.3.15)

$$\begin{aligned} a(t)^n &= \left\{ \sum_{m,m'} A_{m,m'} \sqrt{P_{m'} P_m}\, e^{i(\alpha_{m'} - \alpha_m)} e^{-i(E_{m'} - E_m)t/\hbar} \right\}^n = \\ &= \sum_{M} \sum_{M'} \left(\prod_{k=1}^{n} A_{m_k, m'_k} \sqrt{P_{m_k} P_{m'_k}} \right) e^{i\sum_{k=1}^{n} \alpha_{m'_k} - i\sum_{k=1}^{n} \alpha_{m_k}}\, e^{-i\left(\sum_{k=1}^{n} E_{m'_k} - \sum_{k=1}^{n} E_{m_k} \right) t/\hbar} \end{aligned} \tag{A2.1.3}$$

where $M = (m_1, m_2, \cdots, m_n)$ and $M' = (m'_1, m'_2, \cdots, m'_n)$ are sets of n indices. By performing the time average of eq. (A2.1.3) one derives that, in the absence of energy degeneration, only the contributions in eq. (A2.1.3) where M' is a permutation of M survive. But in such a case, the difference on the phases $\sum_{k=1}^{n} \alpha_{m'_k} - \sum_{k=1}^{n} \alpha_{m_k}$ also vanishes and, therefore, no dependence on the phases would be revealed by the moments $\overline{a^n}$. Therefore $\tilde{p}(q)$ does not have any parametric dependence on the phases and the same conclusion can be drawn for its Fourier transform

$$p(a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dq\, e^{-iqa}\, \tilde{p}(q) \tag{A2.1.4}$$

Which is the distribution function for the observable.

APPENDIX 2.2: EFFECTS OF ENERGY AND FREQUENCY DEGENERACY

In defining the PSD we assumed for the sake of simplicity a non degenerate energy spectrum so that condition (2.3.4) always holds, and also the absence of degeneracy in the frequency spectrum, in order to satisfy condition (2.3.16). In this section we will investigate the consequences of relaxing these conditions by showing how eventually degeneracy on the energy or frequency spectrum has to be treated in the above presented framework. The main difference when one consider the possibility of energy and frequency degeneration is that the equilibrium distribution of observables is not in general independent on the initial phases, but depend on a certain combination of them. In particular the condition (2.3.16) is not generally true in the case our total system consists of parts which does not interact each others. To see this consider for example the energy and frequency spectra of two spins which do not interact, depicted in Figure 2-2,

$$H = \Delta_1 S_z^{(1)} + \Delta_2 S_z^{(2)} \qquad \begin{aligned} \Delta_1 &= 1 \\ \Delta_2 &= 0.75 \end{aligned} \tag{A2.2.1}$$

Even if the energy spectrum is not degenerate, the frequency spectrum is (i.e., the non resonance condition (2.3.16) is not satisfied). In order to properly account these cases it is convenient to analyze the problem in the Liouville Space notation. The basic definitions and the super operator form of the Liouville-Von Neumann equation (2.2.7) are briefly discussed in Section A2.2.1.

Even if one could in principle take into account all the phases dependent conserved quantities which derive from the presence of degeneracy, as it is shown in Section A2.2.2, it is worthy to note that for realistic systems, due to the complexity of internal interactions, one expects degenerate energy eigenvalues to split in nearly located but distinct levels. This is also briefly illustrated in Section A2.2.3.

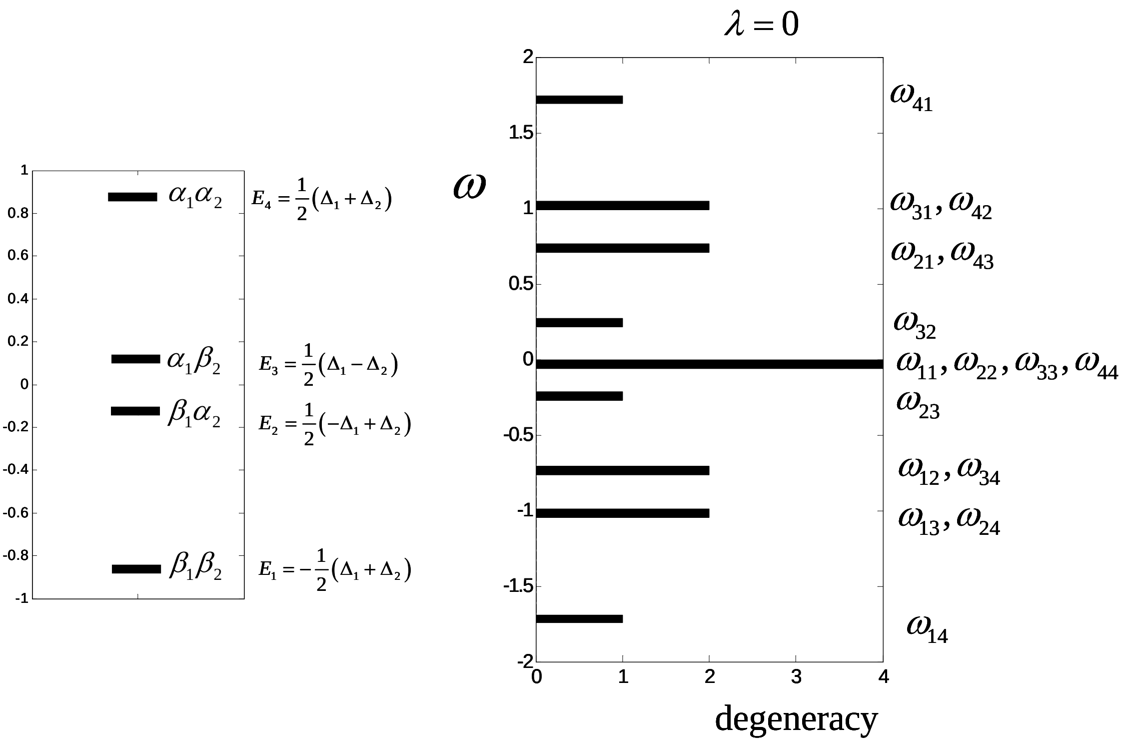


Figure 2- 2: Energy Spectrum (left) and Frequency Spectrum (right) of two non interacting spins with different Zeeman frequencies, the Hamiltonian is given in eq. A2.2.1.

A2.2.1: NOTE ON THE LIOUVILLE SPACE

The von Neumann equation for the evolution of a pure state density matrix can be conveniently cast in a superoperator form as

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}\left[H, \rho(t)\right] = \mathcal{L}\rho(t) \tag{A2.2.2}$$

If we define the Liouville space as the direct product $\mathcal{H} \times \mathcal{H}$ of the Hilbert space of dimension N we can represent the operators as vectors and the superoperators as matrices in this new space of dimension N^2. An operator A in Hilbert space, including the density matrix, is represented by a vector $\mathcal{A}$ in the Liouville space. The scalar product is defined by

$$\left(\mathcal{A}\middle|\mathcal{B}\right) = Tr\left\{A^\dagger B\right\} \tag{A2.2.3}$$

and the norm is $\|\mathcal{A}\| = \sqrt{\left(\mathcal{A}\middle|\mathcal{A}\right)}$. Projectors and theirs adjoint, which are superoperators in the Hilbert space, take the following representation

$$\begin{aligned} \mathcal{N} &= |nn') = |n\rangle\langle n'| \\ \mathcal{N}^{\dagger} &= (nn'| = |n'\rangle\langle n| \end{aligned} \tag{A2.2.4}$$

and constitute an orthonormal basis for the Liouville space

$$(\mathcal{N}|\mathcal{M}) = (nn'|mm') = \delta_{nm}\delta_{n'm'} \tag{A2.2.5}$$

The identity is thus written as $I = \sum_{nn'} |nn')(nn'|$.

As usual any operator and superoperator can be expanded on the chosen basis

$$\mathcal{A} = \sum_{\mathcal{N}=1}^{N^2} (\mathcal{N}|\mathcal{A})\mathcal{N} = \sum_{nn'}^{N^2} A_{nn'} |nn') \tag{A2.2.6}$$

$$\mathcal{L} = \sum_{\mathcal{N}} \sum_{\mathcal{M}} (\mathcal{N}|\mathcal{L}|\mathcal{M}) |\mathcal{N})(\mathcal{M}| \tag{A2.2.7}$$

where

$$(\mathcal{N}|\mathcal{L}|\mathcal{M}) = \mathcal{L}_{nn',mm'} = -\frac{i}{\hbar}\left(H_{nm}\delta_{n'm'} - H_{n'm'}\delta_{nm}\right) \tag{A2.2.8}$$

which is anti-hermitian, i.e. $\mathcal{L}^{\dagger} = -\mathcal{L}$

If n and m indices correspond to the eigenstates of the Hamiltonian we have

$$\mathcal{L}_{nn',mm'} = -\frac{i}{\hbar}\left(E_n - E_{n'}\right)\delta_{nm}\delta_{n'm'} = -i\omega_{nn'}\delta_{nm}\delta_{n'm'} \tag{A2.2.9}$$

that is, we see that the spectrum of the Liouvillian consists of all the frequencies which characterized the evolution of the total system. In fact the evolution of the total density matrix, eq. (A2.2.2), can be written using the Liouville space notation as

$$\rho(t) = \sum_{\mathcal{N}} (\mathcal{N}|\rho(0)) e^{-i(\omega_{\mathcal{N}})t} |\mathcal{N}) \tag{A2.2.10}$$

A2.2.2 MEAN AND VARIANCE OF OBSERVABLES IN LIOUVILLE SPACE: HOW TO ACCOUNT FOR DEGENERACY

Consider the density matrix as a vector in the Liouville space, working in the complete basis corresponding to the energy representation $\left\{\left|\mathcal{N}\right)\right\}$ its time evolution is ruled by the frequencies which characterize the spectrum of the Liouville operator $i\mathcal{L}$. We shell use the following partition of the full Liouville space

$$L = \varepsilon_0 \oplus \varepsilon_{\pm 1} \oplus \varepsilon_{\pm 2} \oplus .... \varepsilon_{\pm j} \tag{A2.2.11}$$

where each $\varepsilon_{\mathcal{N}}$ is defined as the subspace spanned by the set of eigenvectors corresponding to the Liouvillian eigenvalue $\omega_{\mathcal{N}} = E_n - E_{n'}$. For example for $\mathcal{N} = 0$ we write

$$\varepsilon_0 = span\left\{\left|\mathcal{N}\right), \mathcal{N} = 1,..dim\left(\varepsilon_0\right) \;\middle|\; i\mathcal{L}\left|\mathcal{N}\right) = 0\right\} \tag{A2.2.12}$$

Clearly ε_0 has dimension N in the case of a non-degenerate spectrum of the Hamiltonian while all the others are one-dimensional subspaces if the non resonance hypothesis, eq (2.3.16), is satisfied. However the following picture is general and includes the above case as a special one. The expected value of the operator A is now written as a scalar product

$$a(t) = Tr\left(A\rho(t)\right) = \sum_{\left|\mathcal{N}\right)} \left(\mathcal{N}\middle|\mathcal{A}\right) e^{i\omega_{\mathcal{N}} t} \left(\rho(0)\middle|\mathcal{N}\right) \tag{A2.2.13}$$

Averaging over time one excludes all the subspaces different from ε_0 and the summation is thus restricted to this degenerate subspace

$$\overline{a(t)} = \lim_{T\to\infty} \frac{1}{T}\int_0^T a(t)\,dt = \sum\nolimits'_{\left|\mathcal{N}\right)\in\varepsilon_0} \left(\mathcal{N}\middle|\mathcal{A}\right)\left(\rho(0)\middle|\mathcal{N}\right) \tag{A2.2.14}$$

While in the case of a non degenerate spectrum the only terms which survive to the average are those which refer to the same eigenstate, resulting in eq. (2.3.17), in the degenerate case one has to consider also the contribution of the two different but degenerate levels. If, for example there are K pairs of distinct but degenerate eigenstates e_d and $e_{d'}$, the mean value in the Hilbert space notation became

$$\overline{a(t)} = \sum_n A_{nn} P_n + \sum_{(dd')=1}^{K} \left(A_{dd'} \sqrt{P_d P_{d'}} e^{i\Delta\alpha_{d'd}} + A_{d'd} \sqrt{P_d P_{d'}} e^{i\Delta\alpha_{dd'}} \right) = \bar{a} + a_{\deg} \tag{A2.2.15}$$

where the phase differences $\Delta\alpha_{d'd} = \alpha_{d'} - \alpha_{d}$ relative to the degenerate states are now additional conserved quantities. By supposing the matrix elements of the observable being positive, notice that while in the first summation all the terms would give a positive contribution, the summation due to the degeneracy contains positive and negative terms. Given that the single phases are uniformly distributed, so are they relative differences. This means that in the limit of a highly degenerate spectrum the contribution to the average of the observable, (A2.2.15), due to the presence of degeneracy would be small compared to the first one.

The following time dependent product can be written as

$$a(t)a(t)^{*} = \sum_{|\mathcal{N})} \sum_{|\mathcal{M})} (\mathcal{M}|\mathcal{A})(\mathcal{A}|\mathcal{N})(\rho(0)|\mathcal{N})(\mathcal{M}|\rho(0)) e^{i(\omega_{\mathcal{N}} - \omega_{\mathcal{M}})t} \tag{A2.2.16}$$

but now the terms which survive after the time average are all those for which $|\mathcal{N})$ and $|\mathcal{M})$ belong to the same subspace. The variance is thus

$$\sigma_A^2 = \sum_{\mathcal{J}\neq 0} \sum_{|\mathcal{N})\in\varepsilon_{\mathcal{J}}} \sum_{|\mathcal{M})\in\varepsilon_{\mathcal{J}}} (\mathcal{N}|\mathcal{A})(\mathcal{A}|\mathcal{M})(\rho(0)|\mathcal{N})(\mathcal{M}|\rho(0)) \tag{A2.2.17}$$

As before, in the case of frequency degeneracy there are additional contribution to the variance which are given by those transitions for which $\omega_{nn'} + \omega_{m'm} = 0$ but $(m'm) \neq (n'n)$. Again this extra-contribution is phase dependent, say there are K of such a group of four states, then

$$\sigma_A^2 = \sum_{n} \sum_{n'\neq n} P_n P_{n'} A_{nn'} A_{nn'}^{*} + \sum_{(nn'mm')}^{K} \sqrt{P_n P_{n'} P_m P_{m'}}\, e^{i(\Delta\alpha_{nn'} + \Delta\alpha_{m'm})} \tag{A2.2.18}$$

From this treatment one can easily sees that degeneracy in the energy spectrum has to be taken into account in order to correctly evaluate the time average, eq. (A2.2.14), but does not affect the variance of the observable because all the terms pertinent to the ε_0 subspace are cancelled by subtracting the mean value. On the contrary, degenerate frequencies has to be consider in evaluating the variance of the distribution, eq. (A2.2.17), but do not affect the average value of the distribution.

Note that for self adjoint A eq. (A2.2.17) is also equivalent to

$$\sigma_{A^{sa}}^2 = \sum_{\mathcal{J}\neq 0} \sum_{|\mathcal{N})\in\varepsilon_{\mathcal{J}}} \sum_{|\mathcal{M})\in\varepsilon_{\mathcal{J}}} (\mathcal{N}|\mathcal{A})(\mathcal{M}|\mathcal{A})(\rho(0)|\mathcal{N})(\rho(0)|\mathcal{M}) \tag{A2.2.19}$$

If the system is composed of parts which does not interact one has to analyze the spectrum of the Liouville operator in order to correctly identify the basis vectors which contribute to the summation. This problem, however, became less important when an interaction term is added to the Hamiltonian. In fact a generic perturbation removes the degeneracy due to some symmetry both in the energy and in the frequency spectrum (clearly with the exception of the subspace ε_0 of the Liouville space).

A2.2.3 REMOVING THE DEGENERACY

An Hamiltonian which include energetic terms relative to different systems but no interaction between them is on one hand theoretically important because simple and on the other hand quite unrealistic. To see this consider for example to add a purely adiabatic interaction term to the above considered zero order Hamiltonian (A2.2.1)

$$H = \Delta_1 S_z^{(1)} + \Delta_2 S_z^{(2)} + \lambda S_z^{(1)} S_z^{(2)} \tag{A2.2.20}$$

the eigenvectors are not affected and the eigenenergies as a function of the interaction strength parameter reads

$$E_{s_1 s_2} = s_1 \Delta_1 + s_2 \Delta_2 + \lambda s_1 s_2 \tag{A2.2.21}$$

where s_i is the eigenvalue of the spin operator $S_z^{(i)}$. The spectrum as a function of the interaction parameter λ is depicted in Figure 2-3. This interaction is sufficient to remove the initial degeneracy in the Liouville subspaces different from ε_0. However, because the perturbation has the same symmetry of the zero order Hamiltonian, the energy eigenvalues cross for some special values of the interaction parameter. As consequence also the frequency spectra became degenerate for these and others single values of λ.

To analyze the most general case a further small perturbation can be added to the Hamiltonian

$$H = \Delta_1 S_z^{(1)} + \Delta_2 S_z^{(2)} + \lambda S_z^{(1)} S_z^{(2)} + H_I \tag{A2.2.22}$$

where H_I is a self-adjoint matrix with no other symmetries. By removing all the symmetries from the Hamiltonian one sees that the energy levels are never degenerate, because the non crossing rule is valid. The energy and frequency spectra which refer to this case are depicted in Figure 2.4. As before the degeneracy of the zero order frequencies is completely removed by the perturbation (inset A). Also other punctual degeneracy in the frequency spectrum become avoided crossing due to the interaction (inset C). Only for few special values of the strength parameter some accidental degeneracy of frequencies are still present (inset B).

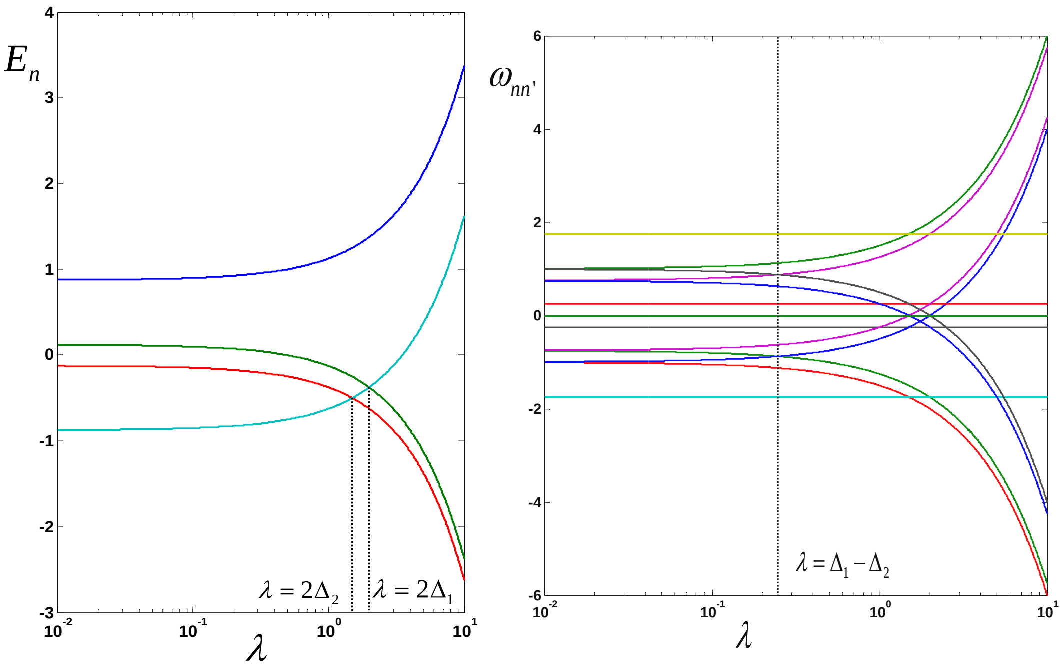


Figure 2-3: Energy Eigenvalue (left) and frequencies (right) as a function of the strength of a purely adiabatic interaction term in the Hamiltonian two spins, see eq. A.2.2.20.

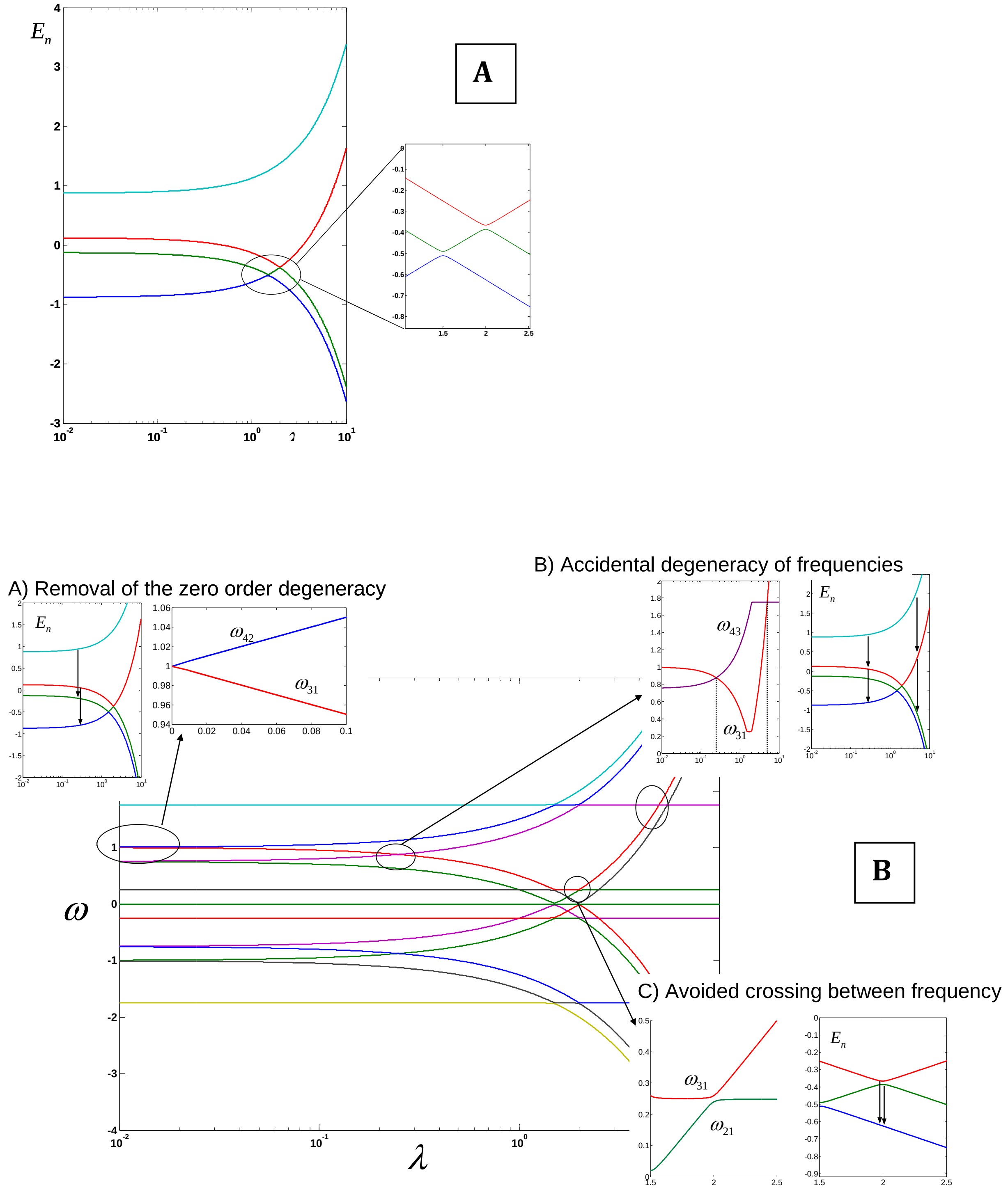


Figure 2-4: Energy Eigenvalue (A) and frequencies (B) as a function of the strength of a purely adiabatic interaction term in the Hamiltonian of two spins. In this case a further perturbation term in the form of a random matrix is added to the Hamiltonian, eq. A.2.2.22.

CHAPTER 3

STATISTICAL ENSEMBLES OF PURE STATES AND ENSEMBLE DISTRIBUTIONS

3.1 INTRODUCTION

By defining the equilibrium distribution function on the basis of the asymptotic time average of an isolated system we have, in principle, completely characterized the equilibrium state from a statistical point of view: the equilibrium value of any phase function (observable) is the time average which can be equivalently computed by integrating over the Pure State Distribution, eq. (2.3.35). This, however, is not the end of the story for the statistical mechanics of an isolated quantum system, since the Pure State Distribution is defined for a given set of populations which we usually do not know.

In this Chapter we thus consider Ensembles of pure states and define probability distributions on such ensembles. The connections with the ergodic foundations of statistical mechanic on the one hand and the standard formulation of statistical ensemble in quantum mechanic on the other hand are also discussed.

It is worth to stress that here by ensemble is always meant an abstract construction for the statistical sampling of the possible pure states of an isolated quantum system. It should not be confused with a real ensemble of systems, each of them described by a single pure state. Such an ensemble cannot exist in the reality due to the uncontrollable effects of the entanglement which prevent the possibility to assign a state vector to a system which is part of a real ensemble of other quantum systems. The use of the ensemble concept in the here presented framework has to be intended as a logical step toward the final purpose which is to find the basis of a statistical description of the populations for an isolated quantum system.

3.2 ENSEMBLE DISTRIBUTIONS

At this point we face the problem that we cannot say anything a priori about the populations which characterize a single isolated quantum system. It seems there are no reasons to assign a superiority of a particular set of populations with respect to any other set which equally satisfies some constraint, for instance the expected value of some thermodynamic quantity such as the energy.

We will thus take a different perspective and consider the statistical properties of different *Ensembles of pure states.* Each element of such an ensemble would be characterized by its particular set P of populations, and the Ensemble Distribution (ED) is described by a probability density $p(P)$ normalized as $\int dPp\left(P\right)=1$. Then, as long as the distribution on the angular parameters is independent of the populations, the overall ensemble probability density is given as

$$p(P,\gamma)=p(P)/(2\pi)^{N-1} \tag{3.2.1}$$

With normalization condition $\int dPd\gamma\, p(P,\gamma)=1$.

This introduces basically two problems in connection with the equilibrium statistic of the considered quantum system:

1. First one has to properly define the Ensemble and thus specifies the corresponding ensembles distribution, eq. (3.2.1). Clearly many choices are possible: all the wavefunctions which have in common required properties, e.g. dimensionality or expected value of some observable, define an ensemble in the meaning here intended. In particular we shall introduce and study the properties of two ensembles:

   Random Pure State Ensemble (RPSE): i.e. the ensemble of all the N-dimensional normalized wavefunction which belong to a certain, finite dimensional, Hilbert space $\mathcal{H}_{\mathcal{RPS}}\subseteq\mathcal{H}$. In general the dimension N of the considered Hilbert space is defined trough a high energy cut off $E_{\max}$, that is

$$\mathcal{H}_{\mathcal{RPS}}=span\left\{\left|e_n\right\rangle\middle|E_n\leq E_{\max}\right\} \tag{3.2.2}$$

   If one deal with Hamiltonian with a bounded spectrum, as in the case of a system of spins, one can also consider the whole Hilbert space, $\mathcal{H}_{\mathcal{RPS}}=\mathcal{H}$.

Fixed Expectation Energy Ensemble (FEEE): i.e., the ensemble of all the N-dimensional normalized wavefunction in $\mathcal{H}_{\mathcal{FEE}}$ characterized by the same value of the expectation energy. This is analogous to the generalized microcanonical ensemble mentioned at the end of Section 2.3 and considered in refs. [Brody, (2005), (2007); Bender, (2005), Naudts, (2006)].

2. By introducing the concept of Ensemble one has to analyze the connection between the Ensemble Distribution and the statistical characterization of the equilibrium of a single system which is based on its temporal evolution. There are of course no obvious reasons to think that average value of a function of interest with respect to an Ensemble Distribution should be related to its time averages along the evolution of a single pure state. As we will discussed this problem present some analogy with the ergodic problem in classical mechanics and also sheds some light on the corresponding, not so well defined, problem of ergodicity in quantum theory, Refs. [Bocchieri (1958), (1959); Pechukas (1984); Casati (1999); Deutsch (1991); Klein (1952); Peres (1984)].

To analyze this points we shell start by consider in the next section the geometry of the phase space.

3.3 WHAT DOES GEOMETRY SAY ABOUT STATISTICS?

An isolated quantum system can be described in a N dimensional complex Hilbert space which is specified by $2N$ real parameters with a normalization constraint and a total phase invariance property. We thus introduce a real phase space Γ of dimension $2N$. Different types of parameterization of the density matrix correspond to different choice of the reference system in such a space. Looking at the state of the system and its evolution from a geometrical point of view turns out to be particularly convenient especially when one has in mind a statistical characterization of such a state. For our purpose the main motivations to introduce a geometrical description are

1. the concept of probability distribution are closely related to the concept of measure in a manifold

2. classical statistical mechanics is formulated in the classical phase space. When quantum mechanics is view from a geometrical point of view, refs. [Anandan, (1994); Brody, (2001); Chruscinski (2006)], many analogies with the statistical mechanics of classical system

become apparent and can be used as guidelines for the statistical mechanics in the quantum case.

3. It will be shown that, by considering the geometry of the quantum phase space, one can characterize the probability distribution of the populations, i.e. the above mentioned Ensemble Distribution.

In Appendix 3.1 we briefly review some basic concepts related to the geometry of a space which will be used later in the discussion, ref. [Dubrovin, (1985)].

Let us now describe the phase space of a generic isolated quantum system from a geometrical point of view. Consider first the expansion of the wave function in an arbitrary orthonormal basis $\left\langle u_i \middle| u_j \right\rangle = \delta_{ij}$

$$\psi = \sum_J^N c_J u_J \qquad c \equiv \left(c_1, c_2 ..., c_N\right) \in \mathbb{C}^N \tag{3.3.1}$$

then it is natural to identify the following set of Cartesian coordinate for the phase space Γ

$$x \equiv \left(\operatorname{Re} c, \operatorname{Im} c\right) \in \mathbb{R}^{2N} \tag{3.3.2}$$

By using this set of coordinates, the scalar product between two vectors of the Hilbert space, i.e. two wavefunction ψ and ψ' represented by the set of coordinate x and x', respectively, can be evaluate as Euclidean scalar product between their representations

$$\left\langle \psi \middle| \psi' \right\rangle = \sum_{k=1}^{2N} x_k x_k^{'} \tag{3.3.3}$$

That is, if no restriction on the space spanned by $\{x\}$ is imposed, then Γ is an Euclidean space with x the corresponding Euclidean coordinate, its metric tensor, eq. (A3.1.7), is the unit tensor. It is interesting to observe that the Schrödinger equation, when written for these coordinates, take the same form of the canonical equation of motion for classical system: let x_{2i} and x_{2i-1} be the real and imaginary part of the i-th coefficient of the state vector expansion in the eigen-energy basis. The time evolution of the state of the system is then determined by the following equation of motion, [Anandan, (1994)]

$$\dot{x}_{2i} = \frac{1}{2\hbar} \frac{\partial E}{\partial y_{2i-1}} \qquad \dot{y}_{2i-1} = -\frac{1}{2\hbar} \frac{\partial E}{\partial x_{2i}} \tag{3.3.4}$$

Where $E = \langle \psi | H | \psi \rangle$ is the expectation value of the Hamiltonian operator. As in the classical case the state of a system at any given time determines uniquely its state at any other time. This time evolution is described by the canonical equations of motion. Being the state of a system represented by a point in the corresponding phase space we can say that a point P_0 during the interval of time (t_0, t) goes over to another point P and the two points determines each other uniquely. During the same interval all the other points of Γ goes over into new definite positions. In other words all the phase space is transformed into itself and in a one to one way.

The normalization condition introduces a constraint on the total space Γ which defines an hyper surface of real dimension $2N-1$. The volume element on this new space turns out to be the standard volume element for a $2N-1$ dimensional hyper sphere. This is shown in Appendix 3.2 by using the generalized spherical coordinate system.

In other words on the set of pure states in a N-dimensional complex vector space there is a unique measure which is invariant under all unitary transformations. One can reasonably call this measure the uniform distribution over the unit sphere of dimension $2N-1$

$$S^{2N-1} = \left\{ \psi \in \mathbb{C}^N \,\middle|\, \langle \psi | \psi \rangle = 1 \right\} \tag{3.3.5}$$

In order to specify the Ensemble Distribution on the populations we may answer the following question: if pure states are distributed uniformly over the unit sphere eq. (3.3.5), how are their corresponding populations P distributed over the populations space?

3.4 RANDOM PURE STATE ENSEMBLE (RPSE)

Let us consider first the simpler case of the Random Pure State Ensemble. All the normalized wave functions which could describe the system of interest belong to this ensemble.

First let us derive an alternative representation of the phase space and the corresponding metric tensor. The transformation is

$$x_{2i-1} = \sqrt{P_i}\cos\alpha_i \qquad x_{2i} = \sqrt{P_i}\sin\alpha_i \tag{3.4.1}$$

for $i = 1 \div N$. Notice that $P \equiv (P_1 ..., P_N)$ are not truly populations as long as they are not yet normalized: $\sum_{n=1}^{N} P_n = \sum_{n=1}^{N} x_n^2 \neq 1$. The Jacobian matrix of the transformation is block diagonal, and the i-th block is

$$A^{(i)} = \begin{pmatrix} \dfrac{\partial x_{2i-1}}{\partial P_i} & \dfrac{\partial x_{2i-1}}{\partial \alpha_i} \\ \dfrac{\partial x_{2i}}{\partial P_i} & \dfrac{\partial x_{2i}}{\partial \alpha_i} \end{pmatrix} = \begin{pmatrix} \left(2\sqrt{P_i}\right)^{-1}\cos\alpha_i & -\sqrt{P_i}\sin\alpha_i \\ \left(2\sqrt{P_i}\right)^{-1}\sin\alpha_i & \sqrt{P_i}\cos\alpha_i \end{pmatrix} \tag{3.4.2}$$

And the metric tensor, according to eq. (A3.1.11), is diagonal with components

$$\begin{aligned} g_{2i-1,2i-1} &= g_{P_iP_i} = \frac{1}{4P_i} \\ g_{2i,2i} &= g_{\gamma_i\gamma_i} = P_i \end{aligned} \tag{3.4.3}$$

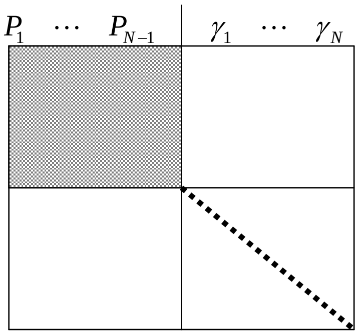
Now let us introduce the normalization constraint as

$$f(P,\alpha) = \sum_{i=1}^{N} P_i - 1 = 0 \tag{3.4.4}$$

Following (A3.1.23) we can thus introduce local coordinates $\alpha_i^{'}$ for $i = 1 \div N$ and $P_i^{'}$ for $i = 1 \div (N-1)$ so that

$$\begin{aligned}
&\alpha_i = \alpha_i^{'} \\
&P_1 = P_1^{'} \\
&\vdots \\
&P_{N-1} = P_{N-1}^{'} \\
&P_N = 1 - \sum_{i=1}^{N-1} P_i^{'}
\end{aligned} \qquad (3.4.5)$$

and specify the metric tensor on the surface defined by eq. (3.4.4) according to the prescription of eq. (A3.1.24). The resulting metric tensor g_{ij} has the following structure



where it results partitioned in two blocks, that on the phases which is diagonal and the block on populations which is not. Explicitly one obtains

$$g_{P_iP_j} = \frac{1}{4P_i}\delta_{ij} + \frac{1}{4\left(1-\sum_{k=1}^{N-1} P_k\right)} \qquad i, j = 1 \div (N-1) \qquad (3.4.6)$$

$$\begin{aligned}
&g_{\gamma_i\gamma_j} = P_i\delta_{ij} \\
&g_{\gamma_N\gamma_N} = 1 - \sum_{k=1}^{N-1} P_k
\end{aligned} \qquad (3.4.7)$$

In order to find the corresponding measure $dV = \sqrt{g}\, dP_1, \ldots dP_{N-1} d\alpha_1, .., d\alpha_N$ we have to calculate the determinant of the metric tensor

$$g = \det\left(g_{ij}\right) \qquad (3.4.8)$$

This can be done by using the following identity for determinants: suppose A is an invertible square matrix and u, v are column vectors. Then it can be verified [Harville, (1997)] that

$$\det\left(A+uv^T\right)=\left(1+v^T A^{-1}u\right)\det\left(A\right) \tag{3.4.9}$$

By identifying A with the diagonal matrix whose entries are $1/\left(4P_i\right)$, the vector v with the vector whose elements are all 1, and the elements of u with the second term of the sum in eq. (3.4.6) we find the population contribution to the volume

$$dV_P=\frac{1}{2^{N-1}}\frac{1}{\sqrt{1-\sum_k^{N-1}P_k}}\prod_{k=1}^{N-1}\frac{1}{\sqrt{P_k}}dP_1,\dots,dP_{N-1} \tag{3.4.10}$$

while the contribution from the phases is

$$dV_\alpha=\sqrt{1-\sum_k^{N-1}P_k}\prod_{k=1}^{N-1}\sqrt{P_k}\,d\alpha_1,\dots,d\alpha_N \tag{3.4.11}$$

So that the total volume element is simply

$$dV=dV_P dV_\alpha=\frac{1}{2^{N-1}}dP_1,\dots,dP_{N-1}d\alpha_1,\dots,d\alpha_N \tag{3.4.12}$$

It turns out that both the phases and the set of populations are uniformly distributed in the phase space.

Note that for the phases this is the same result obtained from the analysis of the pure state distribution. Indeed a uniform distribution on the wavefunction phases α_j implies a uniform distribution on the relative phases γ of eq. (2.3.21).

The uniform distribution on the set of populations P, is instead one of the possible ensemble distribution, in particular the only and appropriate one if no other constraints but normalization is required. Here “uniform” means that if populations space is represented in $\mathbb{R}^{N-1}$ with the axis being the populations $P_1 \dots P_{N-1}$, then the weight attached to any region is proportional to its volume.

In other words the uniform distribution of the wave vectors on the surface of the $2N-1$ corresponding hypersphere induces a uniform measure in the N simplex of the populations

$$\Delta^{N-1}=\left\{\left(P_1,\dots,P_N\right)\in\mathbb{R}^N \,\middle|\, \sum_k P_k=1 \;\; and \;\; P_k\geq 0 \quad for\ all\ k\right\} \tag{3.4.13}$$

This result has already been obtained by means of other arguments by Sykora in ref. [Sykora, (1974)], where its relevance in the framework of quantum information has been discussed.

Now, the average value of some function of a state $A = A(|\psi\rangle)$, for example an expectation value $a = \langle\psi|A|\psi\rangle$, over this generalized ensemble (RPSE) is then defined as

$$\langle a\rangle_{RPS} = \frac{1}{V_N}\int_D A dV_P dV_\alpha = \int_D A(\alpha, P)\, p_{RPS}(\alpha, P)\prod_{k=1}^{N-1} dP_k d\alpha_k d\alpha_N \qquad (3.4.14)$$

where the domain of integration is the region of the phase space characterized by normalized populations and V_N the total volume of such a region. Only in this simple case the total volume, and thus the normalization factor of the distribution, can be explicitly calculated. Indeed it corresponds to the surface area of a $2N-1$ dimensional hypersphere, eq. (3.3.5) and can be calculated by switching to generalized spherical coordinates. This is shown in Appendix 3.2; the final result is eq. (A3.1.32) where the dimension of the space is $M = 2N$ in the present case. The total volume thus reads

$$V_N = S^{2N-1} = \frac{2\pi^N}{(N-1)!} \qquad (3.4.15)$$

It should be explicitly noted that the $(N-1)$ relevant populations are not statistically independent due to the normalization constraint. This is evident if we consider the boundary of the integration domain. Let us specify the order of integration as in eq. (3.4.12), the condition of positivity of the dependent population, say

$$P_N = 1 - \sum_{i=1}^{N-1} P_i > 0 \qquad (3.4.16)$$

define the allowed region in which P_{N-1} can exist

$$P_{N-1} \le b_{N-2} = 1 - \sum_{J=1}^{N-2} P_J \qquad (3.4.17)$$

Then by requiring the upper bound b_{N-2} to be a positive number one find the upper bound for the next integration variable P_{N-2}, and so on. By defining

$$b_K = 1 - \sum_{J=1}^{K} P_J \tag{3.4.18}$$

and by considering that the phase variable are all independent and defined on $\left(0, 2\pi\right]$ one can explicitly define the domain of integration D which appears in (3.4.14) as

$$V_N = \int_D dV_P dV_\alpha = 2\pi^N \int_0^1 dP_1 ... \prod_{k=1}^{N-2} \int_0^{b_K} dP_{K+1} \tag{3.4.19}$$

The normalized probability distribution on the populations (3.2.1) is thus

$$p_{RPS}\left(P_1, ..., P_{N-1}\right) = \left(N-1\right)! \tag{3.4.20}$$

3.5 FIXED EXPECTATION ENERGY ENSEMBLE (FEEE) : THE MEASURE ON THE SURFACE OF CONSTANT ENERGY

If we want to introduce the further constraint of fixed energy expectation value we have to find the measure induced on the $2N-2$ surface defined implicitly by the constraints of normalization and fixed expectation energy.

$$\sum_{i=1}^{N} P_i = 1 \qquad\qquad E = \left\langle \psi \middle| H \middle| \psi \right\rangle = \sum_n P_n E_n \tag{3.5.1}$$

By applying the definition of Appendix 3.1, eq. (A3.1.23), we can define the surface by the following parametric equations

$$\begin{aligned} P_k &= f_1\left(P_1, ...P_{N-2}\right) = \frac{E}{E_k - E_{k'}} - \sum_{i \neq kk'}^{N-2} \frac{E_i}{E_k - E_{k'}} P_i + \frac{E_{k'}}{E_k - E_{k'}} \left(\sum_{i \neq kk'}^{N-2} P_i - 1 \right) \\ P_{k'} &= f_2\left(P_1, ...P_{N-2}\right) = 1 - \sum_{i \neq kk'}^{N-2} P_i - f_1\left(P_1, ...P_{N-2}\right) \end{aligned} \tag{3.5.2}$$

Thus, the metric tensor on the populations, defined according to eq. (A3.1.24) , is

$$g_{P_j P_t} = \frac{1}{4P_j} \delta_{jt} + \frac{1}{4 f_1} \frac{\partial f_1}{\partial P_j} \frac{\partial f_1}{\partial P_t} + \frac{1}{4 f_2} \frac{\partial f_2}{\partial P_j} \frac{\partial f_2}{\partial P_t} \tag{3.5.3}$$

Again we can calculate the determinant of this matrix by using the following general property of the determinant

$$\det\left(A+UV^{\dagger}\right)=\det\left(I+V^{\dagger}A^{-1}U\right)\det\left(A\right) \tag{3.5.4}$$

By defining

$$a_J=\frac{E_{k'}-E_J}{E_k-E_{k'}} \tag{3.5.5}$$

$$R_{11}=\frac{1}{f_1}\sum_{J\neq kk'}^{N-2}P_J a_J^2$$
$$R_{22}=\frac{1}{f_2}\sum_{J\neq kk'}^{N-2}P_J\left(1+a_J\right)^2$$
$$R_{12}=\frac{1}{\sqrt{f_2 f_1}}\sum_{J\neq kk'}^{N-2}P_J a_J\left(1+a_J\right)$$

And after some algebra we find

$$g_P=\left|\det g_{P_iP_j}\right|=\left(\left(1+R_{11}\right)\left(1+R_{22}\right)-R_{12}^2\right)\prod_{J\neq kk'}^{N-2}\frac{1}{4P_J} \tag{3.5.6}$$

Thus one has for the surface element $dV_P=\sqrt{g_P}\prod_{J\neq kk'}^{N-2}dP_J$. On the other hand dV_α remains unchanged so that the total volume element reads

$$dV_{FEED}=dV_P dV_\alpha=$$
$$=\frac{1}{2^{N-2}}\left[\left(f_1+\sum_{J\neq kk'}^{N-2}P_J a_J^2\right)\left(f_2+\sum_{J\neq kk'}^{N-2}P_J\left(1+a_J\right)^2\right)-\left(\sum_{J\neq kk'}^{N-2}P_J a_J\left(1+a_J\right)\right)^2\right]^{1/2}dP_1,\ldots,dP_{N-2}d\alpha_1,\ldots,d\alpha_N$$

This can be recast as

$$dV_{FEED}=$$
$$=\frac{1}{2^{N-2}}\left[\sum_{J\neq kk'}^{N-2}P_J\left(1+a_J\right)a_J-\left(\frac{E-E_{k'}}{E_k-E_{k'}}\right)^2+\left(\frac{E-E_{k'}}{E_k-E_{k'}}\right)\right]^{1/2}dP_1,\ldots,dP_{N-2}d\alpha_1,\ldots,d\alpha_N \tag{3.5.7}$$

The ensemble average of any phase function is thus

$$\begin{aligned} \langle a \rangle_{FEE} &= \frac{1}{V_{FEED}} \int_D a dV_{FEED} = \int_D a p_{FEE}(P,\alpha) dP d\alpha \\ p_{FEE}(P,\alpha) dP d\alpha &= \frac{dV_{FEED}}{V_{FEED}} \end{aligned} \tag{3.5.8}$$

Notice that now the domain of integration is the projection on the $2N-2$ dimensional manifold of those points of the phase space Γ which represents normalized state with the given expectation energy, and it is not reducible to a simple form. Moreover the total volume of the manifold, and thus the normalization constant V_{FEED}, can not be calculated analytically.

3.6 THE CONNECTION WITH THE CLASSICAL ERGODIC PROBLEM

The starting point is that the exact statistical characterization of a single isolated system is given by its particular Pure State Distribution: this means that the actual populations P_0 are fixed and “arbitrary”, in the sense that there are no reasons to assign them a particular functional dependence on the corresponding energy eigenstate or on some others parameters of the problem. The equilibrium distribution on the phases is uniform, that is, all set of phases is, at the equilibrium, equally probable. Notice that this is equivalent to the “random phases hypothesis” of standard quantum statistical mechanics but in this context there are no reasons to postulated it since it emerges naturally from the definition of the pure state distribution itself. However it turns out that quantity of interest averaged over the PSD depend on the particular set of population, and we are not able to specify it. As we have discussed in the previous sections, we can in the best case define ensemble of pure states, each of them with its own population set and introduce a probability measure on this set. This allows to consider the following question:

Since the PSD average of an observable depends on the particular set of population, what is a “typical” set which satisfies a given constraint, for example a given total energy?

We can answer this question by considering the FEE or the RPS Ensemble which give us a probability distribution $p(P) = p(P_1,...,P_K)$ on the set of the K independent populations. Thus if we are interest in studying properties of a “typical” pure state, for example the state of a subsystem, we should choose the population set in a region of high probability.

However, the critical point is that now we do not have any logical connection between the average value of a function of interest with respect to the Ensemble Distribution and the actual equilibrium value of such a function which is defined by its asymptotic time average.

The problem of replacing the dynamical average of an observable with statistical average with respect to an appropriate equilibrium probability distribution is the main point of the ergodic theory. The theorem of Birkhoff, (see Section 2.3), rigorously proves that this is actually possible by choosing as equilibrium probability distribution the uniform distribution over the ergodic subspace of the considered system, that is the portion of the entire phase space which is invariant and metrically indecomposable. While in the classical framework the identification of such metrically indecomposable regions of the phase space is a very difficult task, we have emphasized that in the quantum case the solution of this problem is straightforward. By considering the time evolution of an isolated quantum system the ergodic subspace is easily individuate as the region characterized by a fixed set of populations coordinates, and this leads to the definition of the PSD.

However, in quantum as in classical mechanics, when one ask about the equivalence between time and phase space average one want consider almost always the averages of phase functions on a given surface of constant energy (microcanonical average). With reference to this point it is also interesting to note that the natural quantum counterpart of the constant energy surface which defines the classical microcanonical ensemble appear to be the Fixed Expectation Energy Ensemble. This is strongly suggests by the formal analogy which exists between the Schrödinger equation written for the phase space coordinates, eq. (3.3.4), and the classical Hamiltonian equation of motion. The problem is that the subspace defined by having constant energy is not in general metric indecomposable so that replacing time averages with averages over the space of constant total energy (microcanonical distribution) cannot be rigorously justified. As Ruelle commented (reported as it is cited in ref. [Gallavotti, (2008)])

"… while one would very happy to prove ergodicity because it would justify the use of Gibbs' microcanonical ensemble, real system perhaps are not ergodic but behave nevertheless in much the same way and are well described by Gibbs' ensemble…"

Nonetheless, since in the quantum mechanical framework the clear identification of the metrically indecomposable region of the phase space is possible, one can analyze such a problem from a closer perspective then in the classical case: indeed one should not only take the average over the microcanonical ensemble, but instead look at the dependence of the equilibrium distribution of the quantity of interest on the particular Pure State Distribution.

The resulting analysis will lead us to a solution of the puzzle which is close in spirit to an argument which is also present in the classical formulation of the ergodic theory. In this context the problem is that, on the one hand there will exist almost always some other free integral of motion, independent from the energy constraint, which in theory should be considered when performing the phase space average. On the other hand the wide applicability of statistical mechanic and Gibbs' distributions are out of doubt and call for a physical justification. We briefly recall the central argument to overcome this apparent duality in classical mechanic, along the line drawn by Khinchin, because it gives a useful perception of the statistical nature of the problem. For a more detailed and rigorous treatment of this point we refer the reader to ref. [Khinchin, (1949)]. The main idea is that

1. The majority of physical phase functions which are of interest in statistical physics have a specific structure which makes the value of these functions on the energy surface very near each other at all point except for a set of very small measure.

2. If I is an integral of motion different from the energy integral which has a structure as in 1 then the possibility of replacing time integral with phase average does exist. On the other hand, if I does not have such a structure, the phase function which it represents does not have, as a rule, an actual physical interpretation so that the relation between its different averages have no interest.

These qualitative considerations seem to move the core of the problem from the structure of the phase space to the property of the phase functions in which we are interested in. In classical statistical mechanics these function are typically "sum-functions", i.e. the sum of functions each depending on the dynamical coordinates of only one component. This is surely not the case for quantum phase functions because the state vector $\left|\psi\right\rangle$ describe the entire system and the state vectors of the smaller "components" is not defined at all. However the same arguments (1 and 2) could apply also in this case even if for different reasons. The phase functions we are interested in are indeed sum functions with respect to the global populations, e.g. the Shannon entropy defined in eq. (2.3.12), even if we consider observable referring to one small subsystem, e.g. the equilibrium average RDM eq. (2.4.12).

It is a matter of fact that from the standard quantum statistical mechanics one has the intuition that at least some state functions, which we could call "thermodynamic functions", e.g. the entropy, should not depend on the detail of the quantum state, that is on the particular choice of the populations, but only on other thermodynamic properties such as the energy. Therefore the following further question suggest itself

Do they exist functions whose PS average is approximately the same regardless of the specific set of populations considered? Stated differently: Are some functions of the populations actually independent on the set of populations and dependent only on the fixed energy constraint?

If this is the case this could be the *definition* of what we can call a thermodynamic function. If we denote the global probability distribution on the ensemble phase space as $p_{ED}\left(P,\gamma\right)$ we want to see whether and when

$$\left\langle \cdot \right\rangle_{PSD} = \left\langle \cdot \right\rangle_{ED}$$

Given the inherent complexity of the derived probability density, in order to investigate the properties of the introduced ensembles, and the behavior of the phase functions of interest, we will take two different (complementary) approaches

1. Explicit numerical calculations for simple model systems (ensemble of non interacting $1/2$ spins, harmonic oscillators) by using Monte Carlo sampling techniques. This will permit to numerically generate a statistical sample from the above derived probability density and thus to study the ensemble distribution of some functions of interest.
2. Development of approximate simpler forms of the ensemble distributions valid under certain conditions. Analytical approximations of the geometrical distributions are important to study as the mean value (and the successive moments) of the ensemble distribution of some phase functions depends on the parameters of the problem. They are also necessary in order to consider the limiting behavior for dimension N arbitrarily large which can not be approached by direct numerical calculations.

These two points which are the technical bases which permits further reasoning on the statistical characterization of quantum states will be presented in the next Chapter.

APPENDIX 3.1: BASIC GEOMETRICAL DEFINITIONS: METRIC, VOLUME ELEMENT AND INTEGRATION

The geometrical properties of a space are in general specified by its so called metric which allows one to compute quantities based on lengths and angles from coordinates, [Dubrovin, (1985)].

A3.1.1 LINE ELEMENT AND METRIC TENSOR

Let us first consider a M real dimensional space $\mathbb{R}^M$ whose elements (vectors) are M -tuples of real numbers

$$x := \left\{ \left(x^1,..,x^M \right) \ \middle| x^i \in \mathbb{R} \right\} \tag{A3.1.1}$$

Moreover we assume that such a space has an Euclidean metric such that the norm of the vector x is given as $\|x\| := \sqrt{\langle x|x \rangle}$, where

$$\langle x|x \rangle = \sum_{k=1}^{M} \left(x^k \right)^2 \tag{A3.1.2}$$

Let us now consider a curve in this space defined parametrically as

$$\begin{aligned} x^1 &= f^1(t) \\ &\vdots \\ x^{2N} &= f^{2N}(t) \end{aligned} \tag{A3.1.3}$$

and ask about its length. First define the tangent vector as

$$v(t) = \left(\frac{dx^1}{dt},...,\frac{x^M}{dt} \right) \tag{A3.1.4}$$

The length of a portion $[a,b]$ of the curve parameterized by t is then defined as the integral of the norm of this vector (which is also known as velocity vector giving the intuitive meaning of the length measure)

$$l=\int_a^b \sqrt{\langle v(t)|v(t)\rangle}dt=\int_a^b \|v(t)\|dt=\int_a^b \sqrt{\sum_{k=1}\left(\frac{dx^k}{dt}\right)^2}dt=\int_a^b \sqrt{dl^2} \tag{A3.1.5}$$

where the line element is written in term of the Euclidean coordinates $\{x\}$ as

$$dl^2=\left(dx^1\right)^2+...+\left(dx^M\right)^2 \tag{A3.1.6}$$

It can be shown, but it is just what one naturally expects, that the length of the segment does not depend on the velocity we use to go from a to b. Moreover it should not depend on the choice of the coordinates we use to describe the space. To properly account for this invariance property one introduces the metric tensor g_{ij}. This is the unit tensor when Euclidean coordinates are used

$$g_{ij}^{(x)}=\delta_{ij} \tag{A3.1.7}$$

Consider to switch from the Euclidean coordinates x to another set of generic coordinates $z\equiv\left(z_1...,z_M\right)$, with the transformation defined through a set of functions $x^i=x^i\left(z\right)$ for $i=1\div M$. We suppose also that along the curve the transformation is not singular, that is with a non vanishing determinant for the corresponding Jacobian matrix

$$\det\left(\frac{\partial x^i}{\partial z^j}\right)=\det\begin{pmatrix}\frac{\partial x^1}{\partial z^1} & \cdots & \frac{\partial x^1}{\partial z^M}\\ \vdots & & \vdots\\ \frac{\partial x^M}{\partial z^1} & \cdots & \frac{\partial x^M}{\partial z^M}\end{pmatrix}\neq 0 \tag{A3.1.8}$$

Then, the differential displacement of the components can be specified as

$$dx^j=\sum_k \frac{\partial x^j}{\partial z^k}dz^k \tag{A3.1.9}$$

and therefore the square infinitesimal length, eq. (A3.1.6), can be specified in the new variables

$$dl^2=\sum_{kj} g_{kj}\left(z\right)dz^k dz^j \tag{A3.1.10}$$

with in general a metric tensor which is not the unit tensor and can be z-dependent. Its components in the new representation are given by

$$g_{kj}(z)=\sum_{ih}\frac{\partial x^i}{\partial z^k}g_{ih}(x)\frac{\partial x^h}{\partial z^j} \tag{A3.1.11}$$

where $g_{ik}(x)=\delta_{ik}$ if x are the Euclidean coordinates.

The integration along the curve $z(t)=z(x(t))$ provides a length measure which is independent on the choice of the variables. Furthermore, if one introduces another set of coordinates y with the corresponding transformation law $z=z(y)$, by following the same previously illustrated procedure, one obtains the infinitesimal length in the y-coordinates

$$dl^2=\sum_{kj}g_{kj}(y)dy^k dy^j \tag{A3.1.12}$$

with the following relation

$$g_{kj}(y)=\sum_{ih}\frac{\partial z^i}{\partial y^k}g_{ih}(z)\frac{\partial z^h}{\partial y^j} \tag{A3.1.13}$$

which determines how the metric tensor changes with a transformation of variables.

In conclusion, by explicitly using the metric tensor in the definition of the length in the considered normed space, one can use any coordinate system without warning about the invariance of the distance which is naturally guaranteed by the corresponding transformation of the metric tensor.

A3.1.2. VOLUME ELEMENT, INTEGRATION AND PROBABILITY MEASURE

Having introduced the notion of length in our $\mathbb{R}^M$ space through the definition of the line element (A3.1.10) we can now define the volume element dV which can be integrated over a region $U\in\mathbb{R}^M$ of the space to give the volume of that region. This is defined as

$$dV:=\sqrt{g(x)}dx^1\wedge dx^2\wedge\ldots\wedge dx^M \tag{A3.1.14}$$

where g is the determinant of the metric tensor in the coordinate system $\{x\}$

$$g = \left|\det\left(g_{ij}(x)\right)\right| \tag{A3.1.15}$$

Eq. (A3.1.14) is what is called in differential geometry language a "volume form". The use of the antisymmetric wedge product instead of the symmetric product $dx^1 dx^2 ... dx^M$ is a technical refinement due to the orientation assigned to the region representing the domain of integration. The following equivalence

$$V = \int_U \sqrt{g(x)}dx^1 \wedge dx^2 \wedge ... \wedge dx^M = \int_U \sqrt{g(x)}dx^1 dx^2 ... dx^M \tag{A3.1.16}$$

holds if the domain U is a positive oriented manifold, otherwise one has to change the sign of the last integral. From here on we will always omit the wedge product in specifying the volume element because we are only interest in the *measure*, that is, the absolute value of the volume (A3.1.16). The reason behind this is that probabilities are just particular measures which satisfy the conditions of positivity and normalization. On can easily justify the form $dV := \sqrt{g(x)}dx^1 dx^2 ... dx^M$ for the infinitesimal volume element by taking into account that

1. If x are Euclidean coordinates, $g_{ij} = \delta_{ij}$, then $g = 1$ and one recover the standard form $dV = dx^1 dx^2 ... dx^M$ for the volume element.

2. In the case of a general transformation of coordinates $z \to y$ the invariance of the measure implies the equivalence $\sqrt{g(z)}dz^1 dz^2 ... dz^M = \sqrt{g(y)}dy^1 dy^2 ... dy^M$. According to (A3.1.13) one has

$$\sqrt{\frac{g(y)}{g(z)}} = \left|\det\left(\frac{\partial z^i}{\partial y^j}\right)\right| \tag{A3.1.17}$$

   which is just the Jacobian determinant to change the integration variables well known from the multivariate calculus.

To make more clear this connection between measure and probability let us imagine that coordinate x describes a sample space U. Then the probability for a stochastic variable X to take values belonging to a certain region W of the sample space U is

$$P(W)=\int_{x\in W} p(x)dx \tag{A3.1.18}$$

where we have assumed the existence of the probability density $p(x)$. Notice that $P(W)$ should be positive and normalized

$$P(U)=\int_{U} p(x)dx=1 \tag{A3.1.19}$$

Let us assume that coordinates x have been chosen in such a way that the probability $p(x)dx$ for an outcome with x^j in the infinitesimal interval between x^j and x^j+dx^j for all $j=1\div M$, is proportional to the geometrical volume element $dV:=\sqrt{g(x)}dx^1dx^2...dx^M$. Then, by tacking into account the normalization condition, (A3.1.19), we can specify the probability density as

$$p(x)=\frac{\sqrt{g}}{\int_{U}\sqrt{g}dx} \tag{A3.1.20}$$

In other words, probability is a concept that can be thought as strongly connected with the concept of geometrical measure as defined in eq. (A3.1.16), and by using this connection one can identify the probability distribution function with $\sqrt{g}$ up to a normalization factor.

A3.1.3. METRIC AND VOLUME ELEMENT ON A SURFACE

A K-dimensional surface in a domain of the M-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

$$\begin{aligned} &f_1\left(x^1,...,x^M\right)=0\\ &\vdots\\ &f_{2N-K}\left(x^1,...,x^M\right)=0 \end{aligned} \tag{A3.1.21}$$

The point $P \equiv \left(x_P^1, \ldots, x_P^{2N}\right)$ satisfying eq. (A3.1.22) is said to be non singular if the rank of the matrix $\left(\frac{\partial f_i}{\partial x^j}\right)_{x^i = x_P^i}$ (where $i = 1, \ldots, 2N - K, \quad j = 1, \ldots, 2N$) is equal to $\left(2N - K\right)$. In the neighborhoods of a non singular point one can introduce local coordinates $\left(z^1, \ldots, z^K\right)$ which parametrically defines the surface in the considered point

$$\begin{aligned} & x^1 = z^1 \\ & \vdots \\ & x^K = z^K \\ & x^{K+1} = x^{K+1}\left(z^1, \ldots, z^K\right) \\ & \vdots \\ & x^{2N} = x^{2N}\left(z^1, \ldots, z^K\right) \end{aligned} \tag{A3.1.23}$$

It can be shown, ref. [Dubrovin, (1985)], that the metric of the space induced a metric on the embedded surface; the corresponding metric tensor is given by

$$g_{kk'}\left(z\right) = \sum_{ij=1}^{M} \frac{\partial x^i}{\partial z^k} g_{ij}\left(x\right) \frac{\partial x^j}{\partial z^{k'}} \tag{A3.1.24}$$

where $k, k' = 1, \ldots, K$. As before, once the metric on the surface is known, one can specify the line element, eq. (A3.1.12), and the volume element with the corresponding measure, eq. (A3.1.16).

APPENDIX 3.2: VOLUME AND SURFACE AREA OF THE HYPERSPHERE

As already mentioned in Section 3.3 the normalization condition defines a hypersphere on which the normalized vectors lie. Let us thus consider a hypersphere embedded in a M-dimensional Euclidean space

$$S^{M-1} = \left\{ x \in \mathbb{R}^M \left| \|x\| = R \right. \right\} \tag{A3.2.25}$$

In order to calculate the surface volume one switches to spherical coordinates $\{x_1, \ldots, x_M\} \to \{r, \phi_1, \ldots, \phi_M\}$

$$\begin{aligned} x_1 &= r\cos\phi_1 \\ &\vdots \\ x_J &= r\prod_{i=1}^{J-1}\sin\phi_i \cos\phi_J \\ &\vdots \\ x_M &= r\prod_{i=1}^{2N-1}\sin\phi_i \end{aligned} \tag{A3.2.26}$$

where

$$\begin{aligned} &\phi_J \in [0,\pi] \quad for \;\; 1 \le J \le M-2 \\ &\phi_{M-1} \in [0,2\pi] \end{aligned} \tag{A3.2.27}$$

The determinant of the Jacobian matrix of the transformation specified in eq. (A3.2.26) can be evaluated, ref. [Hassani, (1999)], and reads

$$\left|\det J\left(r\phi\right)\right| = r^{M-1}\prod_{J=1}^{M-2}\left(\sin\phi_J\right)^{M-1-J} \tag{A3.2.28}$$

Thus, the volume element transforms according to

$$\prod_{i=1}^{M} dx_i = r^{M-1} dr \prod_{J=1}^{M-2}\left(\sin\phi_J\right)^{M-1-J} d\phi_J \, d\phi_{M-1} = r^{M-1} dr d\Omega \tag{A3.2.29}$$

where $d\Omega$ contains the dependence on the angular variables and it is the surface element. By integrating the radial displacement one obtains $V_{M-1} = \frac{R^M}{M} S_{M-1}$. The total surface, $S_{M-1} = \int d\Omega$, can be written in terms of the following standard integrals [Dwight, (1961)]

$$I(p) = \int_0^{\pi} \sin^p x dx = \frac{\pi^{1/2}\Gamma\left(\frac{p+1}{2}\right)}{\Gamma\left(\frac{p}{2}+1\right)} \tag{A3.2.30}$$

where $\Gamma(x)$ denotes the Gamma function. Indeed

$$S_{M-1} = \int_0^{2\pi} d\phi_{M-1} \prod_{J=1}^{M-2} \int_0^{\pi} \left(\sin\phi_J\right)^{M-1-J} d\phi_J = (2\pi) I(M-2) I(M-3)\ldots I(2) I(1) \tag{A3.2.31}$$

Thus, by using eq. (A3.2.30), one readily finds

$$S_{M-1} = \frac{(2\pi)\pi^{\frac{M}{2}-1}}{\Gamma\left(\frac{M}{2}\right)} \tag{A3.1.32}$$

CHAPTER 4

DISTRIBUTION OF THE POPULATIONS IN RANDOM QUANTUM STATE:

ANALYTICAL APPROXIMATIONS VS MONTE CARLO SAMPLING

4.1 INTRODUCTION

In this chapter the technical methodologies necessary to investigate the Ensemble Distributions introduced in Chapter 3 are developed. On the one hand approximate forms of the distributions relative to the Random Pure State Ensemble and the Fixed Expected Energy Ensemble are introduced following the idea of W. K. Wootters in *Random quantum states* (Foundations of Physics, 20, 1365, (1990)). On the other hand Monte Carlo numerical sampling of the geometrical distributions is introduced in order to compare the geometrical distributions with the approximate ones. This chapter deals in particular with the validation of the numerical sampling methods as well as the analytical approximation of the distribution. The comparison between the two methodologies is made at the level of the resulting marginal distribution for the single population for both the ensembles. The tools here developed will be apply in the next chapters to the study of the ensemble distributions of some observable pertinent to a spins system and they furnish the basis for discussing the statistical thermodynamic associated to the introduced ensemble.

4.2 CHARACTERIZATION OF THE ENSEMBLE DISTRIBUTIONS BY MONTE CARLO SAMPLING

In order to obtain the average value of any function of the quantum state, i.e. a function $f\left(P,\alpha\right)$ of the parameters $P\equiv\left(P_1,P_2...P_K\right)$ and $\alpha\equiv\left(\alpha_1,\alpha_2,...\alpha_N\right)$, one has to numerically evaluate multidimensional integrals of the type

$$I=\left\langle f\left(P,\alpha\right)\right\rangle=\int_D f\left(P,\alpha\right)p\left(p,\alpha\right)dPd\alpha \tag{4.2.1}$$

with an estimate of the error and in a reasonable number of iterations S (number of steps). The parameter K is the number of independent populations in the considered ensemble, that is $K_{RPSE}=N-1$ and $K_{FEEE}=N-2$. We shall focus only on the ensemble probability distribution function of the populations, because we have already established that the phases are statistical independent and uniformly distributed either in the PSD as in the ED, indeed

$$p\left(P,\alpha\right)=\frac{p\left(P\right)}{\left(2\pi\right)^N} \tag{4.2.2}$$

We can thus easily evaluate the following

$$f_P\left(P\right)=\frac{1}{\left(2\pi\right)^N}\int_0^{2\pi}d\alpha_1...\int_0^{2\pi}d\alpha_N\, f\left(P,\alpha\right) \tag{4.2.3}$$

so reducing eq. (4.2.1) to

$$I=\left\langle f_P\left(P\right)\right\rangle=\int_D f_P\,\left(P\right)p\left(P\right)dP \tag{4.2.4}$$

However the populations Ensemble Distribution, $p\left(P_1,...P_K\right)$, is still a function of K variables which does not factorize, so we have to consider multi-dimensional integration techniques. To study this class of problems deterministic methods of numerical integration (e.g. Newton-Cotes formulae, Gaussian quadratures) are practically useless because the error scales as $S^{-c/d}$ where c is a constant which depend on the method (typically 2 or 4), S is the number of nodal point in the domain of the function, while d denotes the dimension of the considered problem. The wide class of Monte Carlo sampling techniques allow to generate points according to the target ensemble distribution $p\left(P_1,...P_K\right)$. One can thus obtain a statistical sample of the distribution and can ask about the form of marginal distributions

$$p(P_J) = \int_D p(P_1,\ldots P_K) \prod_{i \neq J} dP_i \tag{4.2.5}$$

which can be obtain by making an histogram of the sampled points, or any expected value of phase functions. If we denote as $P^{(i)} \equiv \left\{ P_1^{(i)} \ldots P_K^{(i)} \right\}$ a point of the phase space generated from the wanted distribution, the Monte Carlo estimate of the integral I is given by

$$E = \frac{1}{S} \sum_{i=1}^{S} f_P\left(P^{(i)}\right) \tag{4.2.6}$$

where S is the number of generated point. The law of large number ensures that the estimate converges to the true value as $S \to \infty$. Furthermore, the error on the evaluation of the integral scales as $S^{-1/2}$ regardless of the dimension of the problem.

The choice of the particular algorithm to obtain the statistical sample depends on the target probability distribution. In the following paragraphs we shall separately describe two different methods which are used for sampling the Random Pure State Distribution and the Fixed Expected Energy Distribution of the populations. However let us first introduce the basic idea which permits to derive an analytically tractable but approximate form for the populations distribution $p(P_1,\ldots P_K)$.

4.3 APPROXIMATE DISTRIBUTION OF POPULATIONS FROM MINIMIZATION OF THE INFORMATION FUNCTIONAL

As we have seen before, the ensemble we consider are defined by some constraints. These constraints define a hyper surface in the Hilbert space whose metric properties determines the geometrical distributions. Now we want to use such a constraints as conditions which has to be *approximately* satisfied and then check a posteriori the goodness of our approximation. Imagine to have a set of N random variables $x \equiv (x_1,\ldots,x_N)$ each defined in the domain $[0,\infty]$. We want to find a normalized probability distribution $W(x)$ requiring that, on average, the sum of our variable x is equal to the unity, that is

$$\sum_{k=1}^{N} \langle x_k \rangle = 1 \tag{4.3.1}$$

$$\langle x_k \rangle = \int_0^\infty dx W(x) x_k \qquad \text{where} \qquad dx = \prod_{k=1}^{N} dx_k \tag{4.3.2}$$

The set $x \equiv (x_1, ..., x_N)$ is not strictly an allowed set of populations, because the condition (4.3.1) does not assures that $\sum_{k=1}^{N} x_k = 1$ is true for every single realization of the process of generating x. However we shall construct a probability distribution for this set and check if this could be an approximate form of the geometrical distribution on the "real" populations. Eventually we can formulate a further condition, that is, we require the energy expected values calculated with the variable x to be "on average" equal to some value E

$$\sum_{k=1}^{N} E_k \langle x_k \rangle = E \tag{4.3.3}$$

Of course the probability density has to be normalized

$$\int_0^\infty dx W(x) = 1 \tag{4.3.4}$$

The conditions (4.3.1), (4.3.4) does not specify a unique probability function. The general problem of the specification of the probability function in the absence of guideline for a full characterization of it is as old as the theory of probability itself. The "Principle of Insufficient Reason" of Laplace was an attempt to supply a criterion of choice for the probability if no other stronger reasons are available. The development of information theory and statistical inference has lead to the maximum entropy principle as the rule which permits to determine the less biased distribution according to our initial information. This principle states that, among the infinite set of function $W(x)$ which satisfy our constraints, it is reasonable to choose that which minimize the informational functional, (or equivalently which maximizes the corresponding Shannon entropy functional)

$$I[W] = \int W(x_1, ..., x_N) \ln W(x_1, ..., x_N) \prod_{k=1}^{N} dx_k \tag{4.3.5}$$

Where $I[W]$ denotes a functional dependence of the information content I on the distribution $W(x)$. The minimization procedure has to be performed under the given constraints on the average values eqs. (4.3.1), (4.3.3). For an interesting discussion of this principle and its relation with the field of statistical mechanics we refer the reader to the paper written by Jaynes, [Jaynes (1957)]. The maximum entropy distribution has the property that no possibility is ignored; it assigns positive weight to every situation that is not absolutely excluded by the given information, i.e. the constraints. In other word we select the most homogeneous distribution compatible with the given constraints.

The minimization under constraints can be performed by using the method of Lagrange Multiplier, that is, we introduce three Lagrange multiplier which corresponds to the three constraints eqs. (4.3.1), (4.3.3) and (4.3.4), and thus minimize the following functional

$$\begin{aligned} F[W] &= I[W]-\lambda\left(\sum_k \langle x_k\rangle -1\right)-\mu\left(\sum_k \langle x_k\rangle E_k -U\right)-\eta\left(\int W(x)dx-1\right)= \\ &= \int dxW(x)\left[\log W(x)-\lambda\sum_k x_k-\mu\sum_k E_k x_k-\eta\right]+\lambda+\mu U+\eta \end{aligned} \tag{4.3.6}$$

The functional derivatives which has to be set to zero results in

$$\frac{\delta F[\mathcal{W}]}{\delta \mathcal{W}(\mathbf{x})}=-\log \mathcal{W}(\mathbf{x})-1-\lambda\sum_k x_k-\mu\sum_k E_k x_k-\eta=0 \tag{4.3.7}$$

leading to the a distribution factorized in N independent exponential distributions

$$\begin{aligned} W_{FEEE}(x) &= \prod_{k=1}^{N} W_{FEEE}^{k}(x_k) \\ W_{FEEE}^{k}(x_k) &= \frac{e^{-(\lambda+\mu E_k)x_k}}{(\lambda+\mu E_k)} \end{aligned} \tag{4.3.8}$$

The Lagrange parameters λ and μ are implicitly determined by the following equations

$$\begin{aligned} \sum_{k=1}^{N}\frac{1}{(\lambda+\mu E_k)} &= 1 \\ \sum_{k=1}^{N}\frac{E_k}{(\lambda+\mu E_k)} &= E \end{aligned} \tag{4.3.9}$$

Eq. (4.3.8) is the candidate approximate distribution for the FEE Ensemble. For the RPS Ensemble one follows the same procedure but by considering only the constraints (4.3.1) and (4.3.4). The resulting distribution is factorized into identical exponential distributions for all the components of the random vector x

$$\begin{aligned} W_{RPSE}\left(x\right) &= \prod_{k=1}^{N} W_{RPSE}^{k}\left(x_k\right) \\ W_{RPSE}^{k}\left(x_k\right) &= Ne^{-Nx_k} \end{aligned} \tag{4.3.10}$$

The distributions (4.3.10) for the Random Pure State Ensemble and (4.3.8) for the Fixed Expectation Energy Ensemble are exactly the distributions proposed by Wootters in ref. [Wootters, (1990)] on the basis of different type of considerations. The important feature of these distributions is that they are factorized into single variable distributions. This can never be strictly correct if the random variables are identified with the set of populations, which are not statistically independent due to the constraints. Nevertheless we shall compare these approximate forms of the Ensemble Distributions $W\left(x\right)$ with the numerical sample of the exact ones $p(P)$ derived in the previous chapter for the two Ensembles.

4.4 RANDOM PURE STATE ENSEMBLE DISTRIBUTION:

4.4.1 DIRECT NUMERICAL GENERATION OF THE SAMPLE

As we have seen the $\left(N-1\right)$ independent populations in the Random Pure State Ensemble are uniformly distributed on the simplex defined by the normalization condition $\sum_{k=1}^{N} P_k = 1$.

However if we draw independently $\left(N-1\right)$ populations from the uniform distribution on the possible domain $\left[0,1\right]$ it is clear that the last population, say $P_N = 1 - \sum_{k=1}^{N-1} P_k$, will very likely falls outside the allowed domain.

Nonetheless, the problem of drawing samples from the uniform probability distribution on the N-simplex can be solved directly by a change of variable as explained in the following. One can parameterize the N populations in terms of $N-1$ independent azimuthal angles $\theta_k \in \left[0, \pi/2\right)$ as

$$
\begin{aligned}
&P_1 = \cos^2\theta_1 \\
&\vdots \\
&P_J = \cos^2\theta_J \prod_{i=1}^{J-1} \sin^2\theta_i \\
&\vdots \\
&P_N = \prod_{i=1}^{N-1} \sin^2\theta_i
\end{aligned}
\tag{4.4.1}
$$

This transformation is suggested by the Hurwitz parameterization of the unitary group, see [Życzkowski, (1999), (2001)]. The Jacobian determinant of the transformation reads

$$\{P_1,\dots,P_{N-1}\} \to \{\theta_1,\dots,\theta_{N-1}\}$$

$$J = \prod_{k}^{N-1} 2\cos\theta_k \left(\sin\theta_k\right)^{2(N-k)-1}$$

This means that one can generate populations uniformly on the N simplex by generating independently $(N-1)$ angles according to the probability density

$$p(\theta_k) = 2(N-k)(\sin\theta_k)^{2(N-k)-1}\cos\theta_k \tag{4.4.2}$$

For the k-th angle. To simplify the task we can look for a one dimensional mapping in order to obtain θ as a function of uniformly distributed random variable $0<\xi\le 1$, say $\theta=\phi(\xi)$. By considering that

$$\langle f(\theta)\rangle = \int_0^{\pi/2} f(\theta)\,p(\theta)\,d\theta = \int_0^1 \left[f(\theta)\,p(\theta)\right]_{\theta=\phi(\xi)} \frac{d\theta}{d\xi}\,d\xi = \int_0^1 f(\phi(\xi))\,\hat{p}(\xi)\,d\xi$$

one has $\hat{p}(\xi) = p(\theta(\xi))\dfrac{d\theta}{d\xi}$. Thus we have to find a map $\phi(\xi)$ such that $\hat{p}(\xi) = \text{cost}$, that is

$$\phi'(\xi) = \frac{d\theta}{d\xi} = \frac{1}{p(\theta)}.$$

This leads to the following auxiliary set of variables [Życzkowski, (1999)]

$$\xi_k = \left(\sin\theta_k\right)^{2(N-k)} \tag{4.4.3}$$

that satisfy the previous condition, since their derivative

$$\frac{d\xi_k}{d\theta_k} = 2(N-k)(\sin\theta_k)^{2(N-k)-1}\cos\theta_k$$

is exactly the probability density eq.(4.4.2). In other words we can sample the uniform distribution of the populations in the N dimensional simplex with the following two step algorithm:

1. Draw $(N-1)$ random numbers ξ_k, each of them uniformly distributed within $[0,1]$

2. By virtue of eqs. (4.4.1), (4.4.3), the populations are calculated as

$$\begin{aligned}
&P_1 = 1-\xi_1^{\frac{1}{N-1}}\\
&\vdots\\
&P_J = \left(1-\xi_J^{\frac{1}{N-J}}\right)\prod_{i=1}^{J-1}\xi_i^{\frac{1}{N-i}}\\
&\vdots\\
&P_N = \prod_{i=1}^{N-1}\xi_i^{\frac{1}{N-i}}
\end{aligned} \tag{4.4.4}$$

4.4.2 MARGINAL DISTRIBUTION ON A SINGLE POPULATION IN THE RPSE

It is interesting to note that a random pure state drawn according to the unitarily invariant measure on the hypersphere, (a random pure state from the RPSE) can also be found as a raw, or a column, of a realization of the Unitary Random Matrix Ensemble, [Życzkowski, (1994)]. We shall follow the methodology illustrated in [Pereyra, (1983)] in order to obtain the exact marginal distribution of a single population, eq.(4.2.5), by direct integration of the complete populations' distribution of the RPSE, eq. (3.4.20). By using iteratively the analytical integral

$$\int_a^b (a_J-P)^n\,dP = \left[\frac{(a_J-P)^{n+1}}{-(n+1)}\right]_a^b \tag{4.4.5}$$

one derives the following joint probability density on K populations of the Random Pure State Ensemble

$$p_{RPSE}\left(P_1 \ldots P_K\right) = \left(N-1\right)! \int_0^{b_K} dP_{K+1} \ldots \int_0^{b_{N-2}} dP_{N-1}\, p_{RPSE}\left(P_1, \ldots P_{N-1}\right) = \frac{\left(N-1\right)!}{\left(N-K-1\right)!} b_K^{\left(N-K-1\right)} \qquad (4.4.6)$$

where $b_K = 1 - \sum_{j=1}^{K} P_j$.

For the single state population one thus obtains

$$p_{RPSE}\left(P_J\right) = \left(N-1\right)\left(1-P_J\right)^{N-2} \qquad (4.4.7)$$

which gives the following average population

$$\left\langle P_J \right\rangle = \frac{N-1}{\left(N-2\right)^2 + 3N + 2} \overset{N>>1}{\approx} \frac{1}{N}$$

where the relative error between the exact value and N^{-1} is less then 0.1 for $N > 10$. By considering the equivalence of the N variables and by knowing that their mean value is of the order of $O\left(N^{-1}\right)$, we can expand the logarithm of (4.4.7) under the assumption $N >> 1$, to obtain

$$p_{RPSE}\left(P_J\right) \approx N e^{-NP_J}$$

which is exactly the approximate distribution $W_{RPS}^{k}\left(P_k\right)$, eq. (4.3.10), derived before.

In Figure 4-1 the comparison is made between the marginal probabilities obtained from the numerical sampling and from the exponential approximate form $W_k^R\left(P_k\right)$, eq. (4.3.10). The approximation became rather good also for Hilbert space of low dimensions, say $N = 8$.

On the basis of these results, it is interesting to look at the statistical behaviour of the sum of the N random variables $x \equiv \left(x_1, \ldots, x_N\right)$ each of them defined in the domain $\left[0, \infty\right]$ and distributed according to eq. (4.3.10). If we define

$$X = \sum_{k=1}^{N} x_k \qquad (4.4.8)$$

we see that, by virtue of the Central Limit Theorem (see Appendix 4.4), X is a normally distributed random variable with mean $\langle X\rangle = 1$, and variance which scales with the dimension N

$$\left\langle \left(X-\langle X\rangle\right)^2\right\rangle = \sum_{k=1}^{N}\left\langle x_k^2\right\rangle + \sum_{k,k'\neq k}^{N(N-1)}\left\langle x_k x_{k'}\right\rangle - 1 = \frac{1}{N} \tag{4.4.9}$$

In other words, as N become very large, the condition of normalization “on average”, eq. (4.3.1), becomes *effectively* a condition on the normalization of each realization of the set. However the exact equivalence is found only in the limit $N \to \infty$. This also means that exactly normalized populations $\{P_1,\dots,P_N\}$, even if they never are strictly statistically independent due to the normalization requirement, *tend to* be independent as the dimension N increases.

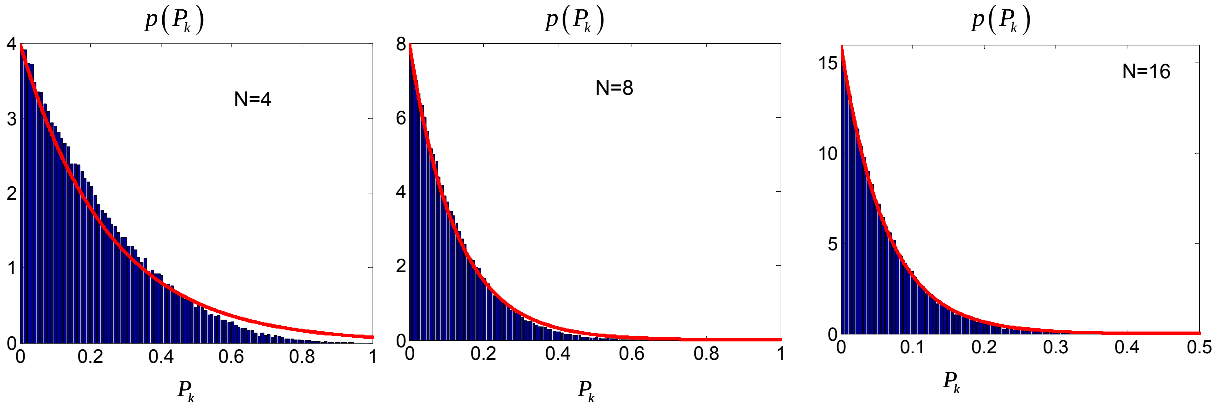


Figure 4- 1: Marginal Distribution of a Single Population in the RPSE: the (normalized) histograms refers to the statistical sample of 10^5 points (in 100 bins) generated by the algorithm described in the text for a system with N equally spaced energy levels. The red lines depicts the corresponding approximate distributions, eq. (4.3.10).

4.5 FIXED EXPECTATION ENERGY ENSEMBLE DISTRIBUTION: MC (MONTE CARLO) METHODS

First notice that we cannot calculate analytically the total volume of the FEEE and thus we do not know the normalization constant of the FEEE distribution. Monte Carlo Markov Chains (MCMC) are methods for drawing a sample from a given multivariate probability distribution (the target distribution) which are known up to a normalizing constant, [Chib, (1995)]. On the other side MCMC methods introduces other difficulties which we briefly discuss in the following, together with the basic theory and the implementations for the problem considered here.

4.5.1 BASIC THEORY OF MARKOV CHAIN

A stochastic process is Markovian if the transition probability between different values of the stochastic (vector) variable X in the corresponding phase space Γ depends only on the stochastic variable’s current state. A Markov chain refers to a sequence of random variables $\left(X_1,...X_t\right)$ generated by a Markov process. A particular chain is defined by its transition kernel, which represents (conditional) probability of moving from a point of the phase space X to another position, say Y. Given some initial distribution $f_{(0)}\left(X\right)$ for the Markov chain and a transition kernel $K\left(X\left|Y\right.\right)$ the probability distribution function for the chain at time t is:

$$f_{(t)}\left(Y\right)=\int K\left(X\left|Y\right.\right)f_{(t-1)}\left(X\right)dX \tag{4.5.1}$$

The main points of Markov chain theory is to determine under which conditions an invariant distribution of the chain exists

$$\int K\left(X\left|Y\right.\right)\pi\left(X\right)dX=\pi\left(Y\right) \tag{4.5.2}$$

and iterations of the transition kernel converges to it

$$f_{(t)}\left(Y\right)\to\pi\left(Y\right)\quad as\quad t\to\infty \tag{4.5.3}$$

The main theorem [Chib, (1995)] asserts that in order to have convergence of the distribution, the chain needs to be irreducible and aperiodic: this means that if X and Y are in the domain of π it is possible to move from X to Y in a finite number of iterations with non zero probability, and the number of moves needs not to be a multiple of some integer.

MCMC turns the theory around: the invariant distribution is fixed and known (it is the target distribution from which one want to draw a sample) but the transition kernel is unknown. To generate a sample from π, the methods find and utilize a transition kernel whose t-th iterate converges to the distribution of interest for large t. That is, if the chain runs for enough number of steps the distribution of the observations generated from the simulation is approximately the target distribution. The point is to find a suitable transition kernel.

4.5.2 METROPOLIS HASTINGS ALGORITHM

The Metropolis-Hastings updating scheme was first described by Hastings [Hastings, (1970)] as a generalization of the Metropolis algorithm of Metropolis et al [Metropolis, (1953)].

Consider the following form of a transition kernel to a state Y of the chain which lies within some set A

$$K\left(X\middle|A\right)=\int_A p\left(X,Y\right)dY+r\left(X\right)I_A\left(X\right) \tag{4.5.4}$$

Here $p\left(X,Y\right)$ is the density associated with selecting a point which is accepted while

$$r\left(X\right)=1-\int_D p\left(X,Y\right)dY \tag{4.5.5}$$

is the probability that the chain remains at the prior value X. $I_A\left(X\right)$ is the indicator function, which is 1 if $X\in A$ and zero otherwise. It can be shown [Tierney, (1994)] that if $p\left(X,Y\right)$ satisfies the detailed balance condition

$$\pi\left(X\right)p\left(X,Y\right)=\pi\left(Y\right)p\left(Y,X\right) \tag{4.5.6}$$

then $\pi\left(X\right)$ is the invariant density of $K\left(X\middle|Y\right)$. The Metropolis-Hasting algorithm gives an easy recipe to construct a markov chain with the required reversibility property eq. (4.5.6).

The algorithm is basically made up by the following steps

1. Start at an arbitrary point X which belong to the domain of π, with $\pi(X)>0$

2. Generate a random variable Y from an arbitrary but fixed proposal distribution $q(X,Y)$, this represents a proposed move from the state X to the state Y

3. Calculate what can be termed the probability of move

$$\alpha(X,Y)=\min\left[1,\frac{\pi(Y)q(Y,X)}{\pi(X)q(X,Y)}\right] \tag{4.5.7}$$

4. Generate a random variable u uniformly from $[0,1]$: if $u<\alpha$ accept the proposal and move to state Y. Otherwise reject the proposal and remain in X, the new sample equals the old one

Repeat 1-4.

Thus, by applying the Metropolis-Hastings updating scheme we sample from $q(X,Y)$ and then accept to move with probability $\alpha(X,Y)$, so that the transition probability is

$$p(X,Y)=q(X,Y)\alpha(X,Y) \tag{4.5.8}$$

One can easily verify that the probability density (4.5.8) satisfies the reversibility condition eq. (4.5.6) and thus the sampling converges to the target distribution.

Some remarks are in order:

Notice that the calculation of α does not require the normalization of the target distribution because this constant cancel out in the ratio.

If the proposal density is symmetric, i.e. $q(X,Y)=q(Y,X)$, the acceptance probability reduces to $\pi(Y)/\pi(X)$; hence, if $\pi(Y)>\pi(X)$, the chain moves to Y, otherwise it moves with probability given by $\pi(Y)/\pi(X)$. This latter is the algorithm originally proposed by Metropolis et al [Metropolis, (1953)].

Although this method must converge to the stationary distribution in the limit of infinite sample size, in practice the progress can be exceedingly slow especially in high dimensional problems. There are many empirical questions such as the number of initial steps that should be discarded from the statistic (the so called “burn in” period) or how long the sampling should be run. A chain is said to be poorly mixing if it stays in small regions of the phase space for long periods of time, as opposed to a well mixing chain that seems to happily explore the phase space. The rate of convergence is strongly dependent on the choice of the initial state of the chain and of the proposal distribution. In the following we briefly discuss three different possible choices that we have used in our calculations.

4.5.3 CHOICE OF THE PROPOSAL DISTRIBUTION $q(X,Y)$

There is an infinite range of choices for the proposal distribution q. In particular one has to choose either a particular *updating scheme*, that is, how the proposal distribution depends on the current state of the chain, and also the *parameters* defining the proposal distribution which can be tuned to reach a well behaving Markov chain. We shall restrict our attention to few special cases which we have applied to the here considered problem:

Random Walk chain (MCRW): in the random walk updating scheme the proposed new value Y equals the current values X plus a random variable Z:

$$Y = X + Z$$

In this case $q(X,Y) = g(Y - X) = g(Z)$ is the density associated to the random variable Z.

In the following we will use, as a common choice, a multivariate normal distribution $G_Z(\mu,\Sigma)$. This is the generalization of the Gaussian distribution for a multidimensional stochastic variable $Z \equiv (z_1, z_2 ... z_N)$

$$G_Z(\mu,\Sigma) = \frac{1}{(2\pi)^{N/2}(\det\Sigma)^{1/2}} \exp\left[-\frac{1}{2}(Z-\mu)^{\mathrm{T}}\Sigma^{-1}(Z-\mu)\right] \tag{4.5.9}$$

where μ is the vector of the average value of the components while Σ is the covariance matrix.

The variance (or in general the covariance matrix) of the proposal distribution can be thought of as a tuning parameter to be adjusted to get a good sampling of the target distribution. One has to consider at least two aspects: the acceptance rate (the percentage of accepted points) and the region of the sample space which is covered by the chain. In large dimension problem, this can become particularly difficult: if for example we take as proposal an N-dimensional normal distribution with unit variance the average radial displacement is roughly proportional to $\sqrt{N}$. That is, large step size which probably lands in a region of phase space with low probability or outside the boundary which defines the domain. In this case we should have a very small acceptance rate with a chain which remains “trapped” in a small region. To maintain a significant acceptance rate as the dimension increases we would have to scale the variance by a factor N: $\sigma^2 \to \sigma^2 / N$. On the other hand such a variance corresponds to a mean radial displacement of $\sigma / \sqrt{N}$, which is often very small compared to the scale of the distribution to be sampled; again we will end with a slow mixing chain. In the following when this scheme is used the proposal distribution will be a multivariate Gaussian with diagonal covariance matrix proportional to the average populations calculated on the basis of the approximate distributions eq. (4.3.8)

$$\begin{aligned}
&\Sigma_P \propto \sigma_k \mathbf{1}_{N-2} \\
&\sigma_k = \langle P_k \rangle = (\lambda + \mu E_k)^{-1}
\end{aligned}$$

this turns out to lead to very accurate predictions of the average values of the populations with respect to the geometrical distribution which we want to sample from. However, when the expectation energy is chosen rather low, this leads to populations much higher than the canonical ones which however represent a point with a positive weight. The point which represents canonical populations, as we will see, has to be considered as an “extreme” point of the phase space, i.e., it lies on the boundary of the domain. This entails that, if the chain is started on a point which is far from the centre of the distribution, as for example in a point near to the canonical one, many of the proposed steps drawn from $\mathrm{G}(0,\Sigma_P)$ are likely to be rejected.

<u>Independence Sampler chain (MCIS):</u> if $q(X,Y) = f(Y)$ then the candidate observation is drawn independently of the current state of the chain. In this case the probability of move is

$$\alpha(X,Y) = \min\left[1, \frac{w(Y)}{w(X)}\right]$$

where $w(Y) = \dfrac{\pi(Y)}{f(Y)}$ is the weight function which one would use in an important sampling. As in that case this can be efficient if $f(Y)$ produces a weight function as close as possible to a constant, that is, a function which well approximates the target distribution. Notice that the samples drawn according to this scheme are not independent from each other, because the probability to move depends on the current state. In the following we will use the above derived approximate distributions

$$f\left(P_1,\ldots P_{N-2}\right)=\prod_{k=1}^{N-2}\left(\lambda+\mu E_k\right)^{-1}e^{-(\lambda+\mu E_k)P_k} \tag{4.5.10}$$

as proposal. Since the population relative to the first eigenvalue has a peculiar distribution as shown by random walk results, we sample the last $N-2$ populations from the exponential distributions (4.5.10) and then determine the first two from the constraints.

We verifies that, for relatively low number of stochastic variables (10-30) this procedure and the random walk chain give coherent results. For higher dimension of the problem random walk became problematic and the independent chain can be more efficient in some cases, the acceptance rate however became smaller as the dimension of the problem increases.

Random Walk with adaptive proposal distribution (AP): Since from MCRW calculations, it turns out that the major difficulty as the number of populations increases and especially at low value of expectation energy, derives from the necessity of making moves which do not land outside the boundaries but large enough to cover in a reasonable number of steps the entire phase space, we will use an adaptive scheme introduced by Haario et al. [Haario, (1999)]. Basically the updating scheme is the same as in the Random Walk chain but the parameters of the proposal distribution are tuned along the chain according to the covariance calculated from a fixed number of previous states. In other words the proposal distribution depends on a certain "history" of the process and the chain is clearly not markovian. The convergence and irreducibility properties of such a chain are thus not obvious and are discussed in [Haario, (1999)]. Our implementation assume as proposal a multivariate Gaussian distribution $G\left(0,\Sigma\right)$ but now the covariance matrix Σ is update every U steps (updating frequency) on the basis of the covariance between the H previous population sets

$$\Sigma=c^2\frac{1}{H-1}\tilde{K}^T\tilde{K}$$

Where H is called the memory parameter, K is the $H\times\left(N-2\right)$ matrix whose rows are the sampled points while $\tilde{K}=K-\left\langle K\right\rangle$. c is a parameter which can be tuned to optimize the acceptance rate, the suggested value reported in [Haario, (1999)] is $c = 2.4/\sqrt{d}$, with d denoting the dimension of the problem.

4.5. IMPLEMENTATION TEST AND ILLUSTRATION OF THE RESULTS FOR $N = 4$

We shall now discuss the application of the above introduced methods to a test case. Consider a spectrum of four equidistant energy levels, the separation is set to one. The FEEE Distribution for the corresponding pure states of dimension $N = 4$ depends on 2 populations and of course on the value of the expectation energy $E = \langle\psi|H|\psi\rangle$. Once fixed the value of the energy we can look at the joint probability distribution of the first two populations

$$p\left(P_1, P_2\right) dP_1 dP_2 = \frac{dV_{P_1P_2}}{\int dV_{P_1P_2}} \tag{4.5.11}$$

and the corresponding domain of integration. The volume element has been derived in Section 3.5. In Figure 4-2 the distribution obtained by numerical quadrature is shown. The fixed expectation energy is set to be $E = 10^{-2}$. One readily notes that the domain of the distribution is a very acute triangle of the entire unit square. Notably the canonical value of the populations, eq. (2.3.41), that is, the set of populations obtained by applying the maximum entropy principle corresponds to the low probability vertex of such a triangle.

This leads to the drawback that if one starts with a random walk chain near this value the steps size has to be very small in order to stay inside the domain, in higher dimension this effect became still more drastic. For this reason, after have performed some test to assure the mixing property of the chains we have usually initialized the chains to a point near the mean value of the populations. Figure 4-3 shows the “time trace” from a MCRW, i.e. the value of the function at each step of the chain, of the entropy function

$$S = -\sum_{k=1}^{N} P_k \ln P_k \tag{4.5.12}$$

for an analogue system with $N = 10$ energy levels. It is evident that if the chain starts near the canonical population set it takes longer to equilibrate and the size of the burn in period increases. In higher dimension a chain which starts near the boundary does not equilibrate in any reasonable time.

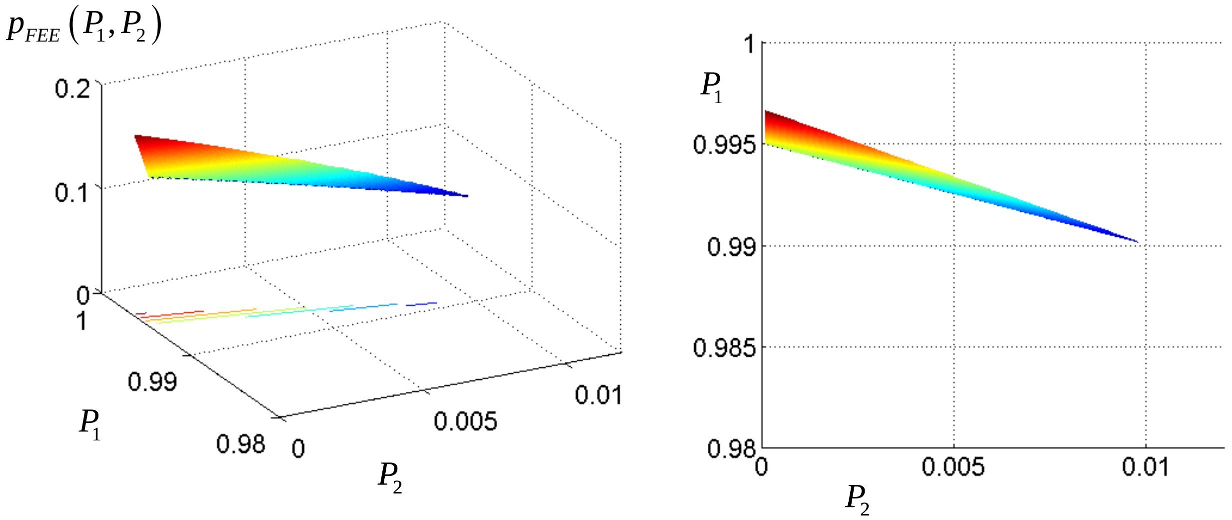


Figure 4- 2: Joint distribution calculated by numerical quadrature of two populations in the FEE Ensemble for the case $N = 4$, and the expectation energy fixed to $E = 10^{-2}$.

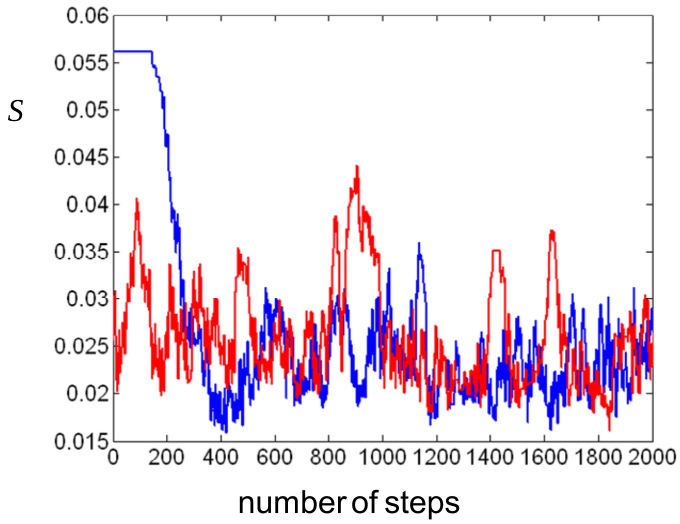


Figure 4- 3: Mixing of the Random Walk Markov chain with multivariate Gaussian proposal as described in the text. The calculations refer to a system with ten equally spaced energy levels. The two paths represent two chains which differ only for the starting value. In the case of canonical initial population (a particular starting point far from the average value of the random variables), represented by the blue line, the burn in period is evident.

Let us now came back to the analysis of the three different type of MC sampling introduced above. In order to check the methods we compare the “exact” single population distribution obtained by quadrature with those obtained with the three MC chains. Thus we are looking at the marginal distribution for a single population

$$p_{FEE}\left(P_k\right)=\int\prod_{i\neq k} dP_i\, p_{FEEE}\left(P_1,\ldots,P_{N-2}\right) \tag{4.5.13}$$

Figure 4-4 shows in particular the probability distribution of P_1 and P_2 obtained by the different chains (MCRW, MCIS, AP) with total number of steps $S=10^5$. All the techniques give distributions which are in excellent agreement with the exact one.

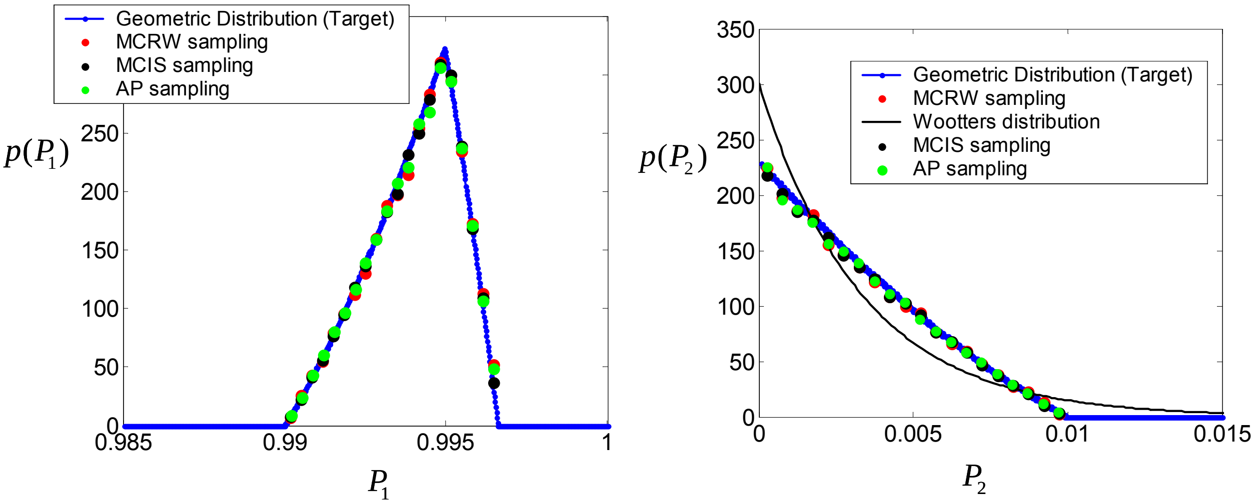


Figure 4- 4: Agreement between the exact marginal geometrical distribution on P_1 and P_2 and the distributions from the different Monte Carlo sampling algorithms. The calculations refer to a spectrum of $N=4$ equidistant energy levels and the expectation value is fixed at $E=10^{-2}$.

Two useful quantities which should be monitored in order to check the convergence of the chain are the estimated average value of the objective function, eq. (4.2.6), and the related error eq. (A4.1.3) as function of the chain’s length. The estimation of the error in a Monte Carlo sampling is treated in Appendix 4.1. The average value and the relative variance are shown in Figure 4-5 for the entropy eq. (4.5.12) and give a criterion for establishing when the chain is long enough on the base of the tolerance admitted for the mean values.

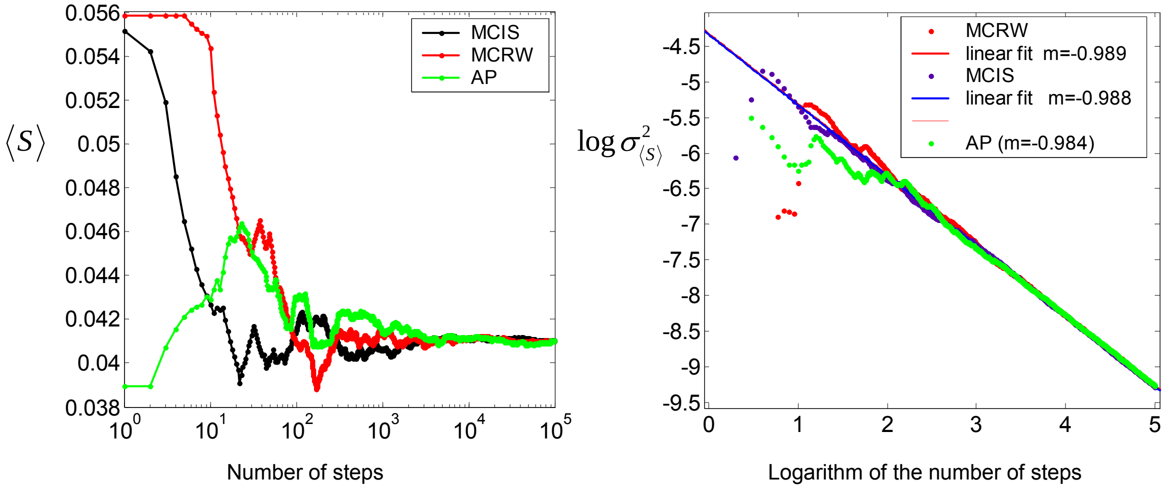


Figure 4- 5: Estimated average and relative error for the entropy function as a function of the chain length. The system is the same of Figure 4-4.

Notice that the variance associated to the estimation of the average value as described in the Appendix 4.1, eq. (A4.1.3), and depicted in the right panel of Figure 4-5 decrease as N^{-1} at least after the first 1000 steps, and this means that the correlation between the sampled points does not make serious deviation from the typical trend of the error predicted for independent sampling.

Finally in Figure 4-6 the distributions of the entropy function obtained from MCRW and MCIS for a ten levels system are compared and a good agreement is established.

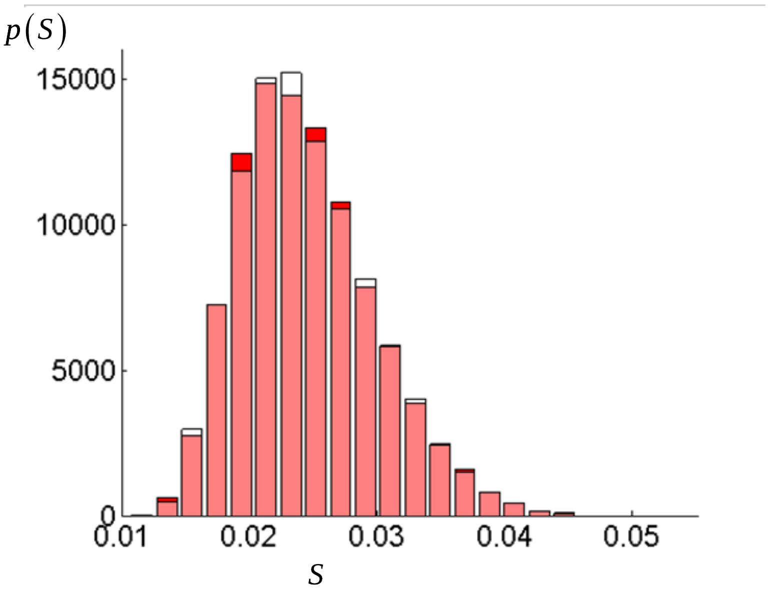


Figure 4- 6: Comparison of the distribution of the entropy function S obtained from RW markov chain (white) and IS chain (red) for a relatively small dimensional problem, i.e. spectrum of $N = 10$ equally spaced energy levels.

4.6 MARGINAL DISTRIBUTION ON A SINGLE POPULATION IN THE FEEE

The aim of this section is to analyze the agreement between the marginal distributions on the single populations which arises from the Fixed Expected Energy Distribution $p_{FEEE}\left(P_k\right)$, eq. (4.5.13), and the exponential approximate distributions $W_{FEE}^k\left(P_k\right)$, eq. (4.3.8). In this case no analytical integration can be carried out because of the complexity of the boundary which defines the integration domain. All we can do is thus to compare the marginal distributions obtained by the Monte Carlo Markov Chain sampling as described above, with the approximate form derived by means of the minimization of the informational functional. First let us briefly look at the behaviour of the average values of the populations as predicted from the approximate distribution

$$\langle P\rangle_W = \left(\lambda + \mu E_k\right)^{-1} \tag{4.6.1}$$

as a function of the energy expectation value E. These can be calculated by solving the linear system of the constraints, eqs. (4.3.9), that is

$$\begin{cases} \sum_{k=1}^{N} \frac{1}{\left(\lambda + \mu E_k\right)} - 1 = 0 \\ \sum_{k=1}^{N} \frac{E_k}{\left(\lambda + \mu E_k\right)} - E = 0 \end{cases}$$

It is easy to show that the populations do not depend on a global shift of the energy scale while the scale of the parameters is given in Appendix 4.2. We are thus free to choose the zero of the energy in correspondence of the first eigenvalue of the Hamiltonian, and this will always be the case if no otherwise specified.

Figure 4-7 shows the average populations, eq. (4.6.1), for a spectrum of ten equally spaced energy levels, that is

$$E_k = k\omega_0 \qquad k = 0 \div 9 \tag{4.6.2}$$

One sees that there is a value of energy for which all the average populations, eq. (4.6.1) became equal, we will refer to this value as the *infinite temperature* energy

$$E_{T\inf} = \frac{1}{N}\sum_{k=2}^{N} E_k \tag{4.6.3}$$

for this value of energy $\lambda \to N$ and $\mu \to 0$ and the mean populations equals those of a Random Pure State Ensemble defined in the same Hilbert space. Moreover for $E < E_{T\inf}$ the two parameters λ and μ are strictly positive. Note that for values of expectation energy higher than $E_{T\inf}$ an inversion of population occurs, and at this point μ changes sign and became negative.

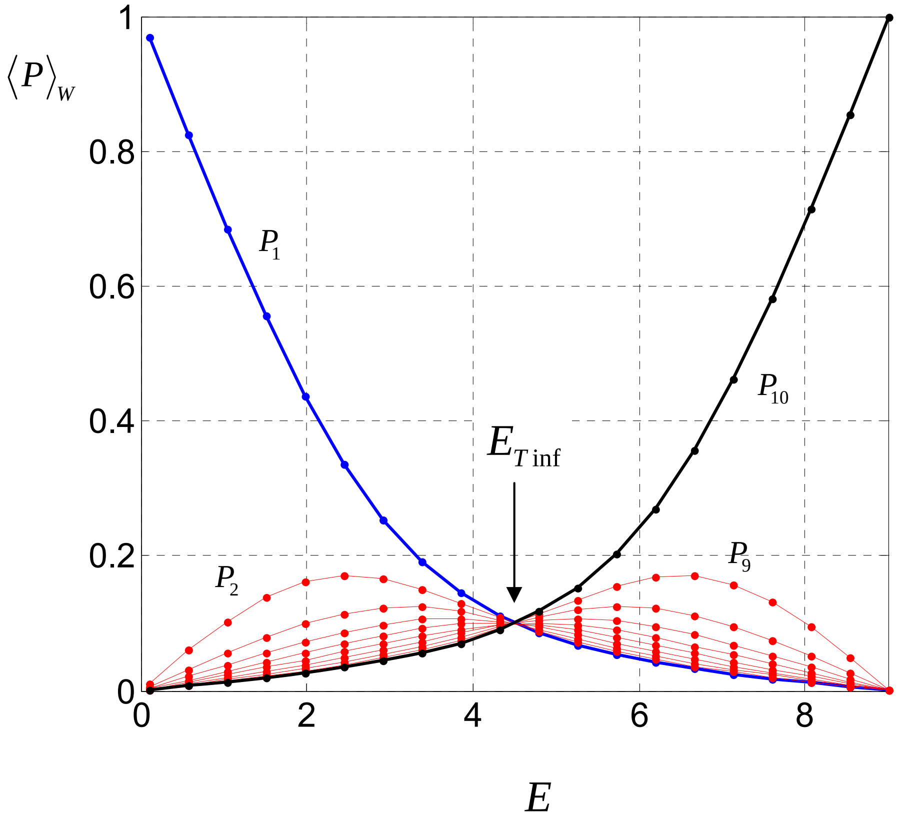


Figure 4-7: Average values of the populations from the approximate FEEE distribution as a function of the energy expectation value. The calculation refers to a spectrum of $N=10$ equally spaced energy levels.

From now on we will restrict our analysis on the physical meaningful range of expectation value $E < E_{T\inf}$. If one want to consider the case $E > E_{T\inf}$, which can be interpreted as a system with negative temperature, one has just to interchanges the role of P_1 and P_N in the following analysis.

Let us compare the FEEE geometrical distribution with the approximate form derived in Section 4.3: first we have verified that the exponential distributions given in eqs. (4.3.8) are a good approximation of the true $p_{FEEE}\left(P_k\right)$ for all $k \neq 1$ and for all the range of possible values of the expectation energy E. Figure 4-8 depicts two (normalized) histograms which refers to the numerical sample of P_3 and P_5 for the Hamiltonian (4.6.2). The expectation value of the energy is an independent parameters and it is set at the value $E = 1.92$ in the reported case. The corresponding distributions

$$W_{FEE}\left(P_k\right) = \frac{e^{-(\lambda+\mu E_k)P_k}}{\left(\lambda+\mu E_k\right)} \tag{4.6.4}$$

are superimposed to the histograms (continuous line).

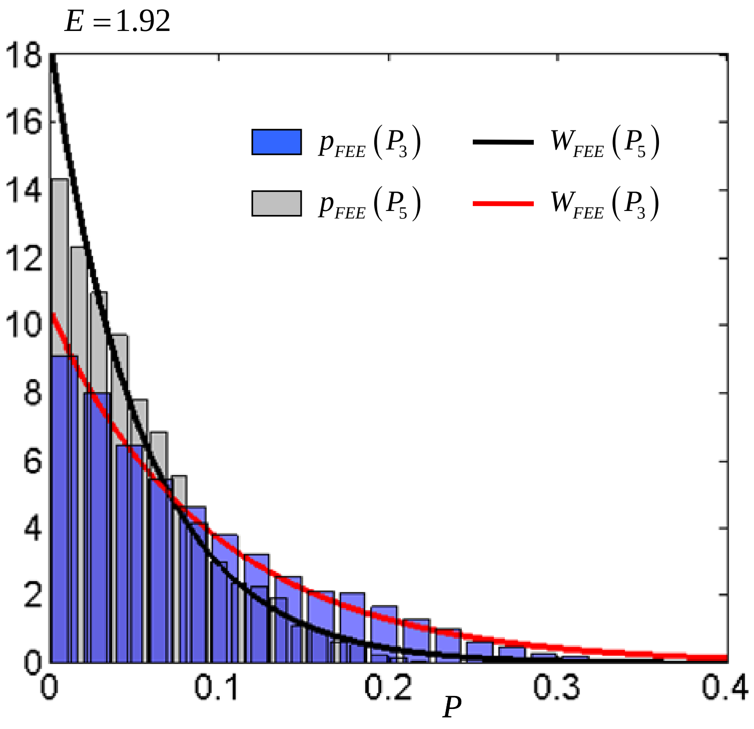


Figure 4- 8: Marginal distributions of P_3 and P_5 (histograms) obtained from a Random Walk Chain (10^5 sampled points) for a $N = 10$ equally spaced energy levels system, and corresponding analytical approximation (solid lines). The expected value of the energy is fixed at $E = 1.92$.

On the other hand the exponential approximation completely misses the salient features of the distributions of the first populations, as it results evident from figures 4-9. Indeed, for $E < E_{T\inf}$ the sampled distribution of the first population is a rather peaked function and became more peaked as the expectation energy diminishes. (For the case $E > E_{T\inf}$ the same considerations can be made for the population of the last energy level). Notably, even if the exponential distribution is not a good approximation for the marginal distribution of P_1, in particular for small values of the energy, nevertheless the predicted average $\langle P_1 \rangle_W = 1/\lambda$ is a good estimation of the average obtained from the sampling of the geometrical distribution, as depicted in figure 4-10.

This implies that we can use the exponential approximations for the distribution of P_1 in order to calculate average value of its linear function but we have to pay attention in the case we want to analyze non linear function, as for example the entropy. Average value of non linear functions depends in fact on the distributions of the stochastic variable and not only on its average. For this reason we derive another form of analytical approximation for the Fixed Expectation Energy Distribution, $p_{FEEE}(P_k)$, which is useful in the range of small E.

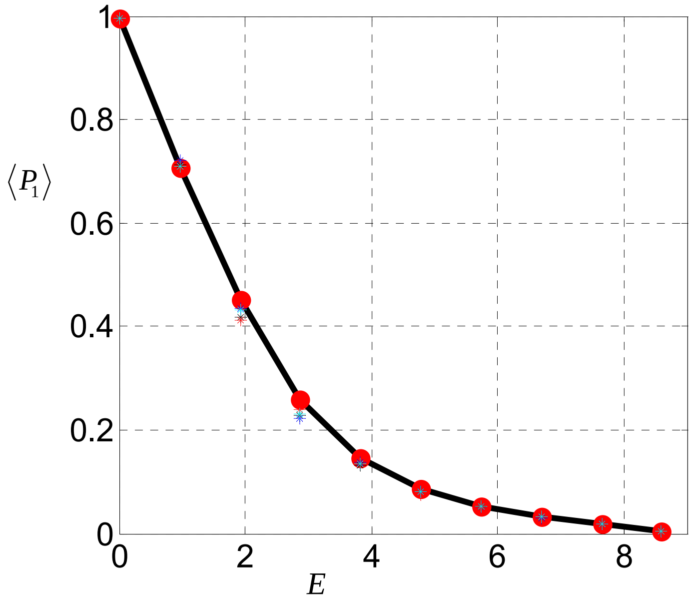


Figure 4- 9: Mean value of the first population P_1: prediction on the base of the approximate distribution $\langle P_1 \rangle_W = \dfrac{1}{\lambda}$ (red dot) and average values obtain from four sampling of the geometrical distribution.

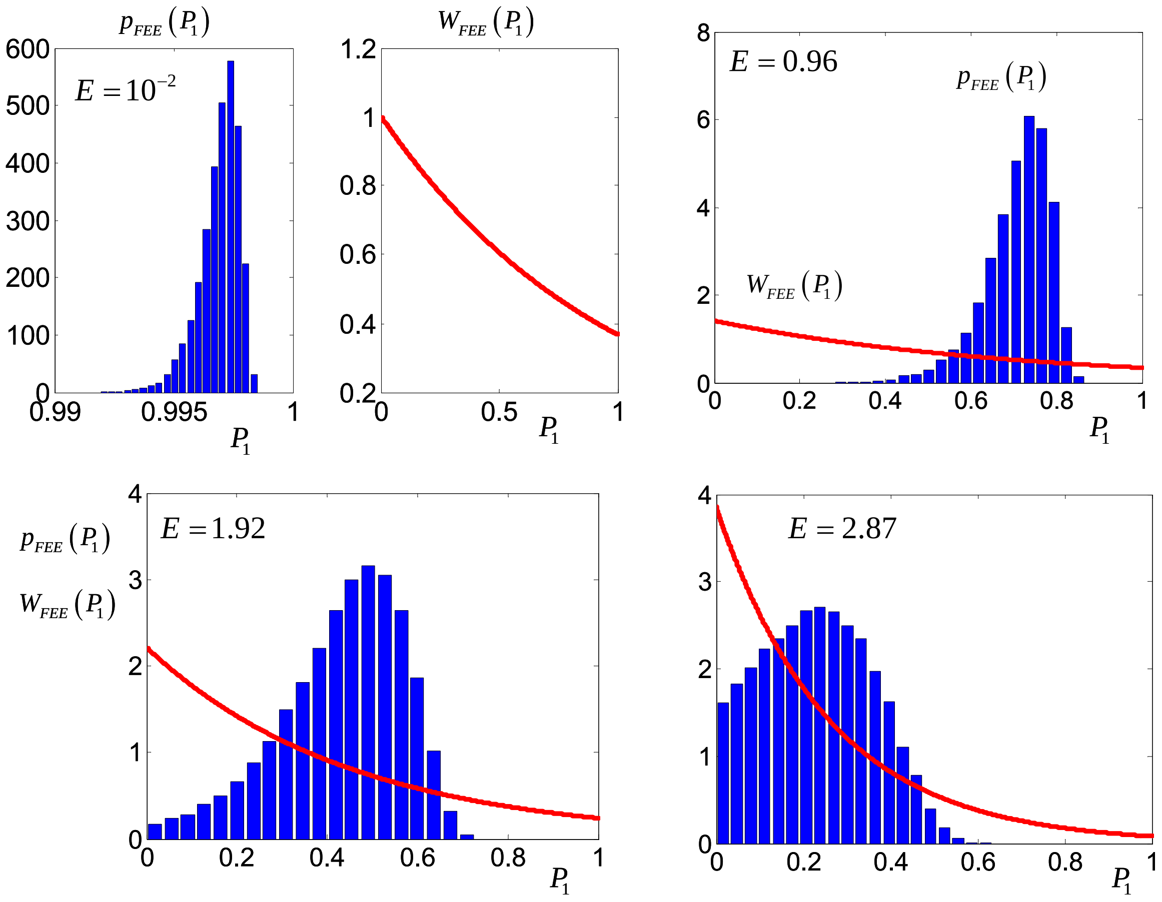


Figure 4- 10: Distribution of the first population P_1 obtained by the numerical sampling and corresponding analytical approximations $W_{FEE}(P_1)$ (red lines). The system is the same as in Figures 4-7 and 4-8. The panels refer to different values of the expectation energy, for this population the geometrical marginal distribution is completely different from the exponential approximation as commented in the text.

4.7 SECOND FORM FOR THE APPROXIMATE FEE DISTRIBUTION

In order to obtain a better approximation we want to take into account the peculiar behaviour of the distribution of the first population. The idea is to use again the same procedure of minimization of the information functional eq. (4.3.5), but now we restrict the space of the allowed function and consider only functions of the form

$$W_{II}\left(x_1,\dots,x_N\right)=w_1\left(\mathbf{a}\middle|x_1\right)w_{II}\left(\hat{x}\right) \tag{4.7.1}$$

where $\hat{x}=\left\{x_2,\dots,x_N\right\}$. That is, we now know that the distribution on the first variable is different from the others and thus we use this information by specifying $w_1\left(\mathbf{a}\middle|x_1\right)$ as a function of a set of parameters $\mathbf{a}=\left\{a_1,a_2\dots,a_j\right\}$. The procedure for the minimization of the information functional then gives the values of $\mathbf{a}$ and the form of $w_{II}\left(\hat{x}\right)$. Such a procedure is described in Appendix 4.3 and for $w_{II}\left(\hat{x}\right)$ one find, eq. (A4.3.13)

$$w_{II}\left(\hat{x}\right)=\prod_{k\neq1}^{N}\frac{e^{-(\lambda_2+\mu_2E_k)x_k}}{\left(\lambda_2+\mu_2E_k\right)} \tag{4.7.2}$$

Here we apply it for a particular choice of $w_1\left(\mathbf{a}\middle|x_1\right)$. First note, as depicted in figure 4-11, that the distribution function of P_1 for small values of the expectation values of the Hamiltonian can be approximate with a Gaussian distribution with mean a_1 and standard deviation $\sigma=1\big/\left(\sqrt{2a_2}\right)$, that is

$$w_1\left(\mathbf{a}\middle|x_1\right)=G\left(a_1,a_2\middle|x_1\right)=\sqrt{\frac{a_2}{\pi}}e^{-(x_1-a_1)^2a_2} \tag{4.7.3}$$

The figure also shows that the variance of the distribution decreases as the value of the expectation energy E diminishes. For the trial function (4.7.3) the set of equations (A4.3.17) which determines the parameters λ_2,μ_2 and $\mathbf{a}$ reads

$$\begin{cases} a_1 + \dfrac{1}{\mu_2}\displaystyle\sum_{k=2}^{N}\frac{1}{z_2+E_k} = 1 \\ \dfrac{(N-1)}{\mu_2} + \dfrac{z_2}{\mu_2}\displaystyle\sum_{k=2}^{N}\frac{1}{z_2+E_k} = E \\ \dfrac{\partial}{\partial \mathbf{a}}\left[\dfrac{1}{2} - \log\left(\dfrac{a_2}{\pi}\right) - a_1 z_2 \mu_2\right] = 0 \end{cases} \tag{4.7.4}$$

where $z_2 = \dfrac{\lambda_2}{\mu_2}$.

The solutions of the system gives the following value for the parameters which specifies the distributions (4.7.2) and (4.7.3)

$$\begin{aligned} &\lambda_2 = 0 && a_2 = 0 \\ &\mu_2 = \frac{N-1}{E} && a_1 = 1 - \frac{E}{N-1}\sum_{k\neq 1}^{N}\frac{1}{E_k} \end{aligned} \tag{4.7.5}$$

In conclusion the approximate distribution we derive reads

$$\begin{aligned} &W_{II}(P_1,\ldots,P_N) = \delta(P_1 - a_1)\prod_{k\neq 1}^{N} w_{II}^{(k)}(P_k) \\ &w_{II}^{(k)}(P_k) = \mu_2 E_k e^{-\mu_2 E_k P_k} \end{aligned} \tag{4.7.6}$$

with μ_2 and a_1 specified as in eqs. (4.7.5).

This second form of the approximate distribution is practically equivalent to the previous one for the populations P_k with $k \neq 1$, while it approximates the $p_{FEEE}(P_1)$ with a Dirac delta distribution at its average value given by the parameter a_1

$$\langle P_1 \rangle_{W_{II}} = 1 - \frac{E}{N-1}\sum_{k\neq 1}^{N}\frac{1}{E_k} \tag{4.7.7}$$

This is surely a better approximation of the real distribution with respect to the exponential one for low value of E/N. This is not the case when the energy is near the infinite temperature values, as one can see from figure 4-11.

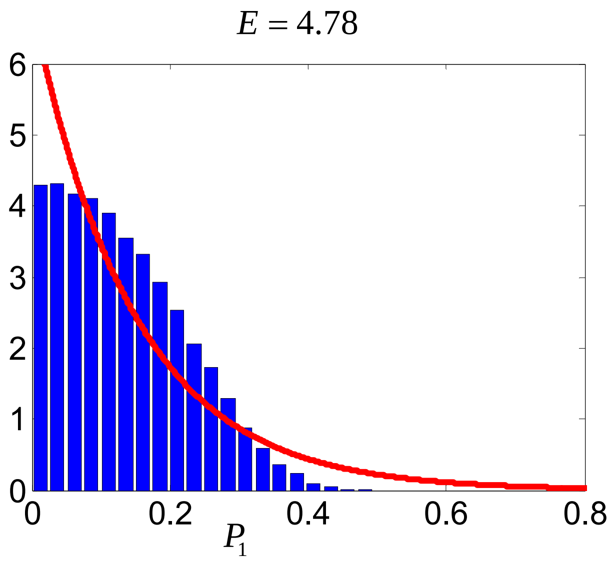


Figure 4- 11: Distribution of the first population P_1 obtained by the numerical sampling and corresponding analytical approximations $W_{FEE}\left(P_1\right)$ (red lines). In this case the expectation energy is near the value corresponding to the infinite temperature condition which in this case is $E_{T\inf} = 4.5$.

Around $E \approx E_{T\inf}$ one has to pay attention and use the RPSE distribution because also the ensemble distribution of the first population tends to an exponential function. Moreover the average value of P_1 predicted from the distribution (4.7.6) deviate from the real one, as one can see in Figure 4-13. Nevertheless this second approximation to the FEE Distribution is particularly convenient as long as it is directly specified on the base of the free parameter E .The average populations different from the first reads

$$\left\langle P_{J\neq 1}\right\rangle_{W_{II}} = \frac{E}{\left(N-1\right)}\frac{1}{E_J} \qquad (4.7.8)$$

In the next chapter we will use the sampling methods and analytical approximations developed in this Chapter for investigating the ensemble distribution of some properties of interest as the equilibrium average of the reduced density matrix for a subsystem of the total isolated system or collective functions of the entire quantum state such as the entropy.

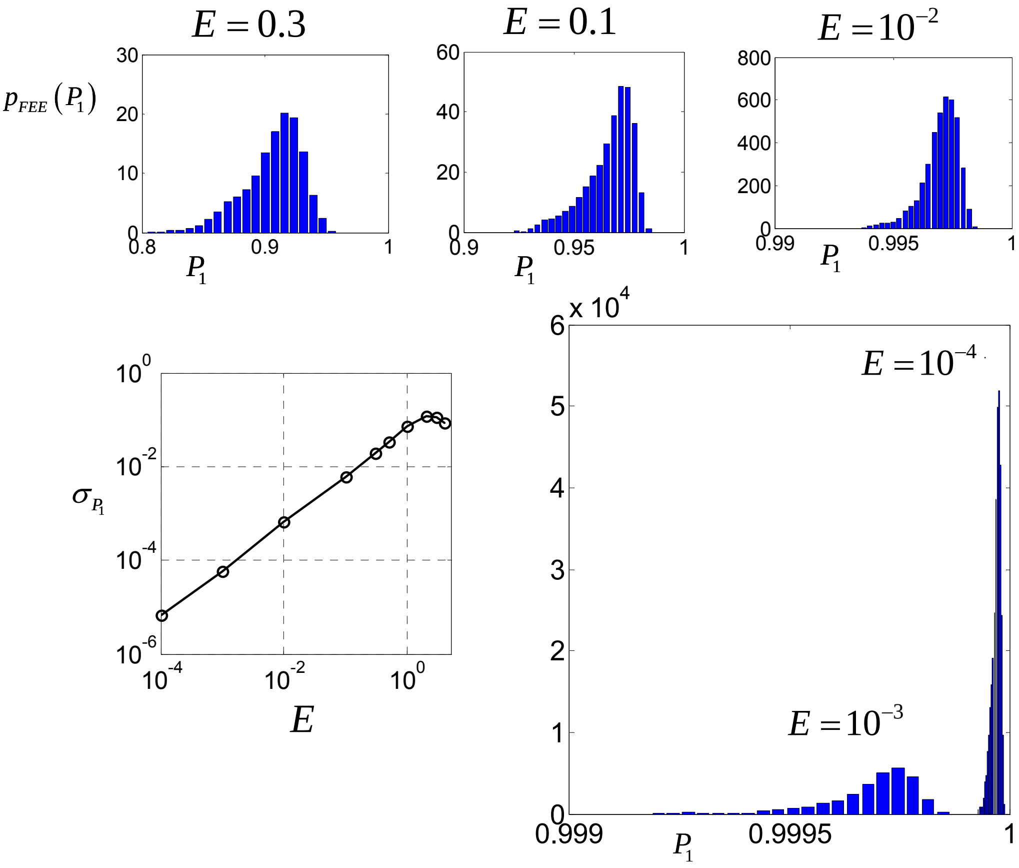


Figure 4- 12: Sampled Distribution of the first population P_1 for low values of the expectation energy. On the low left panel the standard deviation of the distributions as function of the expectation energy is depicted.

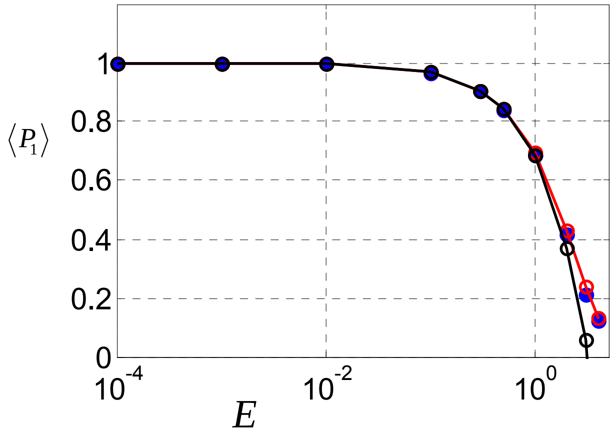


Figure 4- 13: Mean value of the first population P_1: comparison between the prediction on the base of the first approximate distribution $\langle P_1 \rangle_W = 1/\lambda$ (red dot), according to the second form of the approximation, $\langle P_1 \rangle_{W_2} = a_1$ (black dot) and average values obtain from the numerical sampling of the geometrical distribution (blue dot).

APPENDIX 4.1: ROUGH ESTIMATION OF THE ERROR IN MCMC METHOD

As already mentioned the Monte Carlo estimate of a multivariate integral on $x=\{x_1,...,x_d\}$ after S sampled points is given by

$$E=\frac{1}{S}\sum_{i=1}^{S}f\left(P^{(i)}\right) \tag{A4.1.1}$$

If I is the exact value of the integral then the error associated to the Monte Carlo estimation is, in the simplest case of an independent sampling, related to the variance of the function itself and the number of collected points

$$s^2\left(E\right)=\frac{\sigma^2\left(f\right)}{S} \tag{A4.1.2}$$

The fact that a chain produces points which can be highly correlated can introduce other factors in the estimation of the error but we will see that in the present case the basic theory is sufficient to analyze the result.

Of course in practice one usually does not know the exact variance of the objective function and thus uses the Monte Carlo estimate

$$S^2\left(f\right)=\frac{1}{S-1}\sum_{n=1}^{S}\left(f\left(x_n\right)-E\right)^2 \tag{A4.1.3}$$

It seems worthy to state explicitly that Monte Carlo techniques give only a probabilistic error bound, that is, we can only give a probability that Monte Carlo estimate lie within a certain range of the true value.

APPENDIX 4.2: SCALE OF THE λ, μ PARAMETERS UNDER AN ENERGY SHIFT

Consider the average value of the k-th population

$$\langle P_k \rangle_W = \frac{1}{(\lambda + \mu E_k)} = \frac{1}{\mu} \frac{1}{(z + E_k)} \tag{A4.2.1}$$

Where we have defined $z = \lambda / \mu$. From the normalization requirement one find

$$\mu = \sum_k \frac{1}{E_k + z} \tag{A4.2.2}$$

and thus populations can be written as function of the parameter z as

$$\langle P \rangle_W = \frac{(E_k + z)^{-1}}{\sum_k^N (E_k + z)^{-1}} \tag{A4.2.3}$$

After an energy shift spectrum is specified as $\tilde{E}_k = E_k + \Delta E$ and the mean populations reads

$$\langle P \rangle_W = \frac{(\tilde{E}_k + \tilde{z})^{-1}}{\sum_k^N (\tilde{E}_k + \tilde{z})^{-1}} \tag{A4.2.4}$$

where $\tilde{z} = z - \Delta E$

The corresponding expectation energy E is shifted by Δ as expected

$$\tilde{E} = \frac{\sum_k^N \frac{\tilde{E}_k}{(\tilde{E}_k + \tilde{z})}}{\sum_k^N (\tilde{E}_k + \tilde{z})^{-1}} = \frac{\sum_k \frac{E_k}{E_k + z}}{\sum_k (E_k + z)^{-1}} + \Delta = E + \Delta \tag{A4.2.5}$$

Given that $\tilde{z} = \tilde{\lambda} / \tilde{\mu}$, one obtains the scaling rule for the parameters

$$\begin{aligned} \tilde{\lambda} &= \lambda - \mu \Delta E \\ \tilde{\mu} &= \mu \end{aligned} \tag{A4.2.6}$$

APPENDIX 4.3: DERIVATION OF THE MAXIMUM ENTROPY DISTRIBUTION IN A RESTRICTED SPACE OF CANDIDATE FUNCTIONS

The problem we want to solve is the minimization of the information functional

$$I\left[W\right]=\int W\left(x_1,\dots,x_N\right)\log W\left(x_1,\dots,x_N\right)\prod_{k=1}^{N}dx_k \tag{A4.3.1}$$

with function of the form

$$W\left(x_1,\dots,x_N\right)=w_1\left(\mathbf{a}\middle|x_1\right)w\left(\hat{x}\right) \tag{A4.3.2}$$

where $\hat{x}=\left\{x_2,\dots,x_N\right\}$ and we can choose a specific function parametrically dependent on the set $\mathbf{a}=\left\{a_1,a_2\dots,a_j\right\}$ for describing the probability distribution of the first variable. Naturally, such a function has to be properly normalized

$$\int dx_1 w_1\left(\mathbf{a}\middle|x_1\right)=1 \tag{A4.3.3}$$

The information functional can be written as

$$I\left[W\right]=\int dx_1 w_1\left(\mathbf{a}\middle|x_1\right)\log w_1\left(\mathbf{a}\middle|x_1\right)+\int d\hat{x}w\left(\hat{x}\right)\log w\left(\hat{x}\right)=I_1\left(\mathbf{a}\right)+I\left[w\right] \tag{A4.3.4}$$

The constraints are of course the same as before, that is normalization of the average populations, fixed value for the average expectation energy and normalization of the probability density:

$$\sum_{k=1}^{N}\left\langle x_k\right\rangle=1 \tag{A4.3.5}$$

$$\sum_{k=1}^{N}E_k\left\langle x_k\right\rangle=E \tag{A4.3.6}$$

$$\int_0^\infty d\hat{x}w\left(\hat{x}\right)=1 \tag{A4.3.7}$$

But now the average value of the first population is expressed as

$$\left\langle x_1\right\rangle=X_1\left(\mathbf{a}\right)=\int dx_1 w_1\left(\mathbf{a}\middle|x_1\right)x_1 \tag{A4.3.8}$$

By introducing the Lagrange multiplier the functional to minimizes reads

$$\begin{aligned} F\left(\left[w\right],\mathbf{a}\right) &= I_1\left(\mathbf{a}\right)+I\left[w\right]-\lambda\left(\sum_k \left\langle x_k\right\rangle -1\right)-\mu\left(\sum_k \left\langle x_k\right\rangle E_k - E\right)-\eta\left(\int w\left(\hat{x}\right)d\hat{x}-1\right)= \\ &= I_1\left(\mathbf{a}\right)-X_1\left(\mathbf{a}\right)\left(\lambda+\mu E_1\right)+\int d\hat{x}w\left(\hat{x}\right)\left[\log w\left(\hat{x}\right)-\lambda\sum_{k\neq 1} x_k-\mu\sum_{k\neq 1} E_k x_k-\eta\right]+\lambda+\mu E+\eta \end{aligned} \tag{A4.3.9}$$

Actually $F\left(\left[w\right],\mathbf{a}\right)$ is a functional of $w\left(\hat{x}\right)$ and an ordinary function of the parameters $\mathbf{a}$.

The minimization thus requires setting to zero the following derivatives

$$\frac{\partial F}{\partial \mathbf{a}}=\frac{\partial}{\partial \mathbf{a}}\left[I_1\left(\mathbf{a}\right)-X_1\left(\mathbf{a}\right)\left(\lambda+\mu E_1\right)\right]=0 \tag{A4.3.10}$$

$$\frac{\delta F\left[w\right]}{\delta w\left(\hat{x}\right)}=-\log w\left(\hat{x}\right)-1-\lambda\sum_{k\neq 1} x_k-\mu\sum_{k\neq 1} E_k x_k-\eta=0 \tag{A4.3.11}$$

From (A4.3.11) one obtains

$$w\left(\hat{x}\right)=\exp\left[-\left(1+\eta\right)-\lambda\sum_{k\neq 1} x_k-\mu\sum_{k\neq 1} E_k x_k\right]=\prod_{k\neq 1}^{N} w_k\left(x_k\right) \tag{A4.3.12}$$

this, by taking into account the normalization condition (A4.3.7), can be written as

$$w_k\left(x_k\right)=\frac{e^{-\left(\lambda+\mu E_k\right)x_k}}{\left(\lambda+\mu E_k\right)} \qquad k\neq 1 \tag{A4.3.13}$$

So that the average values are expressed as before

$$\left\langle x_k\right\rangle=\frac{1}{\left(\lambda+\mu E_k\right)} \qquad k\neq 1 \tag{A4.3.14}$$

while the parameters λ,μ are determined from the vinculums

$$\begin{aligned} X_1\left(\mathbf{a}\right)+\sum_{k\neq 1}^{N}\frac{1}{\left(\lambda+\mu E_k\right)} &= 1 \\ E_1 X_1\left(\mathbf{a}\right)+\sum_{k\neq 1}^{N}\frac{E_k}{\left(\lambda+\mu E_k\right)} &= E \end{aligned} \tag{A4.3.15}$$

where $\mathbf{a}$ is calculated from the solution of eq. (A4.3.10).

Define the following function

$$S(z)=\sum_{k=2}^{N}\frac{1}{E_k+z} \tag{A4.3.16}$$

where $z=\lambda/\mu$. By assuming the scale of the energy such that $E_1=0$, the equations to be solved for the specification of the parameters are

$$\begin{cases} X_1(\mathbf{a})+\dfrac{S(z)}{\mu}=1 \\ \dfrac{(N-1)}{\mu}+z\dfrac{S(z)}{\mu}=U \\ \dfrac{\partial}{\partial\mathbf{a}}\left[I_1(\mathbf{a})-X_1(\mathbf{a})z\mu\right]=0 \end{cases} \tag{A4.3.17}$$

In conclusion by choosing a parametric function which describes the distribution of the first population, $w_1(\mathbf{a}|x_1)$, and solving the system (A4.3.17) we can specify the approximate maximum entropy distribution as

$$W(x_1,\dots,x_N)=w_1(\mathbf{a}|x_1)\prod_{k\neq 1}^{N}\frac{e^{-(\lambda+\mu E_k)x_k}}{(\lambda+\mu E_k)} \tag{A4.3.18}$$

APPENDIX 4.4: DISTRIBUTION OF SUM OF STOCHASTIC VARIABLE AND CENTRAL LIMIT THEOREM

In order to derive the distribution of $P(X)$ for a stochastic variable

$$X=\sum_{i=1}^{n}x_i \tag{A4.4.1}$$

where x_i are independently distributed random variable with probability density $p_i(x_i)$ it is convenient to introduce the corresponding characteristic function

$$G(q)=\int dXe^{iqX}P(X)=\prod_{k=1}^{n}g_i(q) \tag{A4.4.2}$$

where the functions $g_i(q)$ are the characteristic functions of the distributions $p_i(x_i)$

$$g_i(q)=\int dx_i e^{iqx_i}p_i(x_i) \tag{A4.4.3}$$

In the case we deal with n identical exponentially distributed random variables, $p(x)=\alpha e^{-\alpha x}$, one readily finds

$$G(q)=\left(\frac{i\alpha}{q+i\alpha}\right)^n$$

which is the characteristic function of a Gamma Distribution with parameter (n,α), that is

$$P(X)=\Gamma_{n,\alpha}(X)=\frac{\alpha^n}{(n-1)!}X^{n-1}e^{-\alpha x} \tag{A4.4.4}$$

where n is the shape parameter while α is the rate parameter.

On the other hand the Central Limit Theorem states that if x_i are independent and identically distributed random variables and $p(x)$ has finite mean μ and variance σ^2, then the sum variable (A4.4.1) is distributed, for $N\to\infty$, according to a Normal Distribution with average $M=n\mu$ and variance $\Sigma^2=n\sigma^2$, that is

$$\lim_{n\to\infty}P(X)=G_{M,\Sigma}(X)=\frac{1}{\sigma\sqrt{2\pi n}}e^{-\frac{(X-n\mu)^2}{2n\sigma^2}} \tag{A4.4.5}$$

It is easily verified indeed that the Gamma distribution tends to a Normal one as the shape parameter n increases.

The Central Limit Theorem also applies in the case of random variables that are not identically distributed, as it is the case for the approximate distribution derived for the FEEE:

Let x_i be a random variables defined on the same probability space. Assume that x_i has finite expected value μ_i and finite standard deviation σ_i. Then the sum $X = \sum_{i=1}^{n} x_i$ has average value

$$\langle X \rangle = \sum_{i=1}^{n} \mu_i \tag{A4.4.6}$$

and variance

$$s_n^2 = \sum_{i=1}^{n} \sigma_i^2 \tag{A4.4.7}$$

If the third central moment

$$r^3 = \sum_{i=1}^{n} \overline{\left(\left| x_i - \mu_i \right|^3 \right)} \tag{A4.4.8}$$

exists and is finite for every n, and if it is valid the following (Lyapunov) condition

$$\lim_{n\to\infty} \frac{r_n}{s_n} = 0 \tag{A4.4.9}$$

Then the distribution of X converges to a normal distribution centred at the average value given by eq. (A4.4.6) and variance given by eq. (A4.4.7), that is

$$\lim_{n\to\infty} P(X) = G_{\langle X \rangle, s_n}(X) = \frac{1}{s_n\sqrt{2\pi}} e^{-\frac{(X-\langle X \rangle)^2}{2s_n^2}} \tag{A4.4.10}$$

Notice that for a exponentially distributed random variable, $p(x) = \alpha e^{-\alpha x}$, the n-th moment is simply

$$\langle x^n \rangle = \frac{n!}{\alpha^n} \tag{A4.4.11}$$

CHAPTER 5

TYPICALITY ON THE ENSEMBLES: STUDY OF A SPIN SYSTEM

5.1 INTRODUCTION

Ensembles of spins are convenient systems for investigations of quantum statistical behaviour, since one has to consider a finite dimensional Hilbert space. The numerical calculations of the energy spectra and the time evolution of arbitrary initial states can be performed to machine precision without introducing any artificial truncation of the Hilbert space. Furthermore this kind of model system is the subject of a continuously increasing attention either from a theoretical [Cucchietti, (2005); Suter, (2008)] as well as experimental perspective [Neumann, (2008); Hanson, (2008); Berezovsky, (2008)] because it represents the natural test bed for quantum information protocols.

In this chapter we shall analyze the Ensemble Distribution of the entropy and of the equilibrium average state of a subsystem for a system composed of n non interacting spins. In this and in the following Chapter we will deal with ideal system, i.e. systems composed of non interacting parts. This is convenient and does not cause any drawbacks since we shall focus on the properties of Ensembles Distributions of quantities which does not depend sensibly on the dynamical aspects of the system: in particular we shall consider the ensemble distribution of the entropy, eq. (2.3.12), and of the equilibrium average of the reduced density matrix of a subsystem, as defined in eq. (2.4.14). Instead, the dynamical aspects of the equilibrium state will be considered in the second part of this thesis.

The concept of typicality in the ensemble is introduced and illustrated for the considered systems. The major point is indeed the emergence of properties which does not depend on the detail of the state of the system but are “typical” for the great majority of the wave functions in the considered ensemble.

5.2 ON THE CONCEPT OF TYPICALITY IN QUANTUM STATISTICAL MECHANICS

Recently the concept of *typicality* has been introduced by Goldstein *et al*. [Goldstein, (2006)] and used to provide very strong foundations to the canonical statistics of a quantum subsystem S which is part of a much bigger isolated quantum system $S+E$. The crucial point which emerges from the above mentioned investigation is the following: by choosing at random a pure state ψ from an ensemble of all the wavefunctions which lie on the Hilbert space spanned by a set of Hamiltonian eigenstates

$$H\left|e_j\right\rangle = E_j\left|e_j\right\rangle \qquad E_j \in \left[E, E+\delta E\right] \tag{5.2.1}$$

with the usual condition $\delta E << E$, the corresponding reduced density matrix of a small subsystem defined as

$$\mu = Tr_E\left|\psi\right\rangle\left\langle\psi\right| \tag{5.2.2}$$

is approximately equal to the canonical density matrix

$$\mu_{can} = \frac{e^{-\beta H_S}}{Z} \tag{5.2.3}$$

for the overwhelming majority of the pure state which belong to the initially considered ensemble. Here the important conceptual point which is absent in the standard formulation of quantum statistical mechanics is the idea that the usual statistics (in this case the Gibbs form of the statistical density matrix) originates from the pure state wavefunction itself, without any invocation of real ensemble, randomness or chaos assumptions. Related, less general, results was obtained in ref [Tasaki, (1998)], by assuming that the total independent state is in an eigenstate of the total Hamiltonian.

It is worth to mention here that the ensemble of pure states for which the *Canonical typicality* has been established [Goldstein, (2006)] is a particular case of the Random Pure State Ensemble considered by us: it is an ensemble defined by the uniform measure on the unit sphere in the subspace spanned by the Hamiltonian eigenfunctions $\left|e_j\right\rangle$ with the eigenvalues $E_j \in \left[E, E+\delta E\right]$, that is, the RPSE with the additional constraint defined by the parameter δE, which is assumed to be small in the macroscopic scale.

Nearly at the same time, Popescu *et al* [Popescu, (2006)] presented a very clear and general analysis of the typicality properties of the subsystem density matrix within an approach independent from the standard definitions of microcanonical and canonical distributions used in statistical mechanics. It is worth to briefly summarize here the general setup of this work because it will be useful in the interpretation of our results.

Let us consider a large isolated quantum mechanical system, “the universe”, which can be partitioned into the system, S, and the, comparatively large, environment, E. Let the state of the universe obey some global constraint R which reduces the dimension of the corresponding Hilbert space

$$\mathcal{H}_R \subseteq \mathcal{H}_S \otimes \mathcal{H}_E \tag{5.2.4}$$

where $\mathcal{H}_S$ and $\mathcal{H}_E$ are the Hilbert spaces of the *system* and the *environment*, of dimensions N_S and N_E respectively. Let us define ε_R , the equiprobable state of the universe corresponding to the constraint R, as

$$\varepsilon_R = \frac{1}{N_R}\mathbf{1}_R \tag{5.2.5}$$

where $\mathbf{1}_R$ is the projection operator on $\mathcal{H}_R$ and N_R is the dimension of the total space $\mathcal{H}_R$. Equation (5.2.5) denotes the statistical density matrix corresponding to the maximally mixed state of the universe, that is, it assigns equal probability to each pure state. The generalized canonical state of the system is thus defined as

$$\rho_S = Tr_E \varepsilon_R \tag{5.2.6}$$

Popescu e*t al*. prove that if the universe is in a pure state $\left|\psi\right\rangle$ belonging to H_R, then the reduced state of the system

$$\mu = Tr_E \left|\psi\right\rangle\left\langle\psi\right| \tag{5.2.7}$$

is very close to the canonical state ρ_S defined in eq. (5.2.6) for almost every pure state $\left|\psi\right\rangle \in H_R$. This theorem provides an exponentially small bound to the probability of finding the system in a state that is far from the canonical one. The deviation from the canonical state is characterized by the ratio between the system size and the effective size of the environment. The proof of the theorem comes from geometrical consideration on the Hilbert space and does not involve any dynamical argument.

The above statement is called “general canonical principle” because, as the authors point out, the canonical state (5.2.6) corresponds to the standard canonical state eq. (5.2.3) for a particular choice of the global constraint R, i.e. if the constraint is chosen as the restriction of the Hilbert space according to the condition (5.2.1), which is equivalent to the definition of the ensemble used by Goldstein *et al.* [Goldstein, (2006)].

5.2.1 TYPICALITY FOR ISOLATED SYSTEMS

In a recent contribution, [Reimann, (2007)], Reimann points out that, under rather generic assumptions, the typicality properties already emerge for collective observables pertinent to the whole system without the necessity of a “system plus environment” division. While in [Popescu, (2006)] the foundation of the statistical description for a subsystem is clearly connected to the “*massive entanglement between the subsystem and the rest of the universe*”, this would not be the case for an isolated system which is, by definition, not entangled. In [Reimann, (2007)] the typicality refers to a generalized ensemble defined through a probability density function $p(c)$ for the un-normalized complex coefficients which specify the wavefunction:

$$\psi = \sum \frac{c_n}{\|c\|} |n\rangle \tag{5.2.8}$$

where $c := (c_1, ..., c_n)$ and $\|c\| = \sqrt{\sum |c_n|^2}$. The two key assumptions of Reimann concern the distribution $p(c)$ on the wavefunction coefficients. The first one requires statistical independence

$$p(c) = \prod_{n=1}^{N} p_n(|c_n|) \tag{5.2.9}$$

The second assumption regards the “purity” of the ensemble averaged density matrix and it can be written as

$$\max\left(\frac{\overline{|c_n|^2}}{\overline{\|c\|^2}} \right) << 1 \tag{5.2.10}$$

If the validity of the conditions eqs. (5.2.9) and (5.2.10) is assumed, then the typicality is established as an upper bound to the variance of the ensemble distribution of the expectation value, for a given bounded operator.

The study we shall here present is similar in the spirit to that in ref. [Reimann, (2007)] but the framework is quite different: first we are looking at the Ensemble Distribution of equilibrium value of state functions. Such a value is naturally defined as an asymptotic time averages on the “trajectory”, as explained in Section 2.3, from which a uniform distribution on the phase variables is derived rather than assumed as in [Reimann, (2007]. Secondly we study specific ensembles whose characteristic probability distributions are not arbitrary since they are established from the geometry of the Hilbert space. Moreover we will explore interesting connections between the concept of typicality and the emergence of thermodynamic properties in differently defined ensembles.

It is worthy to note, that the study of the RPS and FEE ensemble distributions developed so far can be used to substantiate the assumptions of Reimann. First we have shown that, at least in the limit of large N, the joint distribution of the populations is well approximated by a factorized probability distribution

$$W(P)=\prod_{k=1}^{N} W^k(P_k) \tag{5.2.11}$$

where the explicit form of the single variable distributions W^k depends on the particular ensemble but in general is exponential, (see eqs. (4.3.8) and (4.3.10))

$$W^k(P_k)=\lambda_k e^{-\lambda_k x_k} \tag{5.2.12}$$

Secondly, since $P_k=|c_k|^2/\|c\|^2$, the condition (5.2.10) is equivalent to require that the maximum of the ensemble average value of a population, is much less than one; in other words it is assumed that, on the average, several energy eigenstates contribute to the specification of the total wavefunctions which belong to the considered ensemble. This condition is naturally satisfied in the Random Pure State Ensemble, for which the average population are all equal and of the order of $O(1/N)$. In the Fixed Expectation Energy Ensemble the maximum of the average population is that corresponding to the ground state. This is, according to eq. (4.7.7), $\langle P_1\rangle_{W_{II}}=1-\frac{E}{N-1}\sum_{k\neq 1}^{N}\frac{1}{E_k}$, thus the validity of the condition

(5.2.10) depends on the total energy and on the energy spectrum; in particular it is not satisfied for small values of the expectation energy.

We emphasize that the above mentioned approaches to the problem of relating the statistical ensemble to the property of a single pure state on the basis of the concept of typicality are of pure "geometrical" character, in the meaning that the dynamics of the quantum state is never invoked. A somewhat different approach based on the analysis of the time evolution can be found in ref. [Jensen, (1985)]. Jensen *et al*. perform a numerical experiment on a cyclic chain of 7 spin in order to compare the equilibrium value of the collective transverse magnetization resulting from the time evolution of a pure state with the standard microcanonical average. The remarkable finding is that the "solution of the Schrödinger equation is reach enough to exhibit statistical behaviour" in the sense that the short time average of the observed $M_x(t)$, calculated from the full knowledge of the initial pure state, is accurately predicted by an ensemble average which requires only the knowledge of the mean energy. This numerical evidence is again relative to initial states which are superposition of energy eigenstates with a distribution which is "reasonably" narrow in energy, as in the case of Goldstein *et al.* [Goldstein, (2006)]. Interestingly the statistical character of the dynamics, as defined in this framework, does not depend on the nearest neighbourhood level spacing statistics of the eigenstates (Wigner-Dyson or Poisson type), while this feature is considered as a central issue in the quantum chaos theory.

In our analysis both the ingredients are present, that is the dynamical evolution on the one hand and the geometrical statistics on the other hand. However they also plays different roles in determining the statistical mechanics of quantum states and this is emphasized by the introduction of the two different probability distributions: the Pure State Distribution on the one hand and the Ensemble Distributions on the other hand.

Let us now focus on this second aspect, i.e. the Ensemble Distributions, and study the eventual typicality property of some functions of interest. As already mentioned we are primarily interested about two kind of functions

1. those which characterize the equilibrium state of a subsystem, i.e. the equilibrium average Reduced Density Matrix as defined in (2.4.14).

$$\bar{\mu} = \sum_s \sum_b P_{sb} \left| s \right\rangle \left\langle s \right| \qquad (5.2.13)$$

2. collective functions such as the Shannon entropy, eq. (2.3.12): $S = -\sum_{k=1}^{N} P_k \ln P_k$

5.3 ENSEMBLE OF n SPINS $1/2$

The system we shall consider is an ensemble of n non interacting $1/2$ spins. Each spin having its Zeeman frequency ω_k. The total number of state is in this case

$$N = 2^n \tag{5.3.1}$$

The M-th eigen energy state will be denoted as $M = \left| m_1^M m_2^M ....m_n^M \right\rangle$ and the corresponding energy is

$$E_M = \sum_{k=1}^{n} \omega_k m_k^M \tag{5.3.2}$$

Where $m_k^M = \mp \frac{1}{2}$

In the case that the spins are all identical with Zeeman splitting $\omega_k = \omega_0$, we obtain a spectrum with $n+1$ energy eigenstates with a binomial degeneracy scheme, by identifying the states $M = \left| m_1^M m_2^M ....m_n^M \right\rangle$ on the basis of the number k of spins “up” one has

$$E_M \to \tilde{E}_k = \omega_0 \left(k - \frac{n}{2} \right) \tag{5.3.3}$$

with the corresponding degeneracy given by

$$d\left(\tilde{E}_k\right) = \binom{n}{k} = \frac{n!}{k!\left(n-k\right)!} = 2^n \mathrm{Bin}(n, \frac{1}{2}) \tag{5.3.4}$$

where $\mathrm{Bin}(n, \frac{1}{2})$ denote the binomial probability distribution with parameter $p = \frac{1}{2}$ and $k = 0 \div n$. If n is at least of the order of 5, the binomial distribution is fairly well approximate by a normal distribution. In order to apply the population distributions previously derived, we set the zero of the energy in correspondence to the first eigen energy

$$E_k = \tilde{E}_k - E_1 = \tilde{E}_k + \frac{n}{2}\omega_0 \tag{5.3.5}$$

The density of state is in general

$$d\left(E_k\right) = \sum_{k=1}^{N} \delta\left(E - E_k\right)$$

which, by using the normal approximation to the binomial, can be written as

$$\tilde{d}\left(E\right) = \frac{2^n}{\sqrt{\pi\, n/2}} e^{-\frac{\left(E-n/2\right)^2}{n/2}} \tag{5.3.6}$$

If the resonance frequency are not identical but somewhat distributed then, when n is large, the spectrum is dense and one can introduces a smoothed density of state

$$g\left(E\right) = \lim_{\varepsilon\to 0} \int_{E-\varepsilon/2}^{E+\varepsilon/2} d\left(E\right) dE \tag{5.3.7}$$

where ε is a small energy interval which contains enough energy levels to guarantee the smoothness of the density function. In the limit of large n and dense spectrum one can thus introduces a Gaussian density of state

$$g\left(E\right) = \frac{N}{\sqrt{2\pi\sigma^2}} e^{-\frac{\left(E-\bar{E}\right)^2}{2\sigma^2}} \tag{5.3.8}$$

with mean $\overline{E} = \frac{1}{2}\sum_{k=1}^{n} \omega_k$ and variance given by

$$\sigma_\omega^2 = \frac{1}{4}\sum_{k=1}^{n} \omega_k^2 \tag{5.3.9}$$

This is shown in Figure 5-1 for $n = 10$: figure 5-1-A shows the binomial degeneracy of a spectrum of 10 identical spins with $\omega_0 = 1$ and the corresponding Gaussian envelope, in 5-1-B the resonance frequency of each spin has been modified by adding a random number drawn from a normal distribution with standard deviation $\sigma = 10^{-1}$.

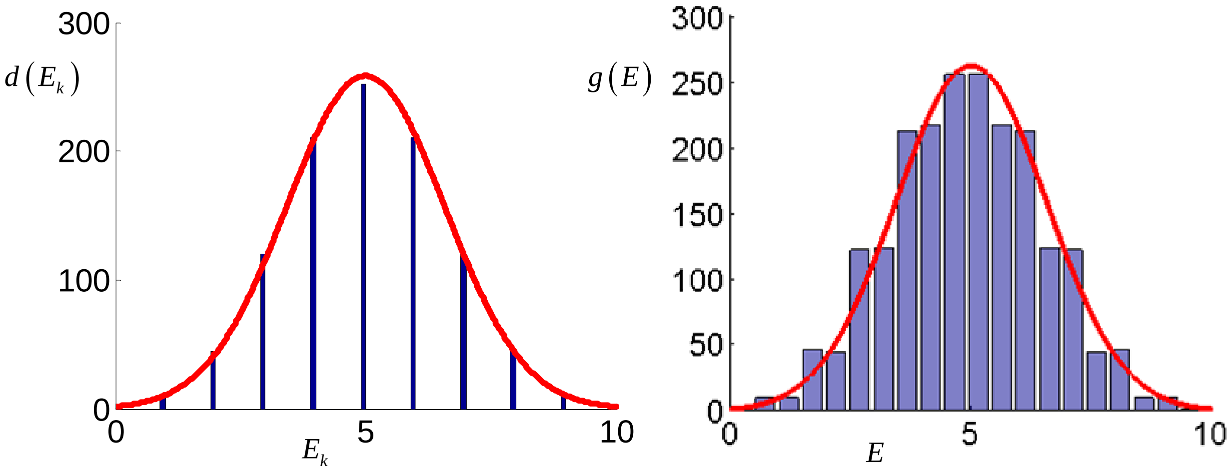


Figure 5- 1: Energy spectrum of A) $n=10$ identical spins $1/2$ with $\omega_0=1$ B) $n=10$ spins with different energy separations.

5.4 THE FIXED EXPECTATION ENERGY ENSEMBLE

Because for the considered system the energy spectrum is naturally bounded we can study the property of the entropy function and the equilibrium average state of a subsystem as a function of the expectation energy $E=\langle\psi|E|\psi\rangle$. The energy *per spin* $\varepsilon=E/n$ is the only independent parameter which defines the Fixed Expectation Energy Ensemble. It has been proposed, [Brody, (2005), (2007); Naudts, (2006)], to consider this ensemble as the real quantum counterpart of the classical microcanonical ensemble. The standard quantum microcanonical set up, see eq. (2.3.40), is indeed not completely satisfactory, first because it relies on the introduction of an arbitrary energy band ΔE and, furthermore because it suggests to consider a quantum system in thermal equilibrium as being in a energy eigenstate, which is in contrast with the superposition principle. The alternative definition proposed in [Brody, (2005)] based on the fixed expected energy is indeed rather appealing since its analogy with the classical microcanonical ensemble results particularly evident from the equation of motion written as in eq. (3.3.4). However its usefulness in the framework of the quantum statistical mechanics requires further investigations. The methodologies developed in chapter 4 can be employed for this purpose.

Figure 5-2 shows the FEE Ensemble Distributions of the first population $p(P_1)$, obtained from the sampling of the geometrical distribution, as a function of the energy per spin. The distributions are fitted with a normal distribution whose variance clearly diminishes as the energy decreases. In the case when the Zeeman frequencies are all identical, the approximate distribution on P_1 introduced in Section 4.7 reads

$$w_{II}\left(P_1\right)=\delta\left(P_1-\overline{P}_1\right) \tag{5.4.1}$$

$$\left\langle P_1\right\rangle=1-\frac{E}{2^n}\sum_{k=1}^{n+1}\binom{n}{k}\frac{1}{E_k} \tag{5.4.2}$$

where the energies are expressed in units of the spin frequency ω_0. In the limit of large n, the binomial coefficient which determines the degeneracy, eq. (5.3.4), is a function of k sharply peaked around $k=n/2$, and in this limit the ensemble average of the first population is a linear function of the energy per spin ε

$$\left\langle P_1\right\rangle=1-2\varepsilon \tag{5.4.3}$$

Note that in order to assure the positivity of this variable the energy per spin has to be lower than that corresponding to the infinite temperature limit as defined in eq. (4.6.3), that is

$$\varepsilon<\frac{E_{T_{\inf}}}{n}\overset{n\to\infty}{=}\frac{1}{2} \tag{5.4.4}$$

Actually this value is slightly less than $1/2$ for n of the order of 10 as considered here.

In the same limit of large n the ensemble average of the populations different from the first are given by

$$\left\langle P_J\right\rangle=\frac{E}{\left(2^n-1\right)}\frac{1}{E_k}\overset{n\to\infty}{=}\varepsilon\frac{n}{J}2^{-n} \qquad J\neq 1 \tag{5.4.5}$$

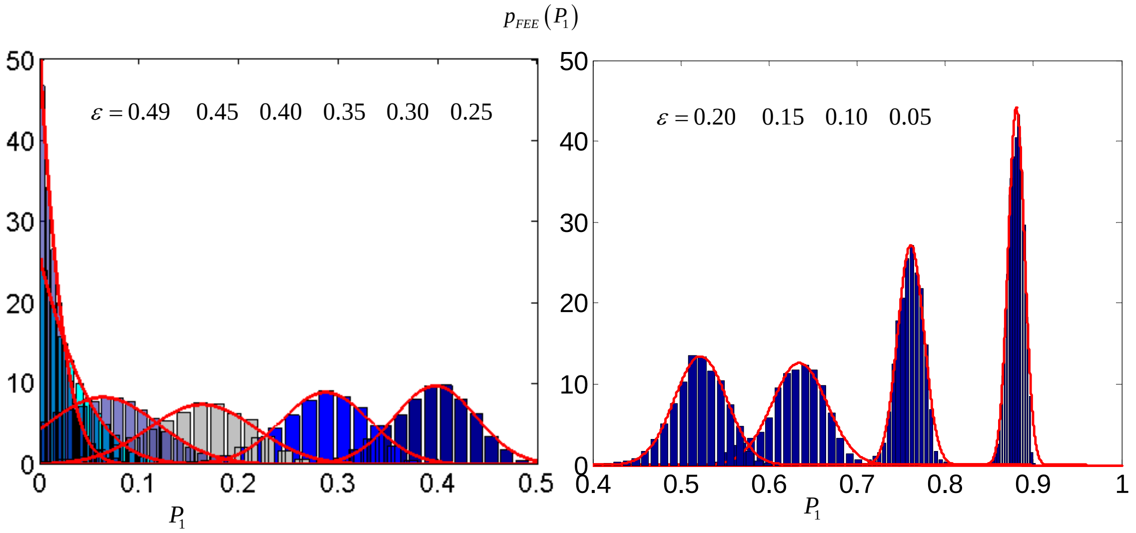
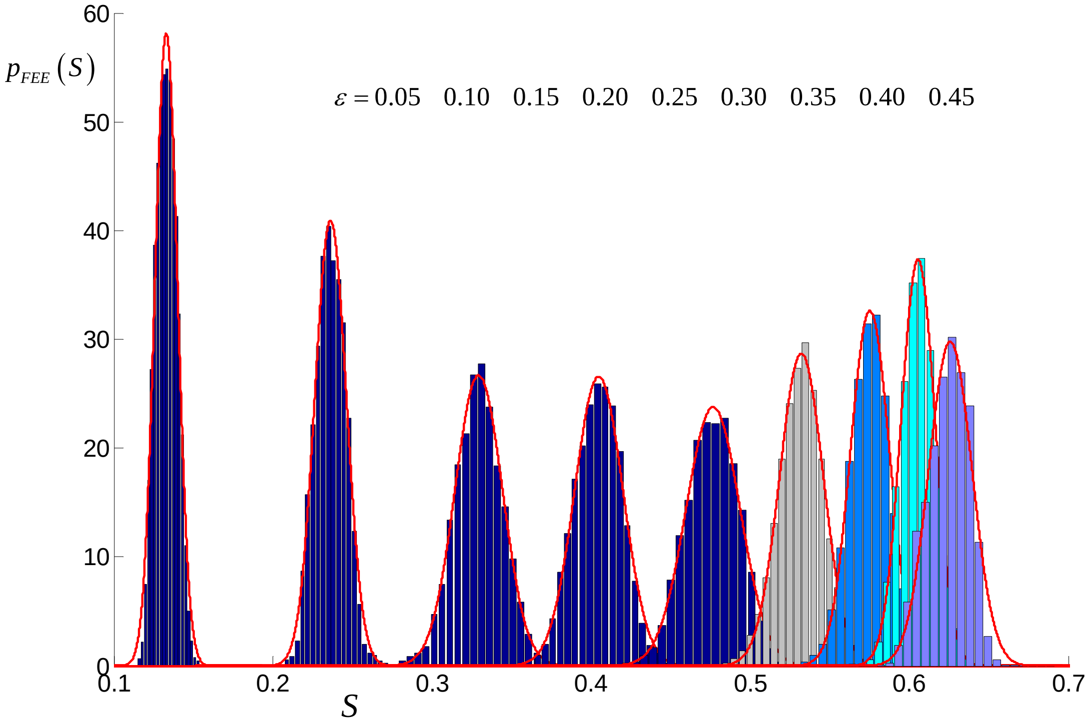


Figure 5- 2: Sampled FEE Distribution of the first population P_1 as a function of the energy per spin ε. The distributions are fitted with Normal distributions.

5.4.1 ENSEMBLE DISTRIBUTION OF THE ENTROPY

At this point we can study the ensemble distributions of the entropy as defined in eq. (2.3.12). The important evidence is that the Ensemble Distribution of this function is concentrated around a "typical" value which is an increasing function of the energy. In other words the great majority of the possible states which can describe a system composed of n identical spins $1/2$ with fixed energy are also characterized by the same value of the entropy function. This is evident from Figure 5-3 which depicts the ensemble distribution of S obtained by sampling the FEE distribution for a system of $n=6$ and $n=10$ spins $1/2$. One readily notes that the variance of such distributions decreases as the number of considered spins, and hence the dimension of the corresponding Hilbert space, is increased, the calculated variances are reported in Figure 5-3.



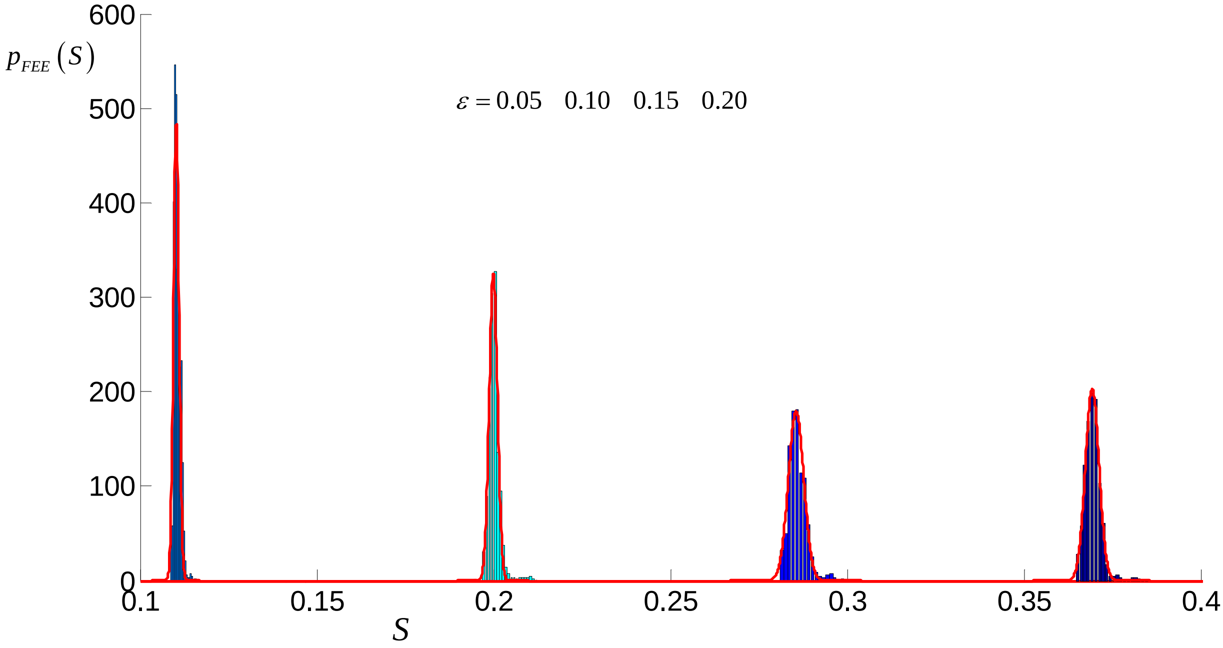


Figure 5- 3: Ensemble distribution of the entropy from the sampling of the geometric fixed expectation energy distribution. The (normalized) histograms refer to different values of the energy per spin as indicated in the figure, and they are fitted with a Gaussian distribution. The upper panel refers to a system of $n = 6$ spins while the lower panel is the sampling for $n = 10$

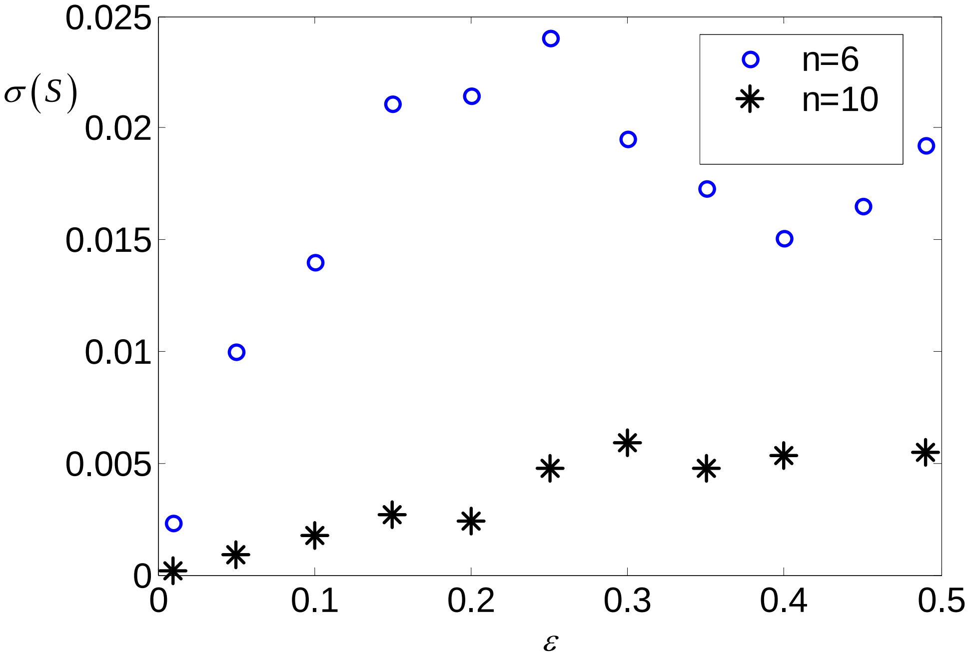


Figure 5- 4: Standard deviation of the Ensemble Distribution of the Entropy function depicted in Figure 5-3 as a function of the energy per spin

Since practically all the states of the ensemble are characterized by a value of entropy which is very close to its ensemble average when n is moderately large, we study this average as a function of the energy. The analytical approximation of the distributions previously derived is very convenient for this purpose because the averages can be calculated analytically. Being a non linear function of the set of stochastic variables $\{P_1,...,P_N\}$ the average entropy in the ensemble depends on the distributions of the stochastic variables and not just on their averages $\{\langle P_1\rangle,...,\langle P_N\rangle\}$.

According to the distribution introduced by Wootters, eqs. (4.3.8), the average entropy reads

$$\langle S\rangle_{W_{FEE}} = -\sum_{k=1}^{N}\langle P_k\rangle_{W_{FEE}}\ln\langle P_J\rangle_{W_{FEE}} - (1-\gamma) \qquad (5.4.6)$$

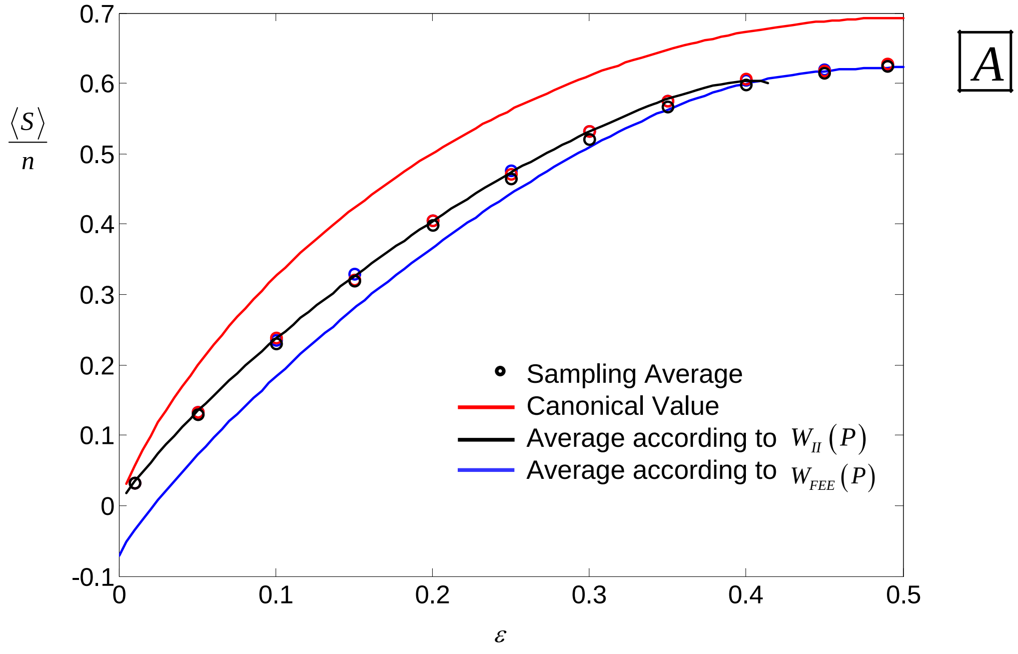
where $\gamma = 0.5772$ is the Eulero constant, and the average populations reads $\langle P_J\rangle_{W_{FEE}} = (\lambda+\mu E_J)^{-1}$. In Figure 5-5 the average entropy per spin $\langle S\rangle_{W_{FEE}}/n$ as a function of the energy per spin is depicted. The symbols refer to the averages obtained from numerical sampling of the geometrical FEE Distribution while the blue lines are the averages according to the Wootters distribution, i.e. eq. (5.4.6). Due to the difference between the approximate form of the distribution of the first population and the real one, discussed in Section 4-6, the average value of the entropy per spin calculated according to the approximate distribution $W_{FEE}(P)$ underestimates in general the real values. Notice also that for low energy and moderate value of spins number n it takes negative values.

Averaging with respect to the alternative distribution $\mathcal{W}_{II}(P_1,\ldots,P_N)$, eq. (4.7.6) derived in Section 4-7 by tacking into account the peculiar behaviour of the distribution of the first population, one gets

$$\langle S\rangle_{W_{II}} = -\sum_{k=1}^{N}\langle P_k\rangle_{W_{II}} \ln\langle P_k\rangle_{W_{II}} - (1-\gamma)\left(1-\langle P_1\rangle_{W_{II}}\right) \tag{5.4.7}$$

where now the ensemble averages of the populations are those given in eqs. (5.4.2)-(5.4.5).

A very good agreement between the average entropy calculated according to $W_{II}(P)$ and the average entropy which result from the sampling of the geometrical distribution is obtained, as depicted in Figure 5-5 for both the considered case. For comparison we have also drawn the entropy corresponding to the global canonical populations, eq. (2.3.41), corresponding to the same value of the expectation energy, eq. (2.3.42). which is, by definition, the maximum value of the entropy compatible with a give value of the expectation energy E.



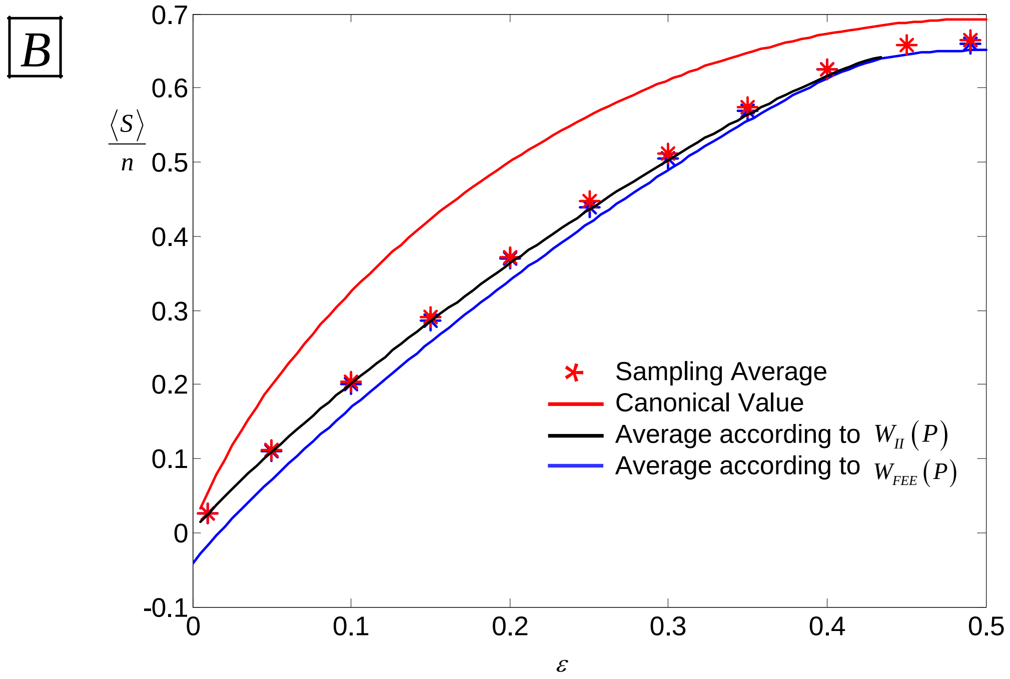


Figure 5- 5: Average Entropy per spin as a function of the energy per spin, Figure A refers to a system of $n=6$ spins while B is the sampling for $n=10$. In the figure are shown the average obtained by the numerical sampling (circle/asterisk), the average according to the Wootters approximation (blue line), the average according to the second approximate form (black dotted line), and the canonical value (red line)

We can thus use eq. (5.4.7) in order to predict the behaviour of the typical entropy per spin in the limit $n \to \infty$. By using the average populations, eqs. (5.4.3) and (5.4.5) one obtains the following average entropy in the limit of large n

$$\langle S\rangle \overset{n\to\infty}{=} n2\varepsilon \ln 2-(1-\gamma)2\varepsilon+2\varepsilon \ln\left(\frac{1-2\varepsilon}{\varepsilon}\right)-\ln(1-2\varepsilon) \tag{5.4.8}$$

which entails a linear relation between the average entropy per spin and the energy per spin in the thermodynamic limit $n \to \infty$, $\varepsilon = E/n = \text{cost}$

$$\frac{\langle S\rangle}{n} \overset{n\to\infty}{=} \varepsilon 2\ln 2 \tag{5.4.9}$$

In figure 5-6 the convergence toward this limiting behaviour is depicted. Even if we have considered for the sake of simplicity the ideal case of identical spins the same behaviour is found also for non identical spins with different Zeeman splitting.

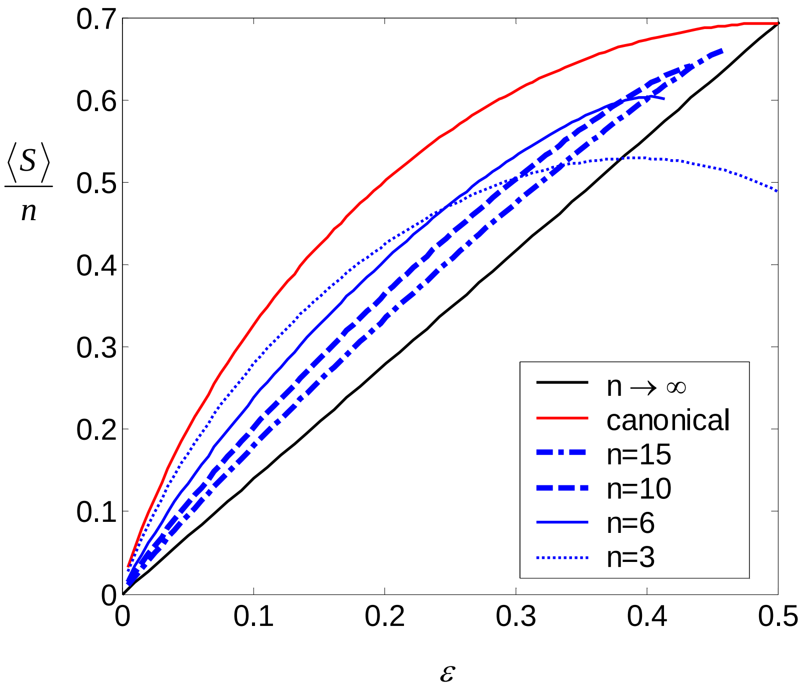


Figure 5- 6: Average Entropy per spin as a function of the energy per spin according to the approximate distribution $W_{II}\left(P_1,\ldots,P_N\right)$. The curve refers to different value of the number of spins as specified in the legend

5.4.2 ENSEMBLE DISTRIBUTION OF THE EQUILIBRIUM STATE OF A SUBSYSTEM

In Section 2.4 the equilibrium average state of a non interacting subsystem was defined through its asymptotic time average and reads

$$\bar{\mu} = \sum_s \sum_b P_{sb} |s\rangle\langle s| \tag{5.4.10}$$

where each populations P_{sb} corresponds to an energy level of the global system which can be expressed as the sum of an energy level of the subsystem and of the environment (bath)

$$E_k = E_s + E_b \tag{5.4.11}$$

From eq. (5.4.10) it appears that the equilibrium state of the subsystem S depends on the detailed specification of the whole pure state, i.e. depends on the specific populations set. We shall now consider the ensemble distribution of the equilibrium average reduced density matrix of n_S spins among the n spins which constitute the whole system. The other $n_B = n - n_S$ spins have to be considered as the environment for the selected subsystem. Figure 5-7A shows the ensemble distribution obtained from the sampling of the FEED for the diagonal element $\bar{\mu}_{\beta\beta}$ of the time averaged reduced density matrix of a single spin which belongs to a six spins system. In the following E_β $\left(E_\alpha\right)$ will denote the lowest (higher) eigen energy of a two level system. The normalized histograms of the sampling refer to different values of the energy per spin and they are fitted with Gaussian distributions whose variance decreases as the energy per spin is lowered. The typicality of the equilibrium reduced density matrix can be seen, in this case, as a direct manifestation of the Central Limit Theorem (Appendix 4.4). An element of the RDM is in fact a sum of $N_B = 2^{n_B}$ random variables exponentially distributed on the ensemble (see eqs. (4.7.6), (4.7.5)), the scale parameter of such distributions reads

$$E_k \mu_2 = \frac{E_k\left(N-1\right)}{E} \tag{5.4.12}$$

For the diagonal element of the RDM which corresponds to $E_s = 0$ there is a contribution due to P_1 whose probability distribution is different from the others, and it is given by a Dirac delta distribution, eq. (5.4.1).

In the simple case of identical spins, the energies E_b of the environment are distributed as the spectrum of n_B identical spins, that is

$$d\left(E_b\right) = \binom{n_B}{b} = \frac{n_B!}{b!\left(n_B - b\right)!} \tag{5.4.13}$$

Thus, it follows from the CLT, eq. (A4.4.10), that, if $N_B = 2^{n_B}$ is large, the Ensemble Distribution of the stochastic variable $\bar{\mu}_{ss}$ is a Gaussian with average

$$\left\langle \bar{\mu}_{ss} \right\rangle = \sum_{b=0}^{n_B} \left\langle P_{sb} \right\rangle = \sum_{b=0}^{n_B} \binom{n_B}{b} \frac{E}{2^n - 1} \frac{1}{\left(E_S + E_b\right)} + \left\langle P_1 \right\rangle \delta_{s1} \tag{5.4.14}$$

and variance

$$\sigma^2\left(\bar{\mu}_{ss}\right) = \sum_{b=0}^{n_B} \binom{n_B}{b}^2 \sigma^2\left(P_{sb}\right) = \sum_{b=0}^{n_B} \binom{n_B}{b}^2 \frac{E^2}{\left(2^n - 1\right)^2} \frac{1}{\left(E_S + E_b\right)^2} \tag{5.4.15}$$

By considering again that the binomial coefficient is very peaked around $b = n_B/2$, and by using the following properties of the binomial coefficients

$$\sum_{b=0}^{n_B} \binom{n_B}{b}^2 = \binom{2n_B}{n_B} \approx \frac{2^{2n_B}}{\sqrt{\pi n_B}} \tag{5.4.16}$$

(where the last relation is obtained by applying the Stirling's approximation for the factorial) the variance (5.4.15) can be estimated as

$$\sigma^2\left(\bar{\mu}_{ss}\right) \approx \frac{E^2}{N_S^2} \frac{1}{\sqrt{\pi n_B}} \frac{1}{\left(E_S + n_B/2\right)^2} \approx \frac{E^2}{N_S^2} \frac{2^2}{\sqrt{\pi}} \frac{1}{n_B^{5/2}} \tag{5.4.17}$$

It turns out that the variance of the distributions of the equilibrium average of the state of a subsystem of spins is proportional to the expectation energy, while it decreases as the number of spins in the environment increases. This is evident also from the performed sampling: Figure 5-7C shows the standard deviation of the obtained distributions for the state of one spin as a function of the energy per spin and for two different sizes of the total system $n = 6$ and $n = 10$.

The average values of the ensemble distribution, eq. (5.4.14), for the diagonal element corresponding to the lower eigenstate of the two level system can be written as

$$\left\langle \bar{\mu}_{\beta\beta} \right\rangle = 1 - \varepsilon \tag{5.4.18}$$

Figure 5-7B shows that the averages obtained from the sampling are actually well fitted by eq (5.4.18), and this average value does not depend, as one expects, on the dimension of the total system.

We thus verify that, while the variance of the ensemble distribution of the RDM elements is inversely proportional to a power of the number of spins in the environment, its average depends only on the energy per spin, thus the existence of a typical value for the equilibrium reduced density matrix is assured when n_B is moderately large. Moreover, since the ensemble distribution is Gaussian, the typical value of the equilibrium average of the diagonal elements of the RDM of a subsystem can be identify with its average, eq. (5.4.18).

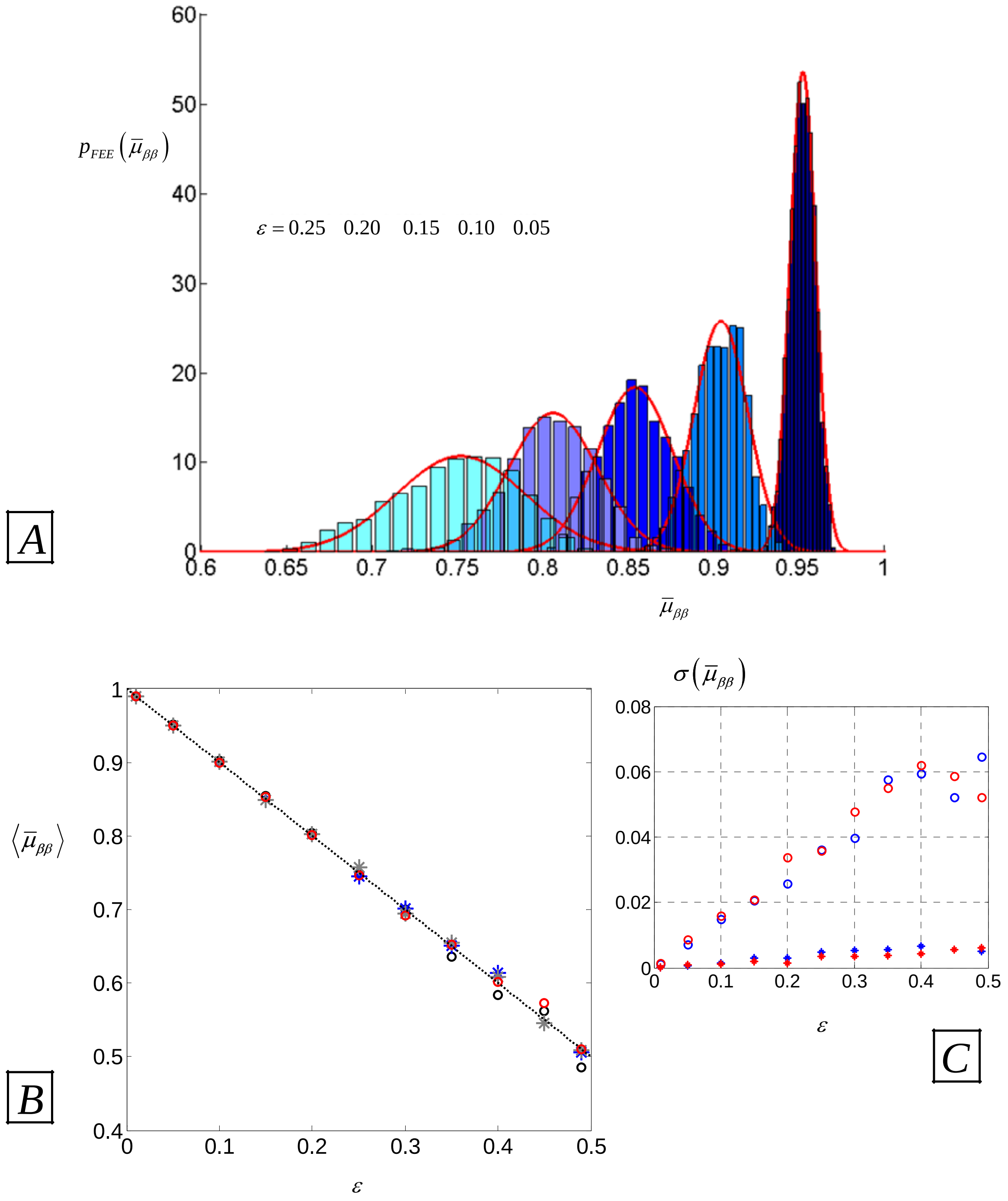


Figure 5- 7: A) Ensemble Distribution for the equilibrium average of the RDM diagonal element $\bar{\mu}_{\beta\beta}$ of a single spin which belongs to a $n=6$ spins system, obtained from the sampling of the FEED of the total system. The red lines are the Gaussian fit. In B) the ensemble average values of the same element of the reduced density matrix are represented: such a parameter does not depend on the total number of spins in the system. The circles refer to the sampling for $n=6$ while the asterisks refer to the case $n=10$, and it is well fitted by eq. (5.4.18) (dotted line). The variances of the sampled distributions are depicted in C) and diminishes as n is increased: the circle refers to $n=6$ while the asterisks refer to $n=10$.

Notice that the diagonal elements of the RDM of a two levels system can be always written in canonical forms

$$\left\langle \bar{\mu}_{\beta\beta} \right\rangle = \frac{e^{-\beta\frac{\omega_0}{2}}}{Q} \qquad \left\langle \bar{\mu}_{\alpha\alpha} \right\rangle = \frac{e^{+\beta\frac{\omega_0}{2}}}{Q} \tag{5.4.19}$$

One can thus think to use the typical reduced state of one spin as a sort of thermometer, and following this idea one can define a local inverse temperature given by

$$\beta_{loc} = -\frac{1}{\omega_0} \ln\left(\frac{\varepsilon}{1-\varepsilon}\right) \tag{5.4.20}$$

which in this case corresponds to the inverse temperature which one would obtain from the canonical form of the global populations, eq. (2.3.41).

5.5 THE RANDOM PURE STATE ENSEMBLE

For a spins system the Random Pure State Ensemble defined on the full Hilbert space can be interpreted as the infinite temperature limit of the Fixed Expected Energy Ensemble. One has indeed that as the energy per spin approaches its infinite temperature value

$$\varepsilon \to \frac{E_{T_{\inf}}}{n} = \frac{1}{2} \tag{5.5.1}$$

the parameters which define the Fixed Expectation Energy Distribution according to the conditions (4.6.9) tend to their limiting values $\lambda \to N$ and $\mu \to 0$. Therefore, the populations distributions $W_{FEE}\left(P_k\right)$ approach the Random Pure State populations distribution as one can see from e.g. Figure 5-2

$$W_{FEE}\left(P_k\right) \to W_{RPS}\left(P_k\right) = Ne^{-NP_k} \tag{5.5.2}$$

where N is determined by the number of spins in the system according to eq. (5.3.1).

5.5.1 TYPICALITY IN THE LIMIT OF INFINITE TEMPERATURE: A TEST FOR THE INDEPENDENCE HYPOTHESIS

In this condition the only free parameter of the problem is the number of spins which constitutes the whole system. It is worth to take advantage of the symmetry underlying the RPSE which implies a very simple form of the analytic approximation of the population distributions, eq. (5.5.2), as well as the availability of the exact joint distribution on K populations, eq. (4.4.6). Thus, we shall study the behaviour of the Ensemble Distribution of our "target" functions, that is, the equilibrium average value of the RDM of a subsystem and the global entropy, as the number of components (spins) n is increased.

First let us look at the ensemble distribution of the Reduced Density Matrix of $n_S < n$ spins, eq. (5.4.10). In this case it is a sum of $N_B = 2^{n-n_S}$ identically distributed random variables. By assuming also that they are independent, that is by using the approximate exponential distribution eq. (5.5.2), one can apply the Central Limit Theorem (Appendix 4.4) to conclude that the probability distribution of the equilibrium value of an element of the RDM $\overline{\mu}_{ss}$ in the ensemble is Gaussian with mean

$$\left\langle \overline{\mu}_{ss} \right\rangle = \frac{N_B}{N} = \frac{1}{N_S} \tag{5.5.3}$$

that is, equal average population for each energy level of the system, and a variance decreasing very rapidly with the number of spins in the system

$$\sigma^2_{\overline{\mu}_{ss}} = \frac{N_B}{N^2} = \frac{1}{N_S}\frac{1}{2^n} \tag{5.5.4}$$

At a first sight the prevision of the CLT about the Ensemble Distribution of the equilibrium RDM is satisfactory as shown in Figure 5-8 in which the subsystem is identified as a single spin.

Interestingly enough, by looking at the variance of the Gaussian distributions as a function of the total number of states, one finds that the actual value of the variance is smaller by a factor 2 than that predicted on the base of the CLT. This, for $n_S = 1$ reads

$$\ln \sigma^{CLT}_{\overline{\mu}_{\beta\beta}} = -\frac{1}{2}\ln N - \frac{1}{2}\ln 2 \tag{5.5.5}$$

This is shown in Figure 5-9A, the results of eq. eq. (5.5.5) are represented with a continuous line, while the red dots are the actual values of the variance resulting from the

Monte Carlo sampling of the geometrical distribution, which depend on the total number of states as

$$\ln \sigma_{\bar{\mu}_{\beta\beta}}^{real} = -\frac{1}{2}\ln N - \ln 2 \tag{5.5.6}$$

and thus they are twice the variance one expects on the basis of the Central Limit Theorem

$$\sigma_{\bar{\mu}_{\beta\beta}}^{CLT} = \frac{1}{\sqrt{2N}} = \sqrt{2}\sigma_{\bar{\mu}_{\beta\beta}}^{real} \tag{5.5.7}$$

The origin of this discrepancy is found in the statistical correlation between the different populations which is neglected in the approximate form of the ensemble distribution. Indeed, the variance of a sum of non independent stochastic variables is

$$\sigma^2\left(\sum x_i\right) = \sum_i \sum_j \operatorname{cov}\left(x_i, x_j\right) \tag{5.5.8}$$

where $\operatorname{cov}\left(x_i, x_i\right) = \sigma_{x_i}^2$, while the covariance for $i \neq j$ is defined as

$$\operatorname{cov}\left(x_i, x_i\right) = \left\langle x_i x_j \right\rangle - \left\langle x_i \right\rangle \left\langle x_j \right\rangle \tag{5.5.9}$$

We can evaluate the covariance of two different populations by means of their joint RPSE probability distribution, from eq. (4.4.6) this is

$$p_{RPSE}\left(P_1, P_2\right) = \left(N-1\right)\left(N-2\right)\left(1-P_1-P_2\right)^{N-3} \tag{5.5.10}$$

The covariance turns out to be $-4/N^3$, and thus it brings a negative contribution to the variance of the reduced density matrix distribution. Explicit calculation for the specific case, $n_S = 1$, gives the following exact variance according to eq. (5.5.8)

$$\sigma_{\bar{\mu}_{\beta\beta}}^2 = \frac{N}{2}\sigma_{P_k}^2 + \frac{N}{2}\left(\frac{N}{2}-1\right)\operatorname{cov}_{k \neq k'}\left(P_k, P_{k'}\right) = \frac{1}{2N} - \frac{1}{4N} = \frac{1}{4N} = \frac{\sigma_{\bar{\mu}_{\beta\beta}}^{2(CLT)}}{2} \tag{5.5.11}$$

which is exactly what one obtains from the numerical sampling. In figure 5-9-B the two contributions to the total variance are separately drawn. From the above analysis one can conclude that:

1. The populations are actually less and less statistically correlated as N increases, the correlation coefficient R is in fact of the order of N^{-1}

$$R_{i,j\neq i}=\frac{\operatorname{cov}\left(P_i,P_j\right)}{\sigma_i\sigma_j}=-\frac{4}{N}$$

2. However, when we are interested to evaluate the variance in the ensemble of a quantity which results from the sum of a great number of populations, that is all the observables pertinent to the subsystem as well as collective functions such as the entropy, the contribution from the correlations is of the same order of that due to the variance of the single populations. Moreover, this is a *negative* contribution which thus enhances the typicality properties of all that quantities which are defined as linear combination of populations with positive coefficients as, e.g. the expectation value of the energy.

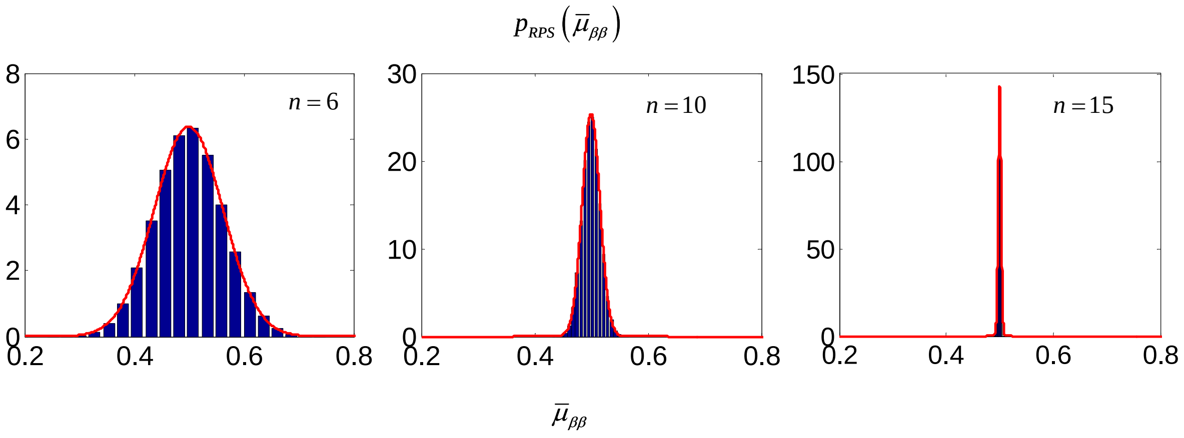


Figure 5- 8: RPS Ensemble Distribution of the $\beta\beta$ element of the equilibrium reduced density matrix of a single spin for different numbers of components in the total system, as specified in the figures.

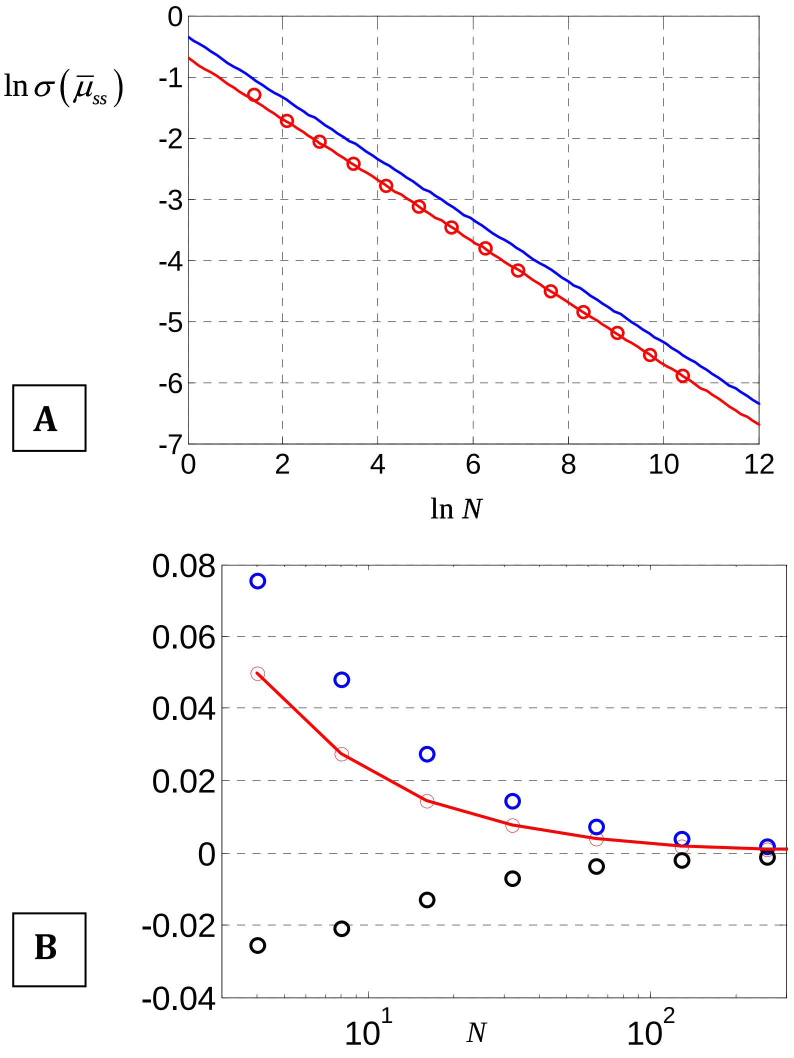


Figure 5- 9: A) Variance of the Ensemble Distribution of the $\beta\beta$ element of the equilibrium reduced density matrix of a single spin as a function of the total dimension of the Hilbert space $N = 2^n$. Blue line: behavior predicted on the base of the statistical independence hypothesis, red line: actual behavior. B) Different contributions to the variance of the RDM elements (red line): positive contribution due to the variance of the single populations (blue dots) and negative contribution due to the statistical correlation between different populations (black dots).

To conclude this section we look at the typical entropy in the RPS, which is given as

$$\langle S \rangle = \ln N - 0.423 \tag{5.5.12}$$

As it is depicted in Figure 5-10 the entropy per spin approaches its maximum value (i.e., $\ln 2$) as the number of spins in the composite system increases while the corresponding variance in the ensemble diminishes. It can be shown that, in the leading order of N,

$$\frac{\sigma_S}{\langle S\rangle}\propto\frac{1}{\sqrt{N}} \tag{5.5.13}$$

Thus the Ensemble Distribution of the entropy becomes sharper and sharper as the number of spins in the system increases.

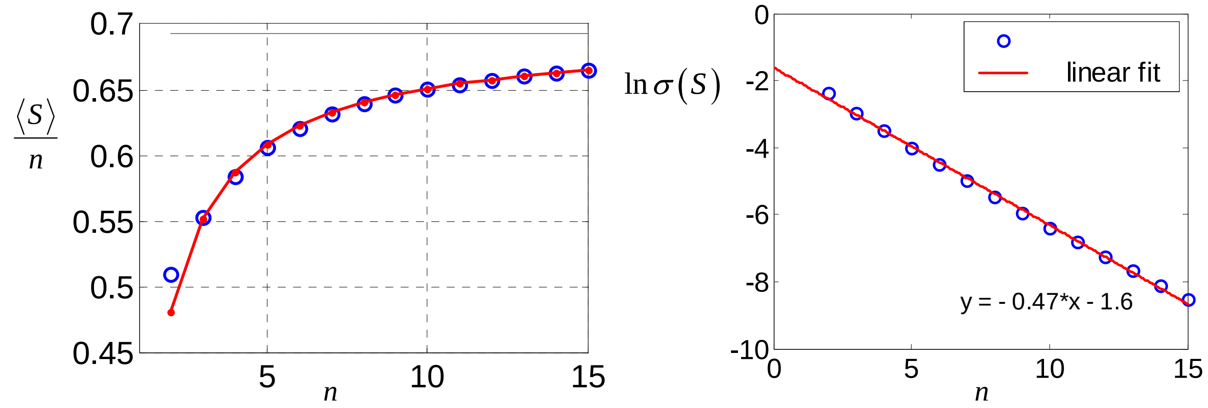


Figure 5- 10: Average value (A) and variance of the RPS Ensemble Distribution of the entropy per spin as a function of the number of spins which form the total system.

At this point we notice that also the expectation value of the Hamiltonian is effectively a function which tends to assume its typical value according to the specification of the considered Hilbert space. In this section we have considered the ensemble of all possible wavefunctions which can describe a system of n spins $1/2$. Despite the fact that pure states characterized by any value of the expectation energy belong to such an ensemble it turns out that, when n is large, by virtue of what we have called “typicality”, the overwhelming majority of such states represents the system in its infinite temperature limit. Indeed, the RPS Ensemble distribution of the expectation energy is centered at the energy corresponding to the infinite temperature condition, and its standard deviation decreases as the system size increases

$$\langle\varepsilon\rangle=\frac{\langle E\rangle}{n}=\frac{1}{2}\qquad\qquad \sigma_E\approx O\left(\frac{n^2}{2^n}\right) \tag{5.5.14}$$

This implies that if we pick at random a wavefunction from this ensemble we will find very likely a system with total energy $E\approx n/2$. From this perspective the Fixed Expectation Energy Ensemble studied before selects states which have extremely low probability of existence with respect to the maximum energy states.

We can thus ask the following question: how can we define Random Pure State Ensembles with a given typical expectation energy different from that corresponding to the infinite temperature condition? One way to obtain this, is that of working with a subspace of the total Hilbert space. In the following Section, we shall illustrate the results of this procedure for the $1/2$ spins system. However, it is worth to point out that the restriction of the Hilbert space to some finite dimension becomes necessary when dealing with systems whose Hamiltonian spectrum is unbounded.

5.5.2 RANDOM PURE STATE WITH TYPICAL ENERGY

Let us now define a RPSE with a typical value of the expectation energy E. The typical value can be identified with the average of the expectation energy ensemble distribution and reads

$$\langle E\rangle(k_{\max})=\frac{1}{N(k_{\max})}\sum_{k=0}^{[k_{\max}]}\binom{n}{k}k\omega_0 \tag{5.5.15}$$

where $k_{\max}$ is the index which identifies the highest energy eigenstate which can be populated, and $[k_{\max}]$ is the greatest integer less then or equal to $k_{\max}$. The number of populated energy levels, and thus the dimension of the Hilbert space on which the RPS Ensemble is defined, reads as

$$N(k_{\max})=\sum_{k=0}^{[k_{\max}]}\binom{n}{k} \tag{5.5.16}$$

It is convenient to use the Gaussian continuous form of the energy density of the spectrum, eq. (5.3.6). If the considered spins are not all identical, the general form (5.3.8) has to be used, but this does not change the properties of the Ensemble Distributions which we want to investigate. In the continuum approximation Eq. (5.5.16) become

$$N(E_{\max})=\frac{2^n}{\sqrt{\pi n/2}}\int_0^{E_{\max}}e^{-\frac{(E-n/2)^2}{n/2}}dE=2^{n-1}\left(1+\operatorname{erf}\left(\frac{E_{\max}-n/2}{\sqrt{n/2}}\right)\right) \tag{5.5.17}$$

where $E_{\max}$ is the maximum energy which is allowed be populated in order to have a RPSE with a typical expectation energy equal to E, $E_{\max}=[k_{\max}]\omega_0$ in the case of identical spins.

However the representation of the spectrum as a continuum can easily describe the more general situation of spins with different Zeeman frequencies.

Let $e_m = E_{\max}/n$ then

$$N\left(e_\mathrm{m}\right) = 2^{n-1}\left(1+\operatorname{erf}\left(\left(e_\mathrm{m}-1/2\right)\sqrt{2n}\right)\right) \tag{5.5.18}$$

and the typical energy as a function of the maximum energy reads

$$\langle E\rangle\left(e_m\right) = \frac{n}{2} - \frac{2^{n-1}\sqrt{n}}{\sqrt{2\pi}}\left(\frac{e^{-\left(e_m-1/2\right)^2 2n}}{N\left(e_m\right)}\right) \tag{5.5.19}$$

The relation between the typical expectation energy and the parameter e_m, eq. (5.5.19), is represented in Figure 5-11 together with the exact discontinuous function, eq. (5.5.15). The figures refer to systems with different numbers of identical spins. As one expects, the real, discontinuous function approaches the continuum approximation as n increases. In the limit $n \to \infty$ for a fixed value of $e_m < 1/2$ the argument of the error function in eq. (5.5.18) tends to $-\infty$, and thus the asymptotic expansion of the complementary error function can be used (we retain just the first term):

$$1+\operatorname{erf}\left(\left(e_\mathrm{m}-1/2\right)\sqrt{2n}\right) = 1-\operatorname{erf}\left(x\right) \qquad x = -\left(e_\mathrm{m}-1/2\right)\sqrt{2n}$$

$$1-\operatorname{erf}\left(x\right) \overset{x\to\infty}{\approx} \frac{e^{-x^2}}{x\sqrt{\pi}}$$

In this limit we obtains

$$N\left(e_\mathrm{m}\right) = 2^{n-1}\frac{e^{-\left(e_\mathrm{m}-1/2\right)^2 2n}}{\left(e_\mathrm{m}-1/2\right)\sqrt{\pi 2n}} \tag{5.5.20}$$

$$\frac{\langle E\rangle}{n}\left(e_m\right) = e_m \tag{5.5.21}$$

It turns out that the typical expectation energy in the RPSE corresponds to the maximum energy level which is populated.

In conclusion the Random Pure State Ensemble is defined in the Hilbert space spanned by the Hamiltonian eigenvectors which corresponds to energies $E_k < E_{\max}$

$$\mathcal{H}_{\mathcal{RPS}} = span\left\{ \left| k \right\rangle \middle| E_k < E_{\max} \right\} \tag{5.5.22}$$

Once defined the active Hilbert space the approximate Ensemble Distributions on the populations are defined as

$$W_{RPS}\left(P_k\right) = N\left(E_{\max}\right) e^{-N\left(E_{\max}\right)P_k} . \tag{5.5.23}$$

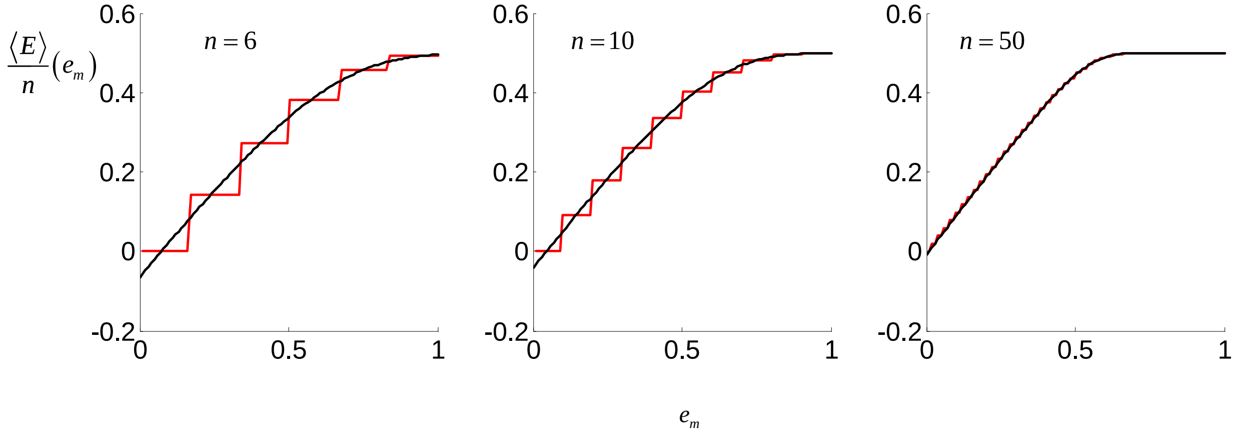


Figure 5- 11: Typical expectation energy per spin of the RPSE as a function of the Maximum energy per spin. The red line is the exact discontinuous function eq. (5.5.15) while the black line represents the continuum approximation, eq. (5.5.19).

5.5.3 ENTROPY AND EQUILIBRIUM STATE OF A SUBSYSTEM

We can now study the behaviour of the RPSE typical entropy as a function of the typical energy in this ensemble. Differently from the FEEE in which the expectation energy is fixed arbitrarily as an independent parameter, here also the energy is a quantity which is distributed on the ensemble. In Figure 5-8 the Ensemble Distribution of the expectation energy and the corresponding distribution of the entropy are shown for a system composed of $n=8$ spins $1/2$. In order to study the entropy as a function of the energy, we exploit the relation between their average values, and this is meaningful in the probabilistic sense since the typicality properties is itself defined in terms of probability.

The ensemble average entropy is, according to eq. (5.5.12)

$$\langle S\rangle = \ln N\left(k_{\max}\right) - 0.423 \tag{5.5.24}$$

where the number of energy levels are related to the energy trough 5.4.15 and corresponds to the dimension of the considered Hilbert space, 5.4.22.

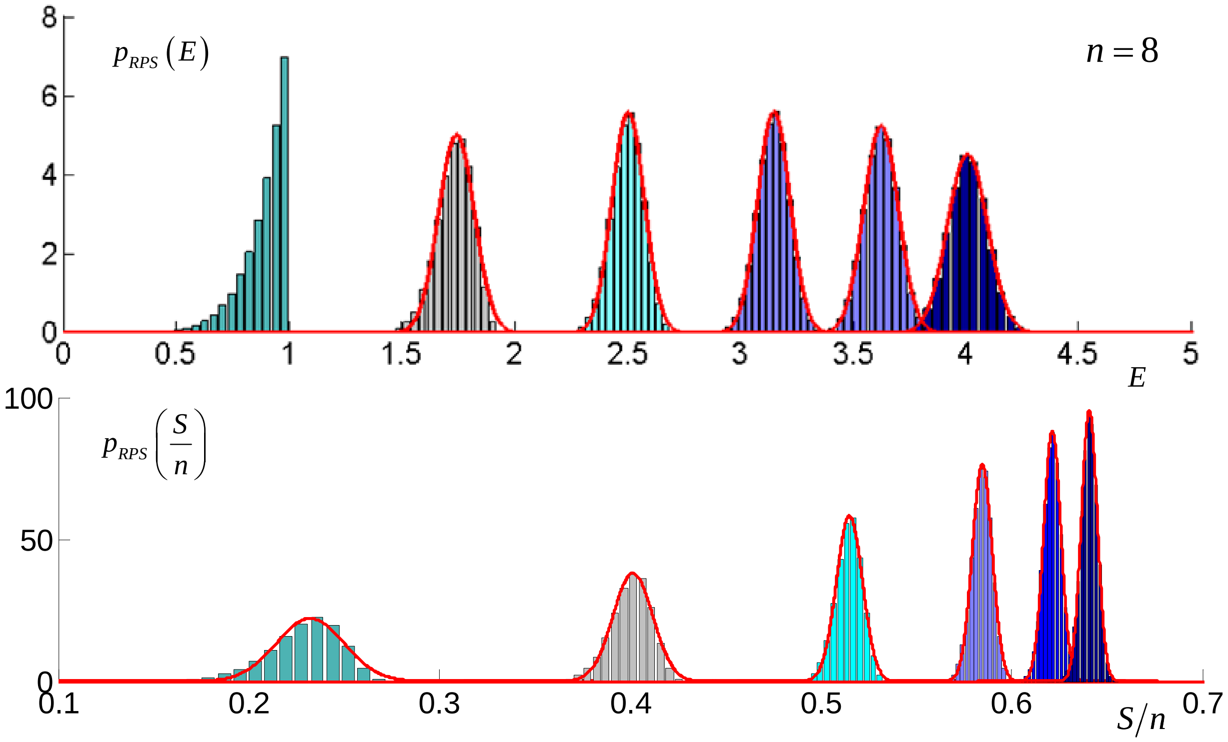


Figure 5- 12: Random Pure State Ensemble Distribution of the expectation energy E and corresponding ensemble distribution of the entropy. The figure refers to a system of $n=8$ identical spins $1/2$.

The typical entropy per spin as a function of the typical Energy per spin is depicted in figure 5-13 for system of different size. The average values calculated according to (5.5.15) and (5.5.24), represented by the dotted black lines, perfectly agree with that obtained from the Monte Carlo sampling of the geometrical distribution performed for $n=6,8,10$. For larger system, $n=50,500$ it is evident that the average entropy approaches its corresponding canonical value even if the populations itself are not canonical at all. The variances of the Ensemble Distributions of the considered functions, energy and entropy, are also shown and they decreases as the number of spins is increased according to the analysis presented above.

In the limit of large n we can use eqs. (5.5.20) and (5.5.21) to calculate the typical entropy per spin as a function of the typical energy per spin and it reads

$$\frac{\langle S\rangle}{n}=\log 2-2\left(\frac{\langle E\rangle}{n}-\frac{1}{2}\right)^2 \tag{5.5.25}$$

This is a valid approximation when the energy is not too low, because for low energy the continuum approximation breaks down and one has to “count” the energy levels according to eq. (5.5.16). Nonetheless the dependence of the typical entropy on the energy implied by eq. (5.5.25) is quite different from the linear relation obtained for the FEEE, eq.(5.4.9). This is a sign that the statistical thermodynamics which arise from the two ensembles is different. This interesting feature will be analyzed in the next Chapter.

Notice that the typicality become “efficient” in selecting the typical value of the considered functions also for systems composed of relatively few spins. In this perspective we can think about the emergence of thermodynamic properties also for mesoscopic systems and without invoking the thermodynamic limit.

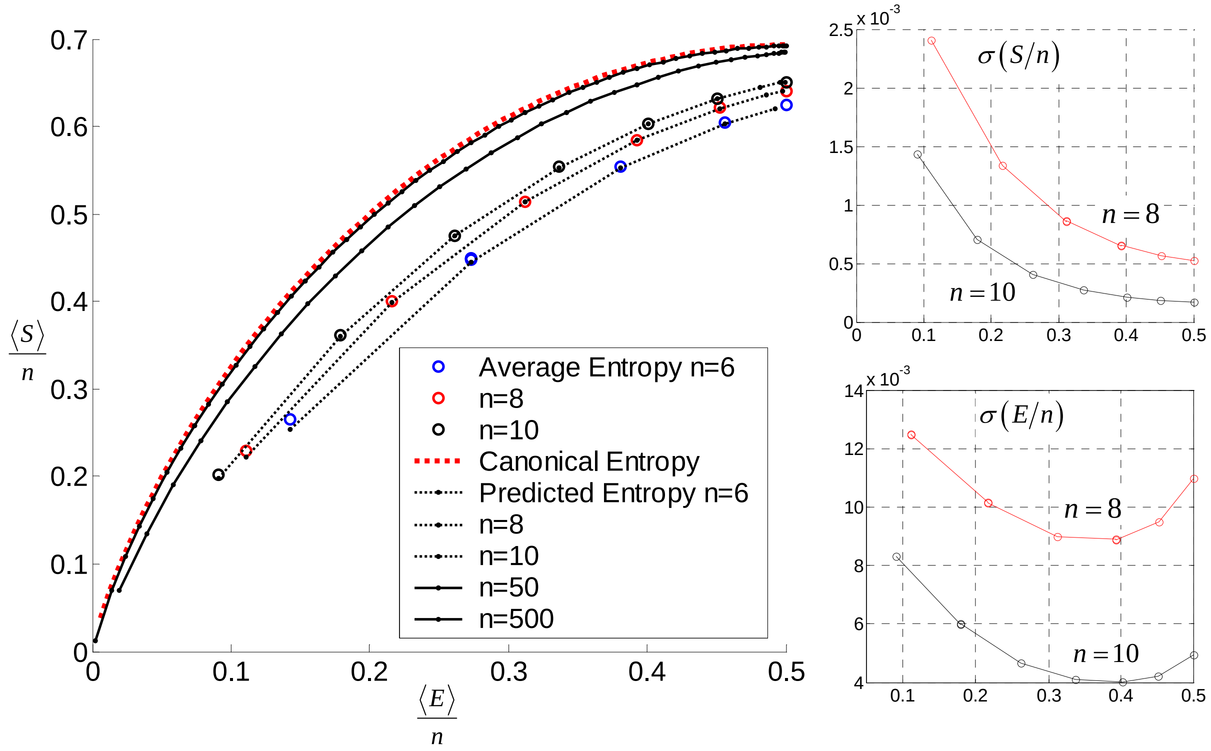


Figure 5- 13: Typical entropy per spin as a function of the typical Energy per spin for different number of components (spin $1/2$) of the system. On the left the figure shown the average obtained from the sampling (circle) and the prediction on the base of the approximate distributions (black lines). The canonical value (red dotted line) is reported for comparison. On the right the variances on the RPSE for the considered functions are depicted as a function of the average energy per spin and for two different numbers of components.

The equilibrium average state of a much smaller subsystem in the RPSE is also characterized by a much peaked distribution as in the case of the FEEE. Its Ensemble Average is, in this case, a sum of the average global populations in the considered Random Pure State Ensemble

$$\langle \bar{\mu}_{ss} \rangle = \sum_{b}^{k_{\max}} \langle P_{sb} \rangle = \frac{N^s(k_{\max})}{N(k_{\max})} \tag{5.5.26}$$

where $\langle P_{sb}\rangle$ are the ensemble averaged population corresponding to $E_{sb}=E_s+E_b\le E_{\max}$. In the case of identical spins, the energy levels E_{sb} which contributes to the summation for the s-th diagonal element of the RDM are distributed as the energies of $n-n_s$ spins centred at $\bar{E}_{m,s}=E_s+\frac{n-1}{2}$. If the subsystem is a single spin, $n_S=1$, one explicitly has

$$\begin{aligned}\langle\bar{\mu}_{\alpha\alpha}\rangle&=\sum_{b}^{k_{\max}}\langle P_{\alpha b}\rangle=\frac{N^{\alpha}\left(k_{\max}\right)}{N\left(k_{\max}\right)}\\N^{\alpha}\left(k_{\max}\right)&=\sum_{k}^{k_{\max}}\binom{n-1}{k-1}\end{aligned}\tag{5.5.27}$$

In this case the average value of the equilibrium RDM as function of the energy per spin resulting from the RPSE is the same as in the FEEE, see Figure 5-7-B, and thus the relation (5.4.18) and what follows is valid as well.

In this section the ensemble properties of the entropy and the equilibrium state of a subsystem have been investigated for the simplest case of a system composed of non interacting spins. By virtue of what we have called here typicality, the functions we have considered are characterized by very sharp distributions on both the ensembles, even for moderate values of the number of spins in the system. For this reason it is meaningful to study the relation between their typical values. The notably evidence that it does exist a most probable value of e.g. the entropy function in the ensembles can be interpreted as the emergence of a possible thermodynamic description of the finite system. Indeed, such a description does not depend on the details of the state of the system itself but only on the "typical" value of some functions which at this point we can denote as thermodynamic functions, such as the energy. In the next chapter we directly consider this possibility by generalizing the analysis presented here to generic systems in order to have a better understanding of the behaviour of these typical values.

CHAPTER 6

CONNECTION WITH THERMODYNAMICS: COMPARISON BETWEEN ENSEMBLES

6.1 INTRODUCTION

For a given system described by a wavefunction in a finite dimensional Hilbert space and characterised by a generic spectrum of the energy, the distributions on the possible set of populations and phases are the broadest ones compatible with the constraints. Nevertheless the concept of typicality discussed in the previous Chapter assures that if N, the dimension of the considered Hilbert space, is large then it exists a typical value of the entropy function that can be considered as the actual value which characterizes any wavefunction which belongs to the ensemble. Moreover, since the Ensemble distribution is in general a Gaussian distribution, such a typical value coincides with the average value. In this chapter we shall discuss the possibility to consider the ensemble average of functions such as the entropy or the energy from a thermodynamical point of view. The resulting statistical thermodynamic which is associated to the ensemble can be thought as emerging from the single pure state which belongs to the considered ensemble.

6.2 DEFINITION OF THE THERMODYNAMIC FUNCTION

In line with the analysis of the $1/2$ spins system of the previous Chapter, we shall concentrate on the existence of a typical entropy in the ensemble which can be studied as function of the expectation energy. By virtue of its typicality, the definition of the thermodynamic entropy is given as the ensemble average of the entropy function. Thus, according to (4.2.4)

$$\langle S \rangle = -k_B \int_D S\left(P_1,\dots,P_K\right) p\left(P_1,\dots,P_K\right) dP_1..dP_K \tag{6.2.1}$$

where k_B is the Boltzmann constant and the probability distribution on the K independent populations has to be specified according to the considered ensemble and can be approximate by the corresponding analytical forms reported in Chapter 4.

On the other hand the expectation energy E shall play the role of the thermodynamic internal energy U. Two different scenarios exists for the internal energy depending on the considered ensemble. In the FEE Ensemble the value of the expectation energy is an independent parameter and it is not distributed in the ensemble of wavefunctions, thus $U = E$, while in the RPS Ensemble the portion of the Hilbert space we consider determines a typical value of the energy expectation value. In this case also the expectation energy is characterized by an ensemble distribution, see for example Figure 5-12, and thus the internal energy is defined as its RPS Ensemble average

$$U = \langle E \rangle = -\int_{D(E_{\max})} E\left(P_1,\dots,P_{N(E_{\max})-1}\right) p_{RPS}\left(P_1,\dots,P_{N(E_{\max})-1}\right) dP_1..dP_{N(E_{\max})-1} \tag{6.2.2}$$

where the function $U = \langle E \rangle \left(E_{\max}\right)$ has to be specified according to the energy spectrum of the considered system.

Once verified the existence of a typical entropy as a function of the typical energy, (or the fixed expectation energy in the case of the FEEE), we want to explore the congruence of such a function from the thermodynamical point of view. Indeed, in order to be a candidate for the role of thermodynamic entropy, an entropic function has to be an extensive quantity. This basically means that, for large enough number of components n, it should be possible to write it as a function of the energy per particle as

$$\langle S \rangle = ns\left(\frac{U}{n}\right) \tag{6.2.3}$$

where $s\left(\frac{U}{n}\right)$ is the entropy of a single particle. The extensivity of the entropy is required in order to define the microcanonical temperature, which is of course an intensive quantity and it is defined according to thermodynamics as

$$\frac{1}{k_B T} = \beta = \frac{d\langle S\rangle}{dU} \tag{6.2.4}$$

The extensive nature of the entropy is often assumed even in those cases in which it is not at all an obvious consequence of the definition itself, see for example the discussion of this point in [Gemmer, (2004)]. According to the definition, eq. (6.2.1), and by using the approximate distribution, eq. (5.5.23) for the populations, the average entropy in the RPSE is given in eq. (5.5.24) and reads

$$\langle S\rangle_{RPS} = \ln N\left(e_{\max}\right) - 0.423 \tag{6.2.5}$$

This is an extensive property, only if the parameter $e_{\mathrm{m}} = E_{\max}/n$ turns out to be directly proportional to the corresponding typical energy per particle $\varepsilon = E/n$ as it is the case for the spins system considered in the previous Chapter, see eq. (5.5.21). Indeed by duplicating the considered system one has $\langle E\rangle' = 2\langle E\rangle$ and if also $E_{\max}^{'} = 2E_{\max}$ then the number of resulting states is just the square of the original number of states, thus also the entropy is increased by a twofold factor. The asymptotic formula of the entropy derived for the spins system, eq. (5.4.25), is indeed of the form (6.2.3).

The average entropy in the Fixed Expectation Energy Ensemble is given in eq. (5.4.7) and reads

$$\langle S\rangle_{W_{II}} = -\sum_{k=1}^{N}\langle P_k\rangle_{W_{II}} \ln\langle P_k\rangle_{W_{II}} - (1-\gamma)\left(1-\langle P_1\rangle_{W_{II}}\right) \tag{6.2.6}$$

Apart from the constant term which does not matter in the large n limit, the entropy (6.2.6) would be naturally extensive if the average populations of the hypothetical doubled size system could be written as the product of the average populations of the original, identical, systems, i.e. $\overline{P}_{k'} = \overline{P}_{k1}\overline{P}_{k2}$, but this is not the case for the FEEE average populations as it is clear from eq. (4.7.7) and (4.7.8). Nevertheless, in the $1/2$ spins system examined in the previous Chapter we have found that the average entropy per spin is a linear function of the energy per spin, and thus is extensive. It remains to verify whether such a property emerges also in more general cases.

The definition of the microcanonical temperature, eq. (6.2.4), is actually the bridge to connect the properties of the whole isolated pure state with the equilibrium state of a subsystem. Indeed the usual canonical state associated to a system in thermal contact with a heat bath is

$$\rho^S \propto \frac{e^{-\beta_{loc} H_S}}{Q} \tag{6.2.7}$$

The canonical state plays a central role in all statistical mechanics. In the classical framework it can be derived from the microcanonical ensemble by assuming that the energy density increases approximately exponentially with the energy. In standard quantum statistical mechanics one can do the same by starting from the postulated form of the microcanonical statistical density matrix. The goal of ref. [Gemmer, (2006)], for example, is to show that the canonical state (6.2.7) can be also derived from a pure state which is a superposition of eigenstates which have about the same energy. Thus, our second focus will be on the typical value of the equilibrium state of a subsystem.

$$\langle \bar{\mu}_{ss} \rangle = \sum_s \sum_b \langle P_{sb} \rangle |s\rangle\langle s| \tag{6.2.8}$$

The points are: is it possible to write the ensemble typical value of the RDM, eq. (6.2.8), in the canonical form (6.2.7)? And if this is the case, does the “local” temperature which appears (6.2.7) agree with the microcanonical temperature defined by (6.2.4)?

In the following we shall answer these questions for our two ensembles.

6.3 STATISTICAL THERMODYNAMICS OF THE FIXED EXPECTATION ENERGY ENSEMBLE

We shall now generalize the analysis proposed in Section 5.4 for systems different from the $1/2$ spins. The average entropy in the FEEE is given in eq. (6.2.6) as a function of the ensemble average populations which reads

$$\langle P_1 \rangle_{W_{II}} = 1 - \frac{U}{N-1} \sum_{k \neq 1}^{N} \frac{1}{E_k} \tag{6.3.1}$$

$$\langle P_{J\neq 1} \rangle_{W_{II}} = \frac{U}{(N-1)} \frac{1}{E_J} \tag{6.3.2}$$

The average populations and consequently the typical value of all the functions of the quantum state depend on the spectral properties of the system Hamiltonian. Let us introduce the following function

$$S_0 = \sum_{k=2}^{N} \frac{1}{E_k} \tag{6.3.3}$$

Let E_N be the highest eigenvalue of the spectrum. We can evaluate the summation in eq. (6.3.3) by introducing the corresponding smoothed density of state, eq. (5.3.7), and solve the resulting integral, that is

$$S_0 = \sum_{k=2}^{N} \frac{1}{E_k} \approx \int_{E_2}^{E_N} \frac{g(E)}{E} dE + R \tag{6.3.4}$$

An estimate of the rest R allows one to quantify the goodness of the continuum approximation. We can use the formula of the rest of a numerical integration which uses the trapezoidal scheme, since our transformation of the summation into an integral is in fact the inverse operation. This however depends on the specific model of the spectral density and reads

$$R = \frac{(b-a)^3}{12n^3} \frac{\sum_{i}^{n} f''(\zeta_i)}{n} \qquad x_i < \zeta_i < x_i + h \tag{6.3.5}$$

where $(b-a) = E_N - E_2$ are the integration interval, n is the number of intervals of length h, and $f''(\zeta_i)$ is the second derivative of the integrand evaluated at a point which belong to the segment.

Let us introduce the scaled internal energy $u = U/N$, after some algebra the FEEE typical entropy, eq. (6.2.6), can be written as

$$\langle S \rangle_{FEE}(u) = -(1-uS_0)\ln(1-uS_0) - uS_0 \ln u + uF_0 - 0.423uS_0 \tag{6.3.6}$$

where we have defined another quantity characteristic of the considered spectrum which has to be evaluated

$$F_0 = \sum_{k=2}^{N} \frac{\ln E_k}{E_k} \approx \int_{E_2}^{E_N} \frac{g(E)\ln E}{E} dE + R \tag{6.3.7}$$

The functions (6.3.4) and (6.3.7) can be evaluated for general models of spectral density as reported in Appendix 6.1. In the next section we will discuss what happens in the case of the spectrum of a harmonic oscillator, which is the simplest system characterized by an unbounded energy spectrum.

6.3.1 UNBOUNDED ENERGY SPECTRUM: THE HARMONIC OSCILLATOR CASE

The energy spectrum of a harmonic oscillator (shifted such as $E_1 = 0$) reads

$$E_k = k\omega_0 \qquad k = 0 \div (N-1) \tag{6.3.8}$$

Where ω_0 is the characteristic frequency of the considered oscillator while N is its number of energy levels. In the Fixed Expectation Energy Ensemble there are in principle no reasons to restrict the number of the energy states which can be populated. The entropy, eq. (6.3.6), thus depends on two parameters: the expectation energy and the dimension of the considered Hilbert space N. Since our first aim is to establish the existence of the function $\langle S \rangle (U)$ it is natural to ask if the average entropy of a single Harmonic oscillator reaches a constant value for some N large enough. Notice that for a fixed value of the internal energy U, the maximum value of the entropy is that obtained with the global canonical populations, that is

$$P_n^{Can} = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \tag{6.3.9}$$

$$\max\left(S\left(U\right)\right) = S_{Can}\left(U\right) = \sum_n P_n^{Can} \ln P_n^{Can} \tag{6.3.10}$$

$$U = \sum_n P_n^{Can} E_n \tag{6.3.11}$$

The canonical entropy, for large enough N, depend only on the internal energy U, as is shown in Figure 6-1.

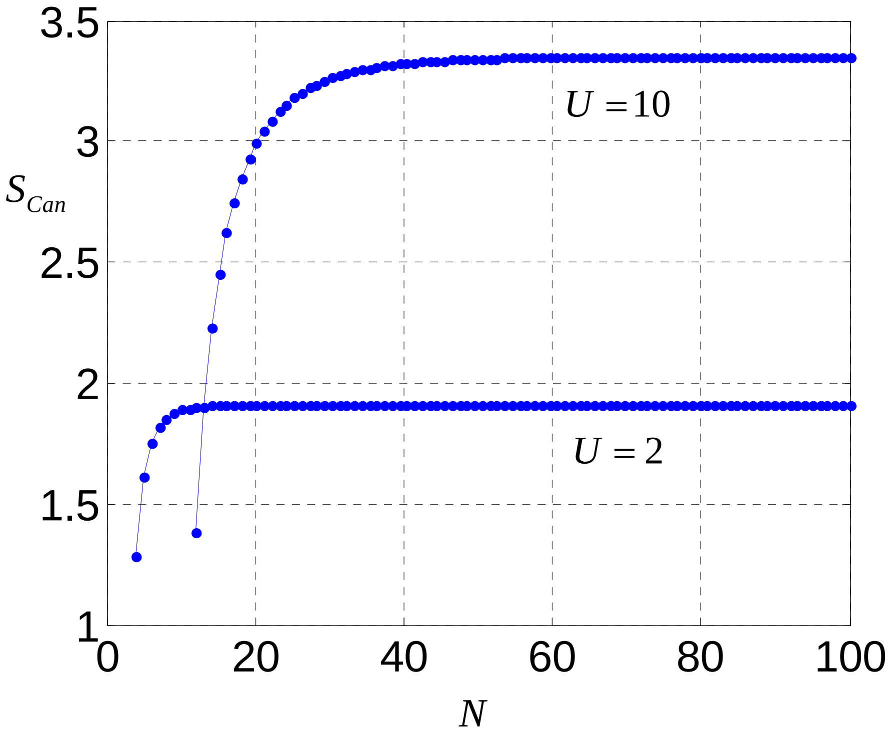


Figure 6- 1: Canonical entropy as a function of the number of energy eigenstates with a non vanishing population. The considered system is a single harmonic oscillator with $\omega_0 = 1$.

In order to evaluate the behavior of the FEEE typical entropy eq. (6.3.6) for large N it is sufficient to specify the functions S_0, eq. (6.3.4), and F_0, eq. (6.3.7), for the spectrum of the Harmonic oscillators. By choosing ω_0 as the unit of the energy scale, S_0 is the harmonic series which asymptotically tends to

$$S_0 \approx \ln\left(N-1\right) \tag{6.3.12}$$

while F_0 can be evaluated, within an absolute error smaller then $1/10$, as

$$F_0 \approx \frac{\ln^2\left(N-1\right)}{2} \tag{6.3.13}$$

In Figure 6-2 the entropy as a function of the number N of energy eigenstates with a non vanishing population N is represented. The circles are the average values obtained from the numerical sampling of the geometrical distributions corresponding to the FEEE of a harmonic oscillator for different N in the range between 50 and 3000 and for two different values of the internal energy U. The dotted lines represent the trend predicted from eq. (6.3.6), by using the estimates of eqs. (6.3.12) and (6.3.13), and a good agreement is found. As it clearly appears, the typical FEEE entropy does not reach a finite asymptotic value. On the contrary it tends to zero as $N \to \infty$, *independently* of the value of the expectation energy U. This peculiar behaviour of the entropy function can be better understood by considering the average populations as a function of N and for a fixed value of the expectation energy. This is shown in Figure 6-3, where, as before, the circles corresponds to the average of the first population P_1 from the sampling of its geometrical ensemble distribution while the dotted line are the prediction from the analytical approximation, eq. (6.3.1). The results show that $\langle P_1 \rangle \to 1$ for $N \to \infty$ regardless of the value of the expectation energy. This rather paradoxical result points out that the Fixed Expectation Energy Ensemble is well defined only for Hilbert spaces of finite, even if arbitrarily large, dimensions. This is true for a large class of models of spectral density, as one can easily understand by rewriting eq. (6.3.1) as

$$\langle P_1 \rangle = 1 - U \frac{S_0}{N-1} \tag{6.3.14}$$

Thus it is clear that, whenever the function S_0 grows slower than linearly with N, the first population tends to one for $N \to \infty$. This is true for the harmonic oscillator, for which S_0 is given in (6.3.12), but it is also true for the generic spectral models described in the Appendix 6.1.

Thus a necessary condition for the existence of the FEEE Ensemble is to consider finite dimensional Hilbert space: this condition is naturally met for systems whose Hamiltonian is a bounded operator as it is the case for spins system. In the other cases one has to truncate the Hilbert space in correspondence of some maximum energy E_N. We shall analyze in the next paragraph the behaviour of the typical entropy for a system composed of n subsystems each with a bounded spectrum. As prototype of this kind of system we will consider an ensemble of n spins with spin quantum number J.

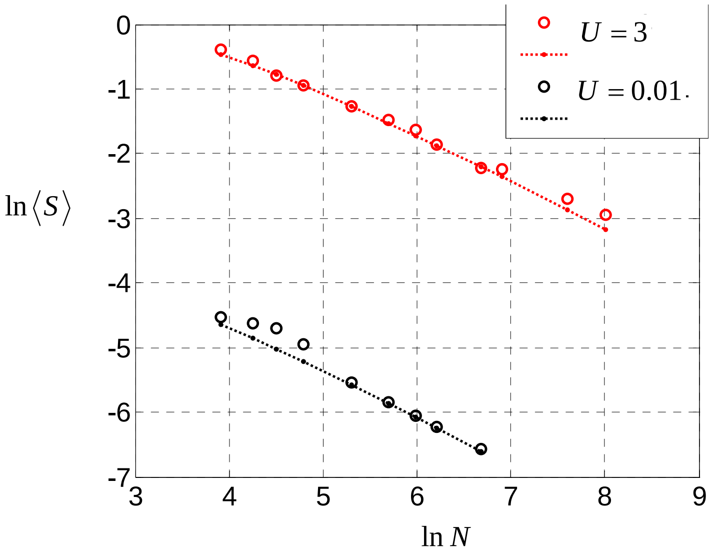


Figure 6- 2: log-log diagram of the typical FEEE entropy as a function of the number of energy eigenstates with a non vanishing population. The considered system is a single harmonic oscillator with $\omega_0 = 1$. The circles represent the average values obtained from the numerical sampling of the geometrical distributions while the dotted lines are the corresponding trend predicted from eq. (6.3.6). The two data sets refer to different values of the internal energy U, as specified in the inset.

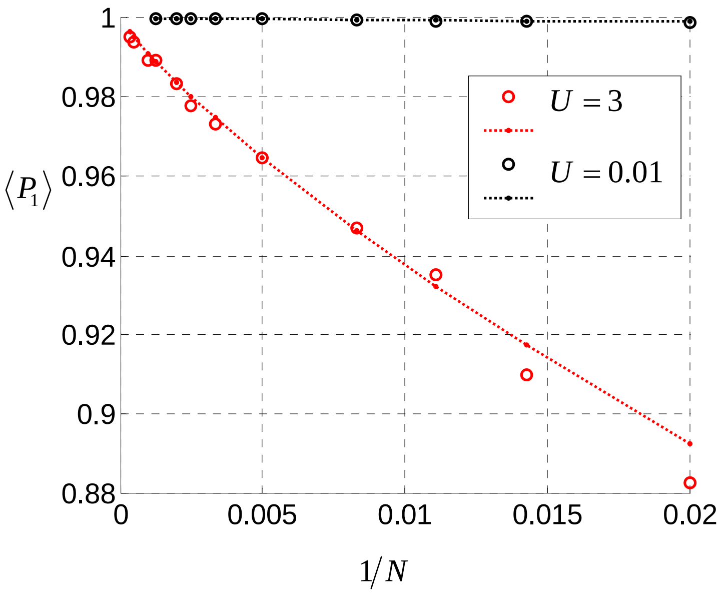


Figure 6- 3: Average value of the first population as a function of the number of energy eigenstates with a non vanishing population. The considered system is the same as in Figure 6-2. The circles represent the average values obtained from the numerical sampling of the geometrical distributions while the dotted lines are the corresponding trend predicted from the analytical approximation eq. (6.3.14). The two data sets refer to different values of the internal energy U, as specified in the inset.

6.3.2 FEEE OF COMPOSITE SYSTEMS

We shall now analyze the typical FEEE entropy as a function of the internal energy for a composite system.

We first assume that each component, when considered isolated, can be described in a finite dimensional Hilbert space. The Hilbert space of the total system is thus the tensor product of n Hilbert spaces, each of dimension $\left(2J+1\right)$

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_1 .... \otimes \mathcal{H}_n$$

Thus, the total Hilbert space is spanned by a basis set of energy eigenvectors of overall dimension $N = \left(2J+1\right)^n$. This is the case of a system of n spins with spin quantum number equal to J. However, the analysis is more general because the results does not depend on the peculiar form of the energy spectrum of each subsystem as long as it is bounded, because the energy density of such a composite system is given by the convolution of the single component energy density. If the energy spectrum of each component is bounded, that is, if the moments of the normalized energy density function exist and are finite, then, by virtue of the Central Limit Theorem, the total energy density can be in general well approximate with a Gaussian function. For the sake of simplicity we now refer to the spectrum of n spins J. The energy levels of the composite spectrum, if the origin of the energy axes is set in correspondence of the first eigenvalue, are given by

$$E_M = \left(\sum_{j=1}^{n} m_j \right) \omega_0 + nJ \tag{6.3.15}$$

where each index m_j can take one of the $\left(2J+1\right)$ values $-J, -J+1, ..., J$. In the simpler case of identical spins, the spectrum consists of $2nJ+1$ distinct energy levels whose density is a function peaked around its average value given by

$$\overline{E_M} = nJ\omega_0 \tag{6.3.16}$$

This is shown in Figure 6-4 for the case of ten spins with $J = 1$ together with the Gaussian Envelope of the corresponding smoothed density of states.

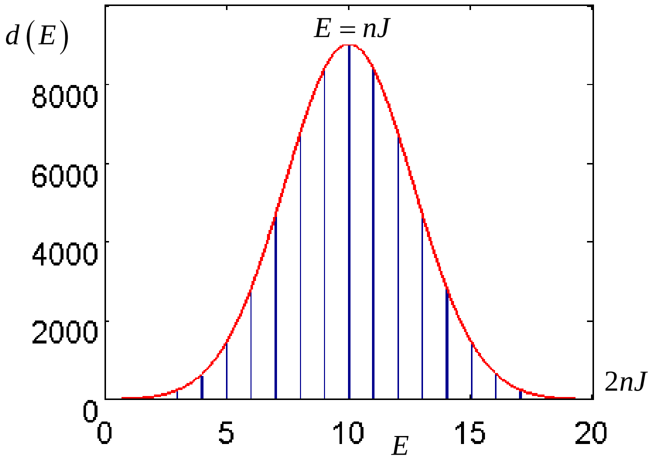


Figure 6- 4: Spectrum of ten identical spins $J = 1$ with $\omega_0 = 1$. The histogram shows the discrete spectrum with the corresponding degeneracy while the red continuous line is the corresponding Gaussian smoothed density of states.

The function S_0 can thus be evaluated as

$$S_0 = \frac{N}{nJ\omega_0} \tag{6.3.17}$$

The typical energy per components in unit of ω_0 reads

$$\varepsilon = \frac{U}{n\omega_0} \tag{6.3.18}$$

and it ranges between zero and its infinite temperature value $E_{T\inf}/n \approx J$. One finds for the typical FEEE entropy, eq.(6.3.6), the following dependence on the energy per spin

$$\langle S \rangle_{FEE}(\varepsilon) = -\ln\left(1 - \frac{\varepsilon}{J}\right) + \frac{\varepsilon}{J}\ln\left(1 - \frac{\varepsilon}{J}\right) - \frac{\varepsilon}{J}\left(\ln\langle E \rangle - \ln N - \ln(nJ\omega_0) + 0.423\right) \tag{6.3.19}$$

By taking into account that $N = (2J+1)^n$, in the limit of large number of components one finds the following asymptotic behaviour of the entropy per spin as function of the energy per spin

$$\frac{\langle S \rangle_{FEE}}{n} \overset{n>>1}{=} \varepsilon \frac{\ln(2J+1)}{J} \tag{6.3.20}$$

In Figure 6.5 the typical entropy per spin as a function of the energy per spin is represented for a system composed of n three levels systems, i.e. spins with $J=1$. As the number of components n increases the trend of the typical entropy per spin is well described by eq. (6.3.20).

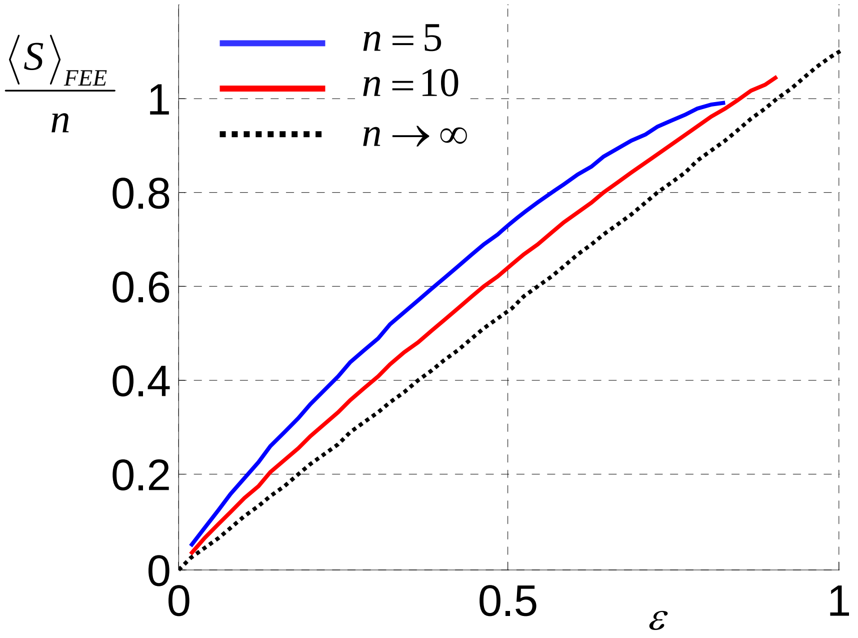


Figure 6- 5: Typical entropy per spin as a function of the Energy for a system composed of n three levels systems, i.e. spins with $J=1$. The three lines refer to different number of components.

It is worth to note that the essence of the result (6.3.20) does not change if one starts with components which are characterized by an unbounded spectrum and then truncate the total energy spectrum of the composite system at some maximum energy E_N. Let us consider for example an ensemble of n harmonic oscillators with characteristic frequency ω_0. The resulting energy levels are highly degenerate and reads

$$E_k = k\omega_0 \qquad\qquad d\left(E_k\right)=\frac{(k+n-1)!}{k!(n-1)!}=\binom{k+n-1}{k} \tag{6.3.21}$$

where $k=0\div N$ and $E_N=N\omega_0$. Differently from the case of the spectrum arising from the convolution of n bounded spectra, in this case the degeneracy of each energy level, and thus also the corresponding smoothed density of states, eq. 5.3.7, rapidly increases with the energy as it is shown in Figure 6-6. This continuously increasing density of states is usually considered a fundamental ingredient for a consistent thermodynamic behaviour (it enters e.g. in the standard demonstration of the equivalence between the microcanonical and the canonical formalism). As already anticipated, also for this kind of spectral density we find a linear dependence of the FEEE typical entropy on the energy per component. Moreover the proportionality constant depends on the maximum energy E_N. This is shown in figure 6-7 for a system composed of n harmonic oscillators and $E_N \propto n$.

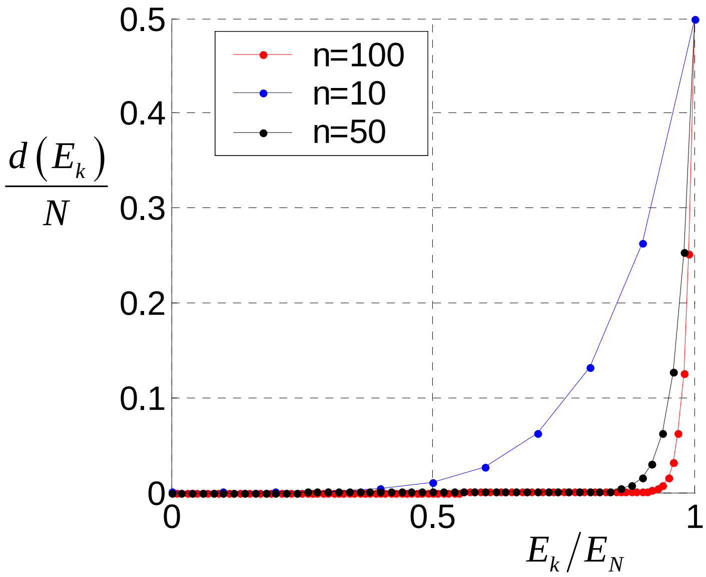


Figure 6- 6: Energy density for a system composed of n harmonic oscillators. The degeneracy is scaled with the total number of energy levels and the energy is scaled with the maximum energy E_N which is chosen proportional to the number of components n.

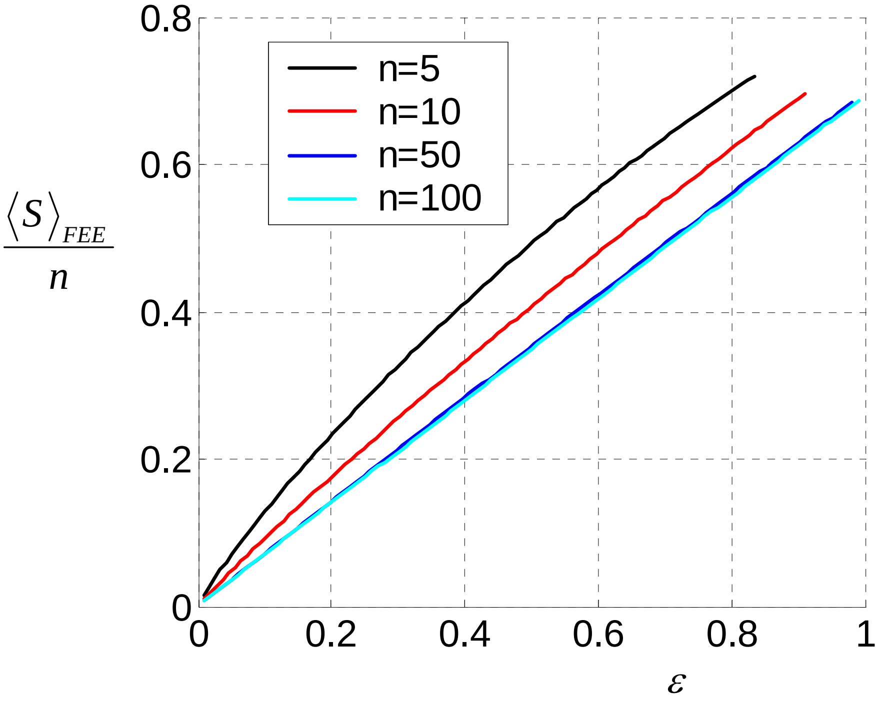


Figure 6- 7: Typical entropy per component as a function of the energy per component for a system composed of n harmonic oscillators. The cut off energy E_N is assumed to be proportional to the number of components in the system.

From a thermodynamical point of view eq. (6.3.20) corresponds to an entropy which is extensive, but from (6.2.4) one would obtain a constant temperature which does not depend on the internal energy of the system.

In order to better understand the implication and the meaning of this evidence, in the following we shall consider the typical equilibrium state of a subsystem in this FEEE ensemble. Note that the asymptotic behaviour of the typical entropy for the system composed of n spins $1/2$, eq. (5.4.9), is a particular case of the more general relation obtained here, eq. (6.3.20). In the case of the ensemble of $1/2$ spins, the equilibrium average of the single spin reduced density matrix can be cast in a canonical form, eq. (5.4.19). As discussed in Section 5.4.2 this fact can be used to define a “local temperature”, eq. (5.4.20). In this case such a local temperature has no relation with the microcanonical temperature, eq. (6.2.4), which would be independent on ε and equal to $2\ln 2$. However, it should be point out that the diagonal elements of a TLS (Two Level System) can be *always* written in a canonical form. We will see this is not the case if the subsystem is, e.g., a spin with $J = 1$.

According to eq. (6.2.8), the ensemble typical value of the equilibrium average reduced density matrix of a subsystem is calculated as a sum of the average global population. For a single spin J, the RDM is a $(2J+1)\times(2J+1)$ matrix and the spectrum of the system of n similar spins is of the type shown in Figure 6.4. The energy eigenvalue of the total system can be expressed as the sum of the eigenen-ergies of the subsystem Hamiltonian, E_k^S, and the energy E_b^B of the $(n-1)$ remaining spins which play the role of the environment. Thus, the typical diagonal elements of the equilibrium RDM can be written as

$$\langle \bar{\mu}_{kk} \rangle = \sum_{b}^{N_B} \langle P_{kb} \rangle = \langle P_1 \rangle \delta_{k1} + \frac{U}{(2J+1)^n} \sum_{b=1}^{(n-1)2J+1} \frac{1}{E_k^S + E_b^B} d(E_b) \tag{6.3.22}$$

where $d(E_b)$ denotes the degeneration of the energy levels of the environment. By inserting eq. (6.3.17) into eq. (6.3.14), the ensemble average of the global ground state population as a function of the typical energy per spins ε (in unit of ω_0) reads

$$\langle P_1 \rangle = 1 - \frac{\varepsilon}{J} \tag{6.3.23}$$

The energy levels of the environment $\left\{E_b^B,\quad b = 1 \div (n-1)2J+1\right\}$ are distributed as in the spectrum of $(n-1)$ spins J. Thus, the degeneracy function $d(E_b)$, in eq. (6.3.22), or the corresponding smoothed density of states, is in substance a Gaussian function whose centre depends on the $k-th$ energy level of the subsystem. Such a function is thus peaked around the energy

$$\overline{d(E_b)} = E_k^S + \overline{E_b} = E_k^S + (n-1)J \tag{6.3.24}$$

By inserting eqs. (6.3.23) and (6.3.24) in the definition of the typical RDM elements, eq. (6.3.22), one obtains the following form of the equilibrium average RDM of a single spin

$$\begin{aligned} \langle \bar{\mu}_{11} \rangle &\overset{n>>1}{\approx} 1 - \frac{2}{2J+1}\varepsilon \\ \langle \bar{\mu}_{kk\neq 1} \rangle &= \frac{U}{(2J+1)} \left(\frac{1}{k+(n-1)J} \right) \overset{n>>1}{\approx} \frac{\varepsilon}{J(2J+1)} \end{aligned} \tag{6.3.25}$$

As usual the energy scale is shifted with respect the ground state energy of the total system and thus $E_1^S = 0$. Notice that the typical value for $\left\langle \overline{\mu}_{\beta\beta} \right\rangle$ found for the spin $1/2$ in the previous Chapter, eq. (5.4.18), is a particular case of eqs. (6.3.25). But now the following question arises: *can these functions of the energy per spin* ε *be written in the canonical form eq.* (6.2.7) *as a function of some local temperature* β_{loc}*, even if different from the (constant) microcanonical temperature defined on the base of the total entropy and energy?*

By looking to eqs. (6.3.25) the answer is evidently negative. In Figure 6-8 this is illustrated for a spin $J = 1$ in a system of n similar spins. In each panel the typical equilibrium average element of the RDM corresponding to one of the three energy eigenvalues of the subsystem is shown as a function of the energy per spin. The blue (red) circle depicts such functions for a system of $n = 5$, ($n = 10$) spins. The black continuous line is the asymptotic value for large n, eqs. (6.3.25). These Figures also show the corresponding canonical RDM elements at the temperature which would results from canonical global populations, eq. (6.3.9)for the same value of the internal energy U.

6.3.3 A REMARK ON TYPICALITY AND STATISTICAL THERMODYNAMIC IN THE FEE ENSEMBLE

As it clearly appears from Figure 6-8 and the discussion above, the typical equilibrium state of a subsystem emerging from the FEE Ensemble is not of the standard Boltzmann form. In the spirit of Popescu et al. [Popescu, (2006)] this would be called the canonical state relative to the constraint of fixed expectation E in the total Hilbert space. As the authors of ref. [Popescu, (2006)] clearly point out, the problem of the existence of a typical value for the RDM of a subsystem has to be considered separated from the problem of finding what this state actually looks like. If the typical state is called a “generalized canonical state”, its actual form will depend on the constraints imposed in defining the Ensemble. In other words if we would define the FEE Ensemble as *all the wavefunctions which are arbitrary superposition of energy eigenstates with energy eigenvalues* E_k *in the range* $\left\langle E \right\rangle \mp \Delta E/2$, with ΔE very small, then we would obtain a typical equilibrium RDM of the Boltzmann form.

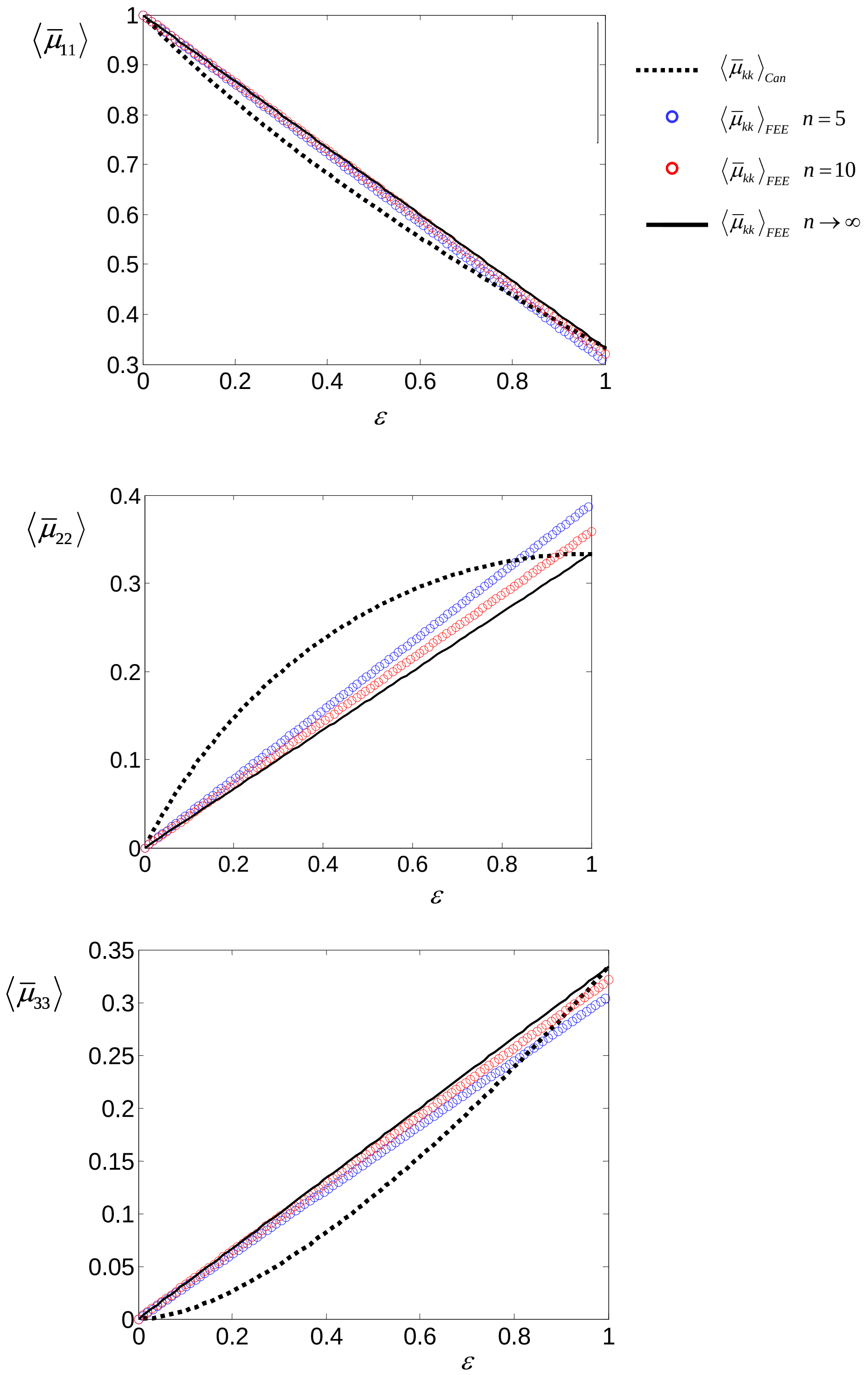


Figure 6- 8: Typical elements of the equilibrium average reduced density matrix of a spin $J=1$ in a system composed of n spins $J=1$. In A, B, C the diagonal elements corresponding to the three energy levels of a spin 1 are separately shown as a function of the energy per spin. The blue (red) circle depict such functions for a system of $n=5$, ($n=10$) spins. The black continuous line is the asymptotic value for large n. For comparison also the elements of the corresponding canonical RDM at the temperature given by eq. (6.3.9) are reported (dotted line).

6.4 STATISTICAL THERMODYNAMIC OF THE RANDOM PURE STATE ENSEMBLE

Let us consider the behaviour of the thermodynamic functions, i.e. typical values of the internal energy and the entropy, and of equilibrium average state of a subsystem in the Random Pure State Ensemble. We recall that this Ensemble includes all the wavefunctions which lie in a Hilbert space of total dimension $N\left(E_{\max}\right)$. The probability distribution on populations is uniform on the N simplex defined by the normalization constraints and can be approximated by a factorized probability distribution derived in Section 4.4.2, namely

$$W_{RPS}\left(P\right)=\prod_{k=1}^{N}W_{RPS}^{k}\left(P_k\right) \qquad W_{RPS}^{k}\left(P_k\right)=Ne^{-NP_k} \tag{6.4.1}$$

As already mentioned in Section 6.2 the internal energy of the Random Pure State Ensemble is not an independent parameter as in the FEEE but it is identified with the typical value of the expectation energy in the Ensemble. Thus, the definition of the internal energy as the average value of the expectation energy, eq. (6.2.2), is meaningful only as long as the ensemble distribution of the expectation energy E is a function peaked at a typical value. We will first show that this is actually the case whenever the density of the energy spectrum is an increasing function of the energy.

To this aim we study for generic system the RPS Ensemble Distribution of the expectation energy

$$E=\sum_{k=1}^{N}P_kE_k \tag{6.4.2}$$

Here $N=N\left(E_{\max}\right)$ is the dimension of the Hilbert space spanned by the non vanishing populations. This is in general a subspace of the full Hilbert space, as illustrated e.g. for the system composed of $1/2$ spins in section 5.4.2. Thus, for the RPSE the finiteness of the considered Hilbert space is guaranteed by the definition of the ensemble, even if the total Hilbert space of the system can be infinite. As in the previous chapter $k_{\max}$ denotes the index of the highest populated energy level. The number of states N depends on $k_{\max}$

$$N\left(k_{\max}\right)=\sum_{k=1}^{k_{\max}}\delta\left(E-E_k\right) \tag{6.4.3}$$

or, by introducing the corresponding smoothed density of states, eq. (5.3.7)

$$N\left(E_{\max}\right)=\int_{0}^{E_{\max}} g\left(E\right)dE \tag{6.4.4}$$

The expectation energy E, being a linear combination of the random variables P_k, can be considered as a random variable in the ensemble with average value

$$\left\langle E\right\rangle = \sum_{k=1}^{N(k_{\max})} \left\langle P_k\right\rangle E_k = \sum_{k=1}^{N(k_{\max})} \frac{E_k}{N\left(k_{\max}\right)} \tag{6.4.5}$$

We can again invoke the Central Limit Theorem to establish that the RPS Ensemble distribution of E converges to a Gaussian distribution with the mean value given by eq. (6.4.5) and the variance given by

$$\sigma_U^2 = \frac{1}{N^2\left(k_{\max}\right)} \sum_{k=1}^{k_{\max}} E_k^2 \approx \frac{1}{N^2\left(E_{\max}\right)} \int_{0}^{E_{\max}} E^2 g\left(E\right)dE \tag{6.4.6}$$

Let us consider the following general energy density, (see Appendix 6.1)

$$g\left(E\right)=\kappa\left(\frac{E}{n}\right)^{\alpha} \qquad\qquad N\left(E_{\max}\right)=\frac{\kappa}{n^{\alpha}\left(\alpha+1\right)}E_{\max}^{\alpha+1} \tag{6.4.7}$$

This is the energy density attributed to an ideal gas if the parameter α is of the order of the number of components n. From eq. (6.4.5) and (6.4.6) one derives that the expectation value of the Hamiltonian is very narrowly distributed around its average value

$$\left\langle E\right\rangle = \frac{\alpha+1}{\alpha+2}E_{\max} \tag{6.4.8}$$

Indeed the variance of its RPS Ensemble Distribution is estimated from eq. (6.4.6) as

$$\sigma_E^2 = \frac{1}{E_{\max}^{\alpha-1}} = \left(\frac{\alpha+1}{\alpha+2}\frac{1}{E}\right)^{\alpha-1} \tag{6.4.9}$$

which decreases rapidly when α is large. As discussed in section (5.4.1) the correlation between the populations which is neglected by assuming the approximate probability density (6.4.1), assures that the variance given in eq. (6.4.9) is still a pessimistic guess.

Thus, for moderately large N and under the hypothesis that the energy density is a weakly increasing function of the energy, the vast majority of the wave functions which can described our system is characterized by the same value of the expectation energy which we identify as the internal energy function $U = \langle E \rangle$.

On the other hand the typical value of the RPSE entropy is given by

$$\langle S \rangle = \ln N\left(E_{\max}\right) - 0.423 \tag{6.4.10}$$

By tacking into account the relation (6.4.8) between the internal energy and $E_{\max}$, one obtains the entropy as a function of the internal energy. For the considered spectral density, eq. (6.4.7) it reads

$$\langle S \rangle = \ln \kappa - \alpha \ln n + (\alpha+1)\ln\left(\frac{\alpha+2}{\alpha+1}U\right) - \log(\alpha+1) - 0.423 \tag{6.4.11}$$

If we assume the energy density of the ideal gas [Gemmer, (2004)] for which $\alpha = n$ we obtain the simple result

$$\frac{\langle S \rangle}{n} \overset{n\to\infty}{\approx} \ln\frac{U}{n} \tag{6.4.12}$$

which gives by means of eq. (6.2.4) the inverse temperature as a function of the internal energy. For this case one obtains

$$\beta = \frac{dS}{dU} \propto \frac{1}{U} \tag{6.4.13}$$

Thus, with the RPSE a reasonable functional dependence of the temperature on the internal energy which characterizes the ideal gas model is recovered, this is shown in Figure 6.9.

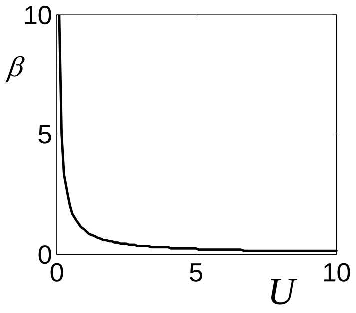


Figure 6- 9: Inverse temperature as a function of the internal energy in the RPSE of an ideal gas

6.4.1 RPSE TYPICAL ENTROPY FOR A COMPOSITE SYSTEM

In the following we shall analyze the behaviour of the typical entropy as a function of the internal energy in the Random Pure State Ensemble which describes our test system composed of n spins J. The analysis is more conveniently performed by using the continuum approximation for the energy density of the total energy spectrum. Thus, we introduce the smoothed density of states for the spectrum of the system which can be written as a Gaussian function whose parameters depend on the quantum spin number J, as

$$\begin{aligned} & g(E) = G_{M,\Sigma}(E) = \frac{(2J+1)^n}{\Sigma\sqrt{2\pi}} e^{-\frac{(E-M)^2}{2\Sigma^2}} \\ & M = \mu J \\ & \Sigma = \sigma_J \sqrt{n} \end{aligned} \qquad (6.4.14)$$

where μ and σ_J are the average and the variance of the spectrum of a single spin J

$$\mu = J\omega_0 \qquad (6.4.15)$$

$$\sigma_J = \sqrt{\sum_{k=1}^{2J} k^2 / (2J+1) - J^2} \qquad (6.4.16)$$

where, as usual, the first eigenvalue is taken as the zero of the energy scale. In terms of energy per spin $e = \dfrac{E}{n\omega_0}$ the density (6.4.14), reads

$$g(e) = \frac{(2J+1)^n}{\sqrt{2\pi\sigma^2}} e^{-\frac{(\varepsilon-J)^2}{2\sigma^2}} \qquad \text{where} \qquad \sigma = \sigma_J / \sqrt{n} \qquad (6.4.17)$$

For convenience of notation we also define the scaled energy per spin $y = \dfrac{(e-J)}{\sqrt{2}\sigma}$.

We have now to establish the maximum energy which can be populated in order to obtain a certain typical value of the expectation energy, i.e. the internal energy as a function of $E_{\max}$. To this aim, one first evaluate the number of populated state as a function of the maximum allowed energy $E_{\max}$

$$N(E_{\max}) = (2J+1)^n \frac{1}{2}\left[1 + erf(y_{\max})\right] \qquad (6.4.18)$$

It is worth to point out that, even if the continuum representation does not cause any problem for almost the whole range of the possible value of the expectation energy and it become a better and better approximation as n increases if the system components are not assume to be identical, it remains an approximation. This means that when one want to consider extremely low value of the expectation energy, and consequently a low value of the maximum energy which can be populated, one has to take into account the discrete nature of the spectrum. In particular the difference between eq. (6.4.4), which is a continuum function of the energy and the real number of states (6.4.3) become important for $E_{\max} \sim E_2$, as it is illustrate in Figure 6-10.

Having in mind this warning one easily finds the relation between the typical energy and the maximum allowed energy. This is given in the general case as

$$U = \frac{1}{N(k_{\max})} \sum_{k=1}^{k_{\max}} d(E_k) E_k \approx \frac{n^2}{N(E_{\max})} \int_0^{e_{\max}} g(e)\, de \tag{6.4.19}$$

For our system by using (6.4.17) and (6.4.18) the internal energy per spin is explicitly given by

$$\varepsilon = \frac{U}{n} = J - \frac{\sqrt{2}\sigma}{\sqrt{\pi}} \frac{e^{-y_{\max}^2}}{1 + erf(y_{\max})} \tag{6.4.20}$$

By considering that the variance of the density (6.4.17) decreases as the number of components n increases, one can use the asymptotic expansion of the complement error function

$$1 - erf(y) \overset{y \to \infty}{\approx} \frac{e^{-y^2}}{y\sqrt{\pi}} \tag{6.4.21}$$

so that in the limit of large n a linear relation between the internal energy and the maximum energy is established

$$\varepsilon = \frac{U}{n} \overset{n>>1}{=} e_{\max} \tag{6.4.22}$$

The identification of the typical value of the expectation energy and the maximum energy which can be populated appears to be, in the RPSE, a property that is quite independent from the detail of the spectral structure of the specific system. Indeed it emerges for the $1/2$ spins system, see eq. (5.5.21), it is recovered here for the case of systems composed by generic J-spins, and, more generally, for systems characterized by a rapidly increasing density of energy levels, see eq (6.4.8).

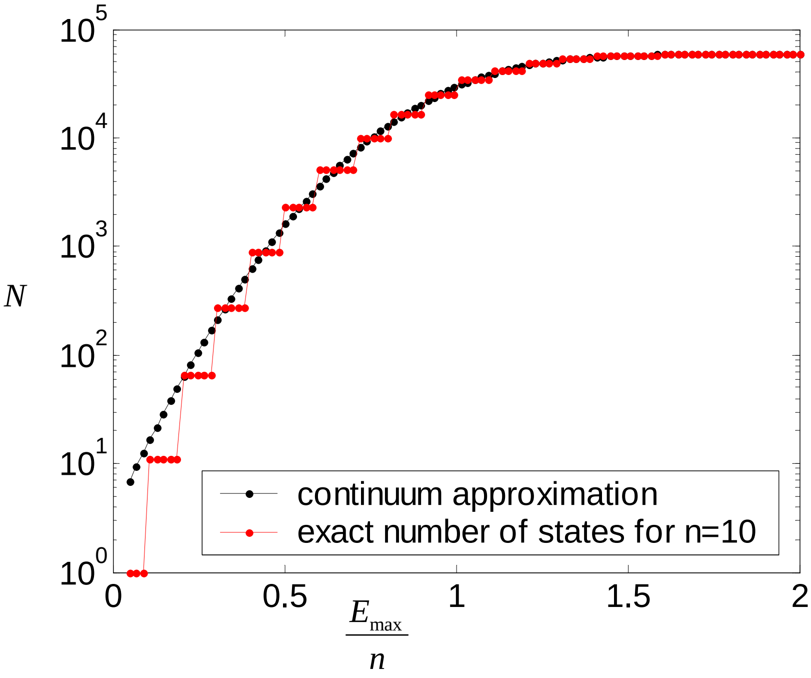


Figure 6- 10: Number of populated states as a function of the scaled maximum energy: the calculation refers to a system of 10 identical spins with $J=1$. The red lines is the exact number of states calculated as the sum in eq. 6.4.3 while the black line is the corresponding result from the continuum approximation of the energy density.

The typical entropy is defined by eq. (6.4.10) on the basis of the number of states eq. (6.4.3) or, when it is possible, by using the continuum approximation, eq (6.4.18). In this case by retaining the leading terms with respect to n, we obtain the following function for the system composed of n spins with value J

$$\frac{S}{n} \overset{n\to\infty}{=} \ln\left(2J+1\right)-\frac{1}{2\sigma_J^2}\left(\varepsilon-J\right)^2 \tag{6.4.23}$$

In figure 6-11 we show the typical entropy per spin as a function of the typical energy per spin for a system composed of different numbers of spins with $J=1$. Remarkably, as n increases, the RPSE typical entropy tends to reach the maximum entropy compatible with the given energy, i.e. the canonical entropy eq. (6.3.10). This Figure also includes the asymptotic formula obtained with the continuum approximation of the energy density, eq. (6.4.23). It fails, as expected, for low value of the energy while it is a good estimation in the high energy limit.

We are now in the position to define the microcanonical temperature in the RPS Ensemble. While the differential relation, eq.(6.2.4), is meaningful only in the thermodynamic limit $n \to \infty,\ \varepsilon = U/n = \text{constant}$, where the entropy and the internal energy become continuous functions, we can define, for finite n, the global temperature as the incremental ratio between entropy and energy, that is

$$\beta = \frac{\langle S\rangle\left(N\left(k_{\max}+1\right)\right)-\langle S\rangle\left(N\left(k_{\max}\right)\right)}{U\left(N\left(k_{\max}+1\right)\right)-U\left(N\left(k_{\max}\right)\right)} \tag{6.4.24}$$

It is worth to note that this temperature converges to that defined by the global canonical population through eq (6.3.11) for n of the order of 100. However we stress that the actual populations of the individual pure states in the RPSE which can be characterized by this temperature are not canonical neither equal to their RPSE average $1/N\left(k_{\max}\right)$. We thus see as the typicality of the entropy and of the energy function in the ensemble can be used as a bridge between the unknown microscopic details of an individual pure state and the existence of thermodynamic quantities, such as the temperature, which depends only of some “gross feature” of the considered pure state.

To complete our analysis it remains to investigate the properties of the typical equilibrium state of a subsystem, i.e. the equilibrium average of the RDM of a single spin J.

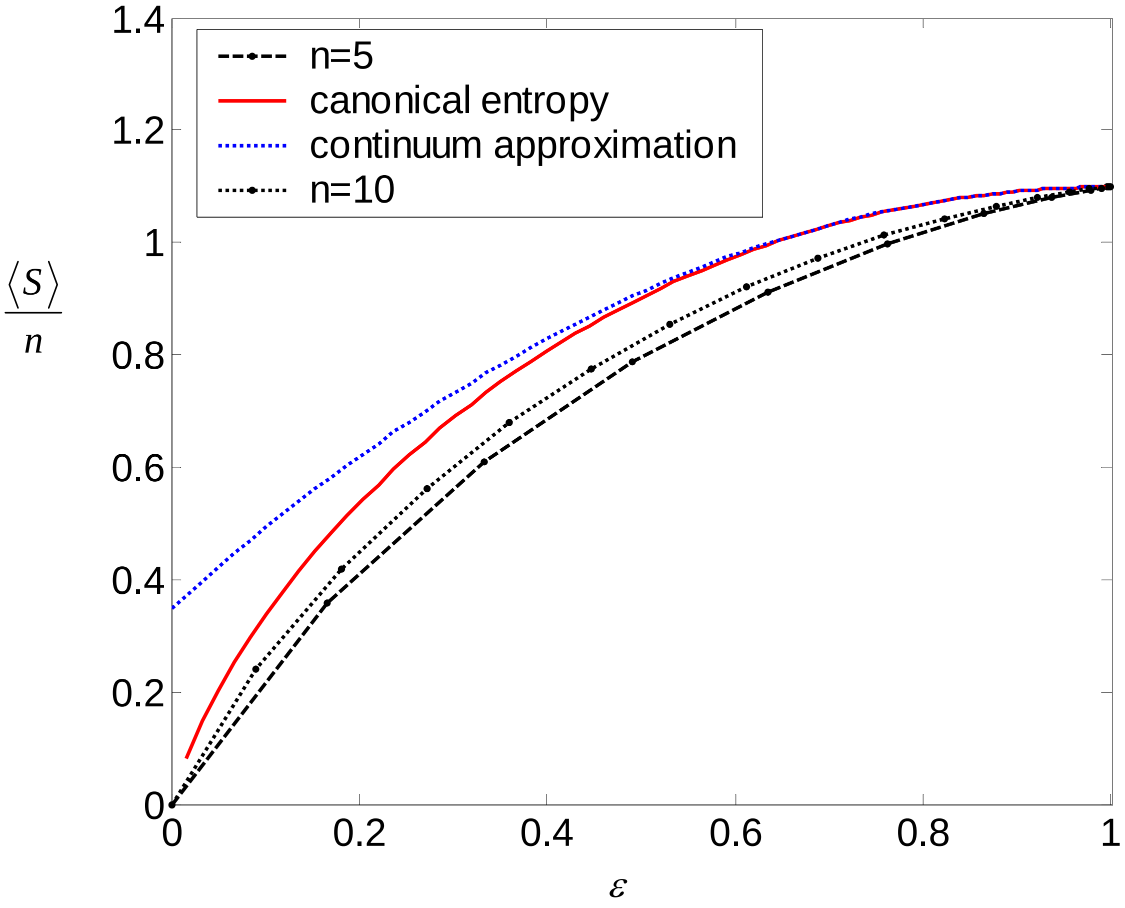


Figure 6- 11: RPSE typical entropy per spin as a function of the internal energy per spin for a system composed of n spins with $J=1$. The black dash and dotted lines refer to the typical entropy calculated according to the exact counting of the states eq. (6.4.3), and for $n=5$, $n=10$ respectively. The blue line is the entropy calculated with the asymptotic continuum approximation, eq. (6.4.23). For comparison, also the entropy obtained with global canonical populations. eq. (6.3.10) is represented (red line).

6.4.2 CANONICAL EQUILIBRIUM STATE FOR A SINGLE SPIN

According to the definition given in eq. (6.2.8), the equilibrium average of the RDM of a subsystem in the RPSE can be calculated as the sum of the average global populations corresponding to those energy levels that correspond to the given value of the subsystem energy E_s, that is

$$\left\langle \overline{\mu}_{ss} \right\rangle = \sum_{b}^{k_{\max} \equiv (sb)_{\max}} \left\langle P_{sb} \right\rangle = \frac{N^{s}\left(k_{\max}\right)}{N\left(k_{\max}\right)} \tag{6.4.25}$$

In Section 5.5.2 this definition has been used to obtain the RDM of a single spin $1/2$. As already mentioned, in that case the parameterization of the resultant two diagonal elements of the RDM in terms of a local temperature is always possible. Indeed we have shown that in both the ensemble of pure states, the FEEE and the RPSE, the equilibrium state of the single spin $1/2$ can be used to define a “local temperature”, eq. (5.4.20). On the other hand we have seen that this is no longer true in the FEEE ensemble for system composed of subsystems whit more than two energy levels, as illustrated in Figure 6-8.

Here we will show that in the RPSE not only a canonical value of the equilibrium RDM elements is recovered for subsystems different from a Two Level System, but also the local temperature which characterized this canonical distribution is actually the microcanonical temperature defined in eq. (6.4.24), if n is large enough.

This is shown in Figure 6-13 for a single spin $J=1$: the circle represents the typical value of the equilibrium RDM elements calculated according to eq, (6.4.25) while the black solid lines are the corresponding canonical form at the temperature calculated according to the definition (6.4.24) for a global system composed of $n=500$ spins. It is worth to note here that the typical equilibrium values of the RDM calculated according to (6.4.25) as a function of the energy per spin, converge to their asymptotic value with respect to the number of component n already for number of components of the order of 10, while the convergence of the typical entropy to its asymptotic value is much slower as can be seen from Figure 6.12.

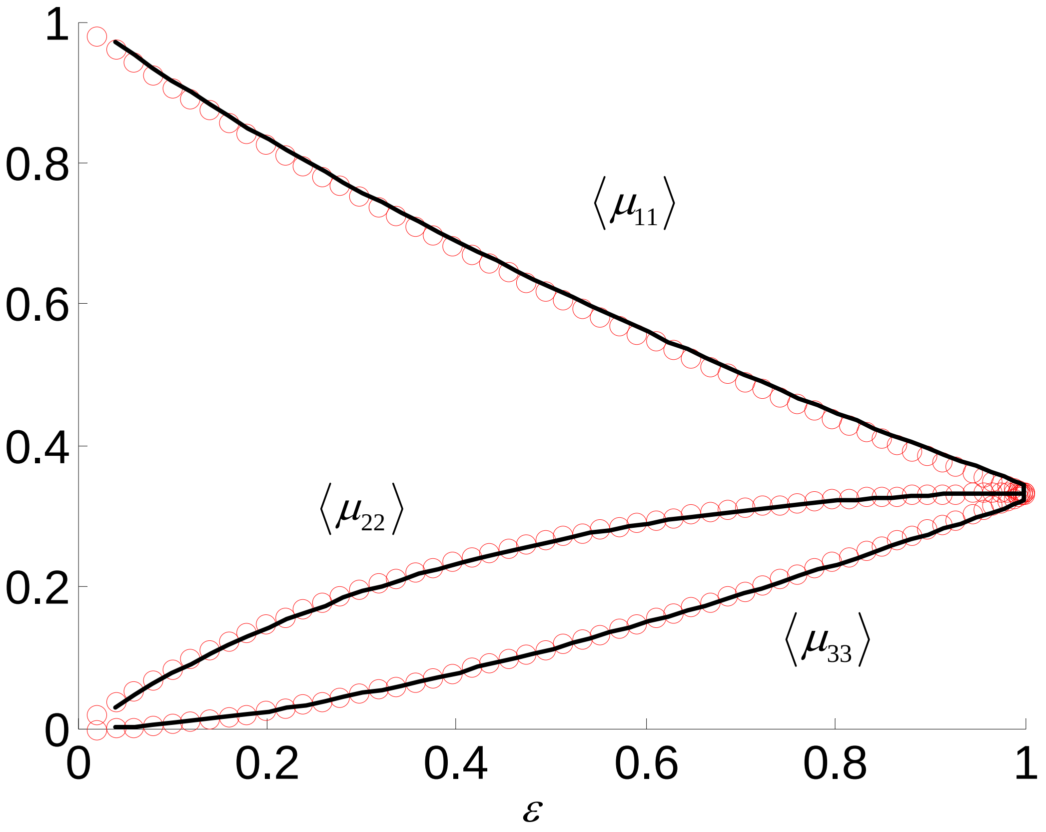


Figure 6- 12: Elements of the Equilibrium RDM of a single spin $J = 1$ in a system composed of $n = 500$ similar spins, as a function of the typical energy per spin. The red circle are the typical elements calculated according to eq. (6.4.25) while the black line are the canonical distribution corresponding to the microcanonical temperature calculated on the base of the RPSE typical entropy as a function of the RPSE typical energy, eq. (6.4.24).

APPENDIX 6.1 : GENERAL MODELS OF SPECTRAL DENSITY

For any system one can introduce a density of energy level $g(E)$. Thus the following integral gives the total number of energy levels

$$\int_{E_2}^{E_N} g(E)\,dE = (N-1) \tag{A6.1.1}$$

while

$$S_0 \approx \int_{E_2}^{E_N} \frac{dE}{E} g(E) \tag{A6.1.2}$$

Here we list some useful and generic model of spectral density

1. *harmonic oscillator*: it is characterized by a constant density of energy levels $g_{ho}(E) = c$ and the above functions are evaluate as

$$(N-1) = c\left(\frac{E_N}{E_2} - 1\right) \qquad S_0 == c\ln\frac{E_N}{E_2} = c\ln\left(\frac{N-1}{c} + 1\right) \propto \ln(N-1) \tag{A6.1.3}$$

2. *Algebraic spectral density* $g_a(E) = kE^{\alpha}$ in which $\alpha > 0$. In this case

$$N = \frac{k}{(\alpha+1)}\left[E_N^{\alpha+1} - E_2^{\alpha+1}\right] \qquad S_0 = \frac{k}{\alpha}\left(E_N^{\alpha} - E_2^{\alpha}\right) \propto N^{\frac{1}{1+\alpha}} \tag{A6.1.4}$$

3. *Exponential spectral density* $g_e(E) = kEe^{\beta E}$

$$N = k\left[e^{\beta E_N}\left(\frac{E_N}{\beta} - \frac{1}{\beta^2}\right) - e^{\beta E_2}\left(\frac{E_2}{\beta} - \frac{1}{\beta^2}\right)\right] \qquad S_0 = \frac{k}{\beta}\left(e^{\beta E_N} - e^{-\beta E_2}\right) \propto \frac{N}{E_N} \tag{A6.1.5}$$

It is worth to mention that an algebraic spectral density characterizes for example the spectra of the ideal gas model where $\alpha = 3n/2$ with n denoting the number of gas particles. More generally it is always assumed that a system composed of many particles is characterized by a spectral density which rapidly increases with the energy. For example such an assumption is essential in order to derive the equivalence of the microcanonical and the canonical formalism in the thermodynamic limit. In [Gemmer, (2004)] a generic derivation of the energy density resulting from the convolution of n "single particle" spectral density is presented. Here we only report the final result which correctly predicts, almost always, a total density of state which is a rapid increasing function of the energy.

4. Typical Spectra for Composite System: The typical energy density of such a system, studied by Gemmer *et al* in ref. [Gemmer, (2004)], is found to be

$$G(E)=\left(R\left(\frac{E}{n}\right)\right)^n e^{\alpha\left(\frac{E}{n}\right)E} \tag{A6.1.6}$$

with

$$R\left(\frac{E}{n}\right)=\int_0^\infty e^{-\frac{E}{n}x}g(x)\,dx$$

Where $g(x)$ is the energy density of one of the n identical components and the quantity on the function at the exponent is explicitly given by

$$\alpha\left(\frac{E}{n}\right)=\frac{1}{\bar{r}\left(\frac{E}{n}\right)} \qquad \bar{r}\left(\frac{E}{n}\right)=\frac{\int_0^\infty xe^{-\frac{E}{n}x}g(x)\,dx}{R\left(\frac{E}{n}\right)} \tag{A6.1.7}$$

CHAPTER 7

IN ITINERE SUMMARY AND SOME REMARKS

7.1 STATISTICAL DESCRIPTION OF QUANTUM SYSTEMS: SINGLE PURE STATE VS ENSEMBLES

It is now worth to discuss some points which emerge from the analysis presented in the previous Chapters. First let us look back at what we have done: the starting point is the definition of the equilibrium properties of an isolated quantum system, parameterized in terms of populations and phases, on the basis of the asymptotic time average of the expectation value of the corresponding observable

$$\begin{aligned} \overline{f(t)} &= \lim_{T\to\infty} \frac{1}{T} \int_0^T dt\, f\left(P,\gamma(t)\right) \\ f\left(P,\gamma(t)\right) &= \left\langle \psi(t) \right| F \left| \psi(t) \right\rangle \end{aligned} \tag{7.1.1}$$

This choice is strictly related to the ergodic foundations of classical statistical mechanics as discussed in Chapter 2. One can rise the objection that such a foundation relies on the assumption that the result of a measure performed on a classical system in equilibrium can be identified with a time averaged properties. On the other hand it is not obvious at all whether a time averaged expectation value is actually related to a quantum measurement. This is of course true, however our standpoint is that a detailed analysis of the quantum measurement process is not essential for the understanding of equilibrium quantum statistical mechanics [Srednicki, (1995)]. On the contrary, one can go a step further and conjecture that a better understanding of the concepts which lie of the basis of the statistical description of quantum states and its dynamics are essential in order to correctly approach the quantum measurement problem. This is however far beyond the scope of the present analysis. On the other hand it is worth to stress that also in the much more understood and robust field of the foundation of classical statistical mechanics, the ergodic theory, which deals with infinite time averages, is not directly related to real measurements which are always performed in a finite time. Indeed the power and the conceptual importance of statistical mechanics derives from the fact that it deals with the entire *distribution* and not only with average values. For this reason the statistical mechanics is the natural bridge between very different descriptions of the same physical system, e.g. from the microscopic to the macroscopic point of view, from the mechanical to the thermodynamical description.

Having identified the equilibrium properties of a quantum pure state, eq. (7.1.1), as the main objective of our study, we have introduced the Pure State Distribution, eq. (2.3.27), in the phase space described by the coordinates $X \equiv \{P, \gamma\}$

$$p(P,\gamma) = \delta(P - P_0)\frac{1}{(2\pi)^{N-1}} \tag{7.1.2}$$

This distribution reflects the characteristics of the temporal evolution ruled by the Schrödinger equation: in the $2N$ dimensional phase space one has N constants of the motion, i.e. the populations, while for time long enough the phase variables take all their possible values with a uniform probability distribution. There is a nice geometrical representation of such an evolution which is pictorially represented in Figure 7-1: we can imagine the phase space as a product of a $(N-1)$ dimensional simplex, built of the populations $(P_1 ... P_N)$, and an $(N-1)$-dimensional torus, built of the phases variables $(\gamma_1 ... \gamma_{N-1})$. Given an initial pure state, the motion of its representative point in the phase space is confined to the torus containing that initial state. From this point of view it is clear that the portion of phase space corresponding to a given expectation energy is not metrically indecomposable, since many different population sets lead to the same expectation value of a given Hamiltonian. Thus, one cannot speak about quantum ergodicity in these terms. Nonetheless the following questions remain meaningful:

Is the infinite time average of a function of interest independent on the initial state of the system $\psi(0)$*?*

If so, is it equal to an appropriate thermal average with respect to some properly defined equilibrium probability distribution?

In other words if the concept of thermal equilibrium is meaningful for a quantum system then we would expect that the equilibrium average $\overline{f}$ of at least some functions of interest depends on the total energy of the system, but it is independent on all other aspects of the initial state. This property has been proposed as a good definition of “quantum ergodicity” [Peres, (1984)].

The above mentioned problem has been discussed in the past by many authors from different points of view: in particular one line of investigation emphasizes the role of “quantum chaos” in order to explain the emergence of thermal behavior in quantum systems [Srednicki (1996), (1994); Peres, (1984), Casati, (1999)] while other approaches point out several aspects of this problem under specific assumptions for the considered system or on in relation to the initial conditions [Deutsch, (1991); Tasaki, (1998)].

More recently the concept of typicality has been introduced and used to give strong foundation to the canonical state of a subsystem, [Goldstein, (2006)]. The more general setting presented in ref [Popescu, (2006)] points out the existence of a typical state for the subsystem which depends on the constraints used to define the total allowed states. In ref [Reimann, (2007)] Reimann proves, under certain hypotheses, that the property of typicality already holds at the level of pure states, that is, it is not a consequence of the massive entanglement of a subsystem of a typical random quantum state with its environment, as argued in [Popescu, (2006)] but it is inherent to the wave function itself.

Our setup allows the analysis of the role of typicality in the emergence of the equilibrium statistical mechanics within a simple but effective theoretical framework. Once recognized the PSD, eq. (7.1.2), as the distribution on the phase space deriving from the temporal evolution of the considered system, in Chapter 3, we have introduced the Ensembles of Pure States. The first key step is the definition of such ensembles and the derivation of the corresponding Ensemble Distributions. We focus on two ensembles:

I. The Random Pure State Ensemble, composed of all the wave functions in a subspace $\mathcal{H}_{RPS}$ of the full Hilbert space of the considered system.

II. The Fixed Expectation Energy Ensemble, composed of all the wave functions in the Hilbert space of the considered system characterized by the same value of the expectation energy of the total Hamiltonian. This Ensemble was introduced as the quantum analogue of the microcanonical ensemble in ref. [Brody, (2005); Naudts, (2006)].

The Ensemble Distributions on the parameters $X \equiv \{P, \gamma\}$ which define a pure state is derived by considering the geometry of the Hilbert space. There is indeed a unique measure on the set of normalized wave function which is invariant under the full group of unitary transformations, [Sykora, (1974)], and this yields a uniform distribution on the surface of the unit sphere defined by the normalization condition $\langle\psi|\psi\rangle = 1$. Starting from such a measure the corresponding RPSE and FEEE Distributions on the populations and phases have been derived in Chapter 3. Two important points which are common to both the ensembles are

I. Populations and phases are statistically independent and the phases are uniformly distributed according to the PSD

$$\begin{aligned} p(P,\gamma) &= p(P)\,p(\gamma) \\ p(\gamma) &= \left(2\pi\right)^{-(N-1)} \end{aligned} \tag{7.1.3}$$

II. The Ensemble probability densities on the independent populations, i.e. $p_{RPSE}\left(P_1,...,P_{N-1}\right)$ and $p_{FEEE}\left(P_1,...,P_{N-2}\right)$, are defined in high dimensional domains with a non trivial topology, because the populations are not statistically independent for the presence of the constraints.

In Chapter 4 the numerical methods for the sampling of the Ensemble Distributions as well as analytical approximations valid in the large N limit have been developed. These allow one to study the Ensemble Distributions of the single populations as well as those of the functions of interest. We focused on two functions of the quantum state: the Shannon entropy associated to the pure state of the whole system (a "collective", non linear function of the global populations) and the equilibrium average of the Reduced Density Matrix of a subsystem. A main point which emerges from the study of the Ensemble Distribution in ideal (non interacting) composite systems, as the system of n spin $1/2$ analyzed in Chapter 5, is the following:

While the Probability Distribution of the populations itself is the broadest one compatible with the constraints of the considered ensemble, the Ensemble Distributions of both the considered observables are, on the contrary, very peaked functions, and this allows their characterization trough their typical values.

The fact that it does not actually exist a set of populations which is preferred or more probable with respect to the other sets equally compatible with the given constraints for an isolated system, was already noted in [Rigol, (2008)]. Evidences were founded in favor of what it is called the "eigenstate thermalization hypothesis", [Srednicki, (1994); Deutsch, (1991)]. This however can occur in large, interacting, many body systems. On the other hand the typicality of the state of a subsystem, or of a collective function such as the entropy, is an evidence which does not depend on the nature of the system but seems to be a simple consequence of the high dimensionality of the phase space together with the structure of the observed functions which are defined as sums of many terms. Another point which is worth to stress is indeed the relation between the considered ensemble distributions and the inherent geometry of the Hilbert space. If one considers that the probability distribution on the parameters of the phase space is directly determined by the geometry of the Hilbert space, then it becomes clear that the existence of a typical value for a large class of observables can be viewed as a manifestation of the “concentration of measure” phenomenon [Hayden, (2006)]: it is a striking fact from elementary geometry of high dimensional surfaces that the uniform measure on the k-sphere, S^k, is strongly concentrated about any equator when k gets large; consequently any polar cap strictly smaller than a hemisphere has a relative volume exponentially small in k. This induces a similar behavior for any slowly varying function on the sphere, which we can understand indeed as a random variable induced by the uniform measure on the sphere: namely, it will take values close to the average except for a set of volume exponentially small in k. This idea is made rigorous in the Levy’s Lemma which is also the main ingredient in the general proof of the typicality given in Popescu e*t al*., [Popescu, (2006)]. Since pure quantum states which lies in a Hilbert space of dimension N can be represented as real unit vectors in a $2N$-dimensional phase space, the above observations on the sphere ensure that, as the dimension of a quantum system becomes large, the behaviour of the typical value of a certain property of the quantum state becomes meaningful. Among the functions which are characterized by this property of typicality we find either properties of the whole system such as its Shannon entropy or properties pertinent to a smaller subsystem, in particular its equilibrium RDM. This fact can be very likely the conceptual bridge between the behaviour of the single, observed, quantum system and the ensemble point of view typical of the statistical mechanics, in the sense that for many properties of interest, it does not matter our impossibility to know the state of the system in detail just for the remarkable fact that almost all quantum states behave in essentially the same way. The importance of this point, already present in classical statistical mechanics, is emphasized by Lebowitz as follows:

> *“Having results for typical microstates rather than averages is not just a mathematical nicety but at the heart of understanding the microscopic origin of observed macroscopic behaviour. We neither have nor do we need ensembles […]. What we do need and can expect is typical behaviour”.*
>
> [Lebowitz, J. L., Boltzmann’s entropy and time’s arrow, Physics Today, 46, 32–38. (1993)]

It is worth to note explicitly that the ensembles we consider, i.e. FEEE and RPSE, are composed of wavefunctions which are general superposition of energy eigenfunctions corresponding to a large range of the eigen energy of the system. Indeed such an energy range is of the order of the internal energy U in the RPSE and still larger in the FEEE. This is in contrast with the usual assumption that the considered quantum state has to be "reasonably narrow" in energy in order to assure the validity of ordinary statistical mechanics, see in particular Tasaki, [Tasaki, (1998)] but also [Rigol, (2008); Jensen, (1985); Goldstein, (2006); Peres, (1984); Deutsch, (1991)].

On the other hand, from the study of the above mentioned ensembles another aspect of the problem emerges: there exists a typical value of the function of interest, but typical among what kind of states?

Indeed different functional dependences between typical values of quantities, e.g. the entropy as a function of the energy, emerge from the study of the two Ensemble Distributions, as discussed for a variety of model systems in Chapter 5 and 6. Specifically we find that the typical FEEE entropy per spin is a linear function of the internal energy per spin. From a thermodynamical point of view this would define a global temperature which does not depend on the internal energy. Curiously one also finds that the typical FEEE equilibrium state of a subsystem is not of the standard canonical form. On the contrary in the RPSE one finds that, as the number of components n gets large, the typical entropy approaches its maximum value, i.e. that corresponding to canonical global populations, even if the populations are not canonical at all. Notably, for the equilibrium state of a subsystem one recover the standard Boltzmann canonical form at the temperature given by the usual thermodynamical relation $dS = \beta dU$.

It is interesting that these results are valid, of course in a probabilistic means, for finite system. It is not necessary to invoke the thermodynamic limit since the property of typicality become effective even in systems made up of relatively few components, as demonstrated in the case of the spins system.

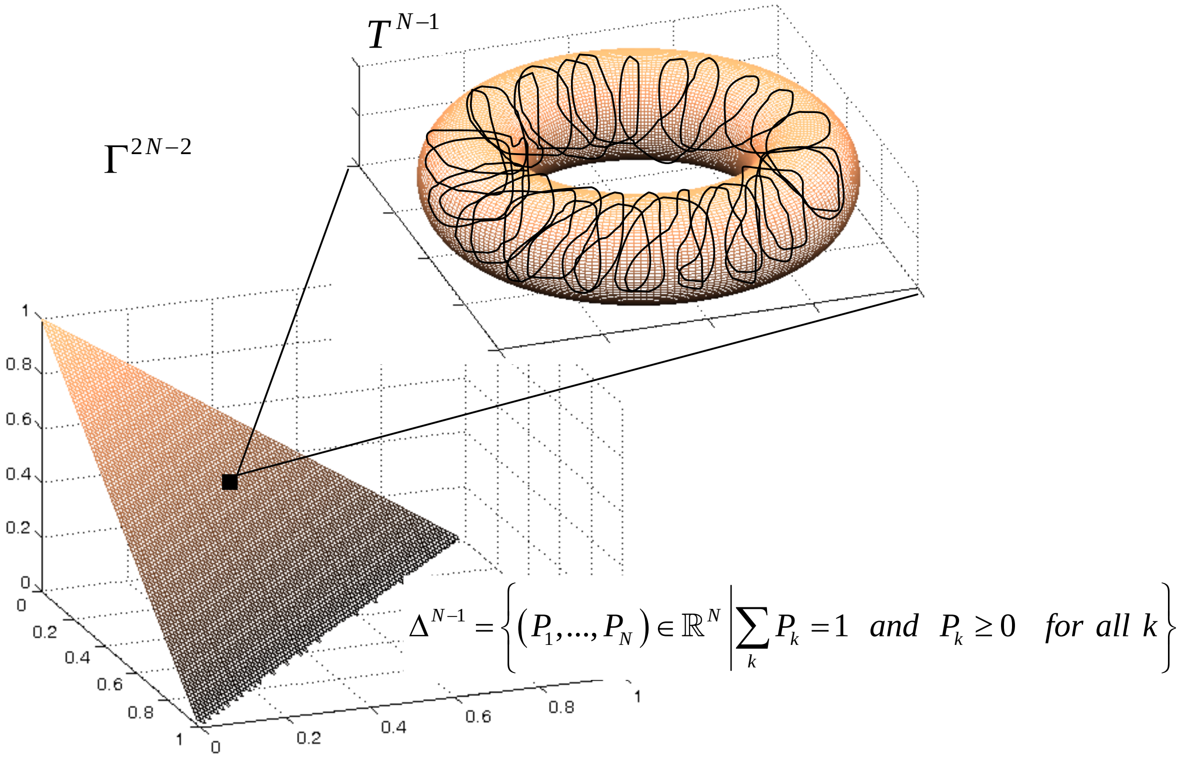


Figure 7- 1: Pictorial Representation of a quantum dynamical trajectory in the corresponding phase space.

7.2 EMERGENCE OF THERMODYNAMICS WITHIN A SINGLE, FINITE DIMENSIONAL, PURE STATE: TYPICALITY AND "THE PRINCIPLE OF MACROSCOPIC UNIFORMITY"

In order to discuss the results on the trend of the thermodynamic functions in the two ensembles, it is interesting to follow an argument presented by Jaynes in [Jaynes, (1957)], where the epistemological aspects of his "subjective statistical mechanics" are carefully considered. First one observes that the statistical character of a theory entails that it makes prediction only when, and to the extent that, it leads to sharp distributions on the observables. In our case the "macroscopic" observable is the value of the entropy, or the elements of the RDM. The emergence of a "typical" value for the function of interest is thus necessary for the mere existence of a statistical theory. On the other hand we have seen that the probability distribution on the parameters of the problem, i.e. populations and phases, is well approximated by means of a maximum entropy distribution, as discussed in Section 4.3. Of course, the maximum entropy distribution depends on the constraints which define the considered Ensemble; such a definition corresponds to our assignments of the weights of the microscopic states. Then, the process of maximum entropy inference is one in which we choose the broadest possible probability distribution over the microscopic states, compatible with the given constraints. Evidently the sharp distribution on the "thermodynamic observable" (entropy or equilibrium state of the subsystem) can emerge only if it is true that for *each* of the overwhelming majority of the microscopic states which have appreciable weight in the considered ensemble, we would obtain the same behaviour of the "macroscopic" functions. With the words of Jaynes

"It is this principle of macroscopic uniformity, which provides the objective content of the calculation, not the probability per sè".

The principle of macroscopic uniformity of Jaynes has the same significance of the typicality of the thermodynamic functions in our ensemble. In the same spirit we can understand the emergence of thermodynamic properties within a single pure quantum state and leave behind the idea of ensembles of pure states which is inconsistent with basic concepts of quantum mechanics as the superposition principle.

From this perspective, if the theory would predict values of macroscopic functions which do not agree with the law of thermodynamics, then it is reasonable to conclude that the hypothesis on the enumeration of the possible state in the ensemble was not correctly given. The two ensembles we have considered can be view as two different rules for selecting the possible states and their weights. Following the above line of reasoning one can interpret the failure of the FEEE in predicting well behaving thermodynamic functions as the falsification of the hypothesis on which the counting rule of the microscopic states is based. More specifically we see that the temperature of the isolated system is not determined only by its expectation energy, because the behavior of macroscopic observables obtained by starting from such an assumption does not agree with thermodynamics, that we know to be experimentally verified. The temperature is instead determined from the number of populated states (in the sense that $E_{\max}$ determines exactly this quantity). It depends only indirectly on the expectation energy E because in the ensemble which predicts well behaving thermodynamic functions, the RPSE, also E is sharply determined by the number of involved states and it is not varied independently as in the FEEE.

In this first part we have considered the statistical characterization of isolated quantum systems, described as pure states. In the second part we will focus on a subsystem which is part of a system plus environment set up. We assume that the global system is described by a pure state and its time evolution is determined on the basis of a given Hamiltonian. First we shall study the equilibrium of such a subsystem: in fact we have just established that the equilibrium average of its corresponding RDM does not depend on the particular choice of the populations of the global state. On the other hand we can now focus on the dynamical aspects of the equilibrium. This implies to consider a single, time evolving, pure state. Later, some insights into the mechanism which underlies the non equilibrium process of the relaxation toward the equilibrium state will be also considered.

PART II:

EQUILIBRIUM DINAMICS AND RELAXATION OF OPEN QUANTUM SYSTEMS

CHAPTER 8

FLUCTUATIONS AT THE EQUILIBRIUM

8.1 INTRODUCTION

In the previous Chapters we have defined the equilibrium average of the state of a quantum system (and thus, of any observables) and we have investigated the statistical behaviour of such a quantity in Ensembles of Pure States. We established that, by virtue of the property of typicality, the equilibrium average of observables of interest is very likely determined by few “macroscopic” characteristic of the system, like its total energy, and does not depend on the details of the wave-function.

In this second part we shall study the dynamical aspect of the equilibrium state, in other words we focus on the fluctuations around the average equilibrium state. This implies the need of studying a single, time evolving, pure quantum state. The connection between the dynamics of the equilibrium fluctuations of an observable and the relaxation toward the equilibrium from a “non typical” initial value is also investigates with the aid of a simple model system.

8.2 VARIANCE OF AN OBSERVABLE ALONG A TRAJECTORY

As a first indication of the amplitude of the equilibrium fluctuations of any observable we shall take the variance of its expectation value along the time evolution of a pure state $\psi\left(t\right)$. This was given in Chapter 2 and reads

$$\sigma_A^2 = \overline{a\left(t\right)a\left(t\right)^*} - \overline{a\left(t\right)}^2 \tag{8.2.1}$$

where $a\left(t\right) = \mathrm{Tr}\left(A\rho\left(t\right)\right)$ and the bar denotes the asymptotic time average or, equivalently, the average with respect the Pure State Distribution, eq. (2.3.35). By introducing the deviation of the density matrix from its equilibrium average, $\delta\rho\left(t\right) = \rho\left(t\right) - \overline{\rho}$, we can write the variance of any observable in terms of the of variances (and covariances) of the time dependent part of the density matrix elements as

$$\sigma_A^2 = \sum_{ss'}\sum_{tt'} A_{ss'}A_{tt'}^*\left(\overline{\delta\rho_{s's}\left(t\right)\delta\rho_{tt'}\left(t\right)}\right) = \sum_{ss'}\sum_{tt'} A_{ss'}A_{tt'}^*\sigma_{s's,t't}^2 \tag{8.2.2}$$

where

$$\sigma_{s's,t't}^2 := \lim_{T\to\infty}\frac{1}{T}\int_0^T dt\delta\rho_{s's}\left(t\right)\delta\rho_{t't}\left(t\right) \tag{8.2.3}$$

While the variance define the average amplitude of fluctuations in the equilibrium state, we now introduce the time correlation function of these fluctuations in order to characterized their dynamical properties. Without loss of generality, it is convenient to shift the expectation value with respect to its equilibrium average $\delta a\left(t\right) = a\left(t\right) - \overline{a\left(t\right)}$. Then we define the time correlation function as

$$C_A\left(\tau\right) = \frac{\overline{\delta a\left(t\right)\delta a\left(t+\tau\right)}}{\sigma_A^2} = \frac{1}{\sigma_A^2}\lim_{t\to\infty}\frac{1}{T}\int_0^T \delta a\left(t\right)\delta a\left(t+\tau\right)dt \tag{8.2.4}$$

Notice that $C_A\left(0\right) = 1$ by construction.

Later we will consider the dynamics of an open quantum system which interacts with its environment. The notation will be that introduced in section 2.4 and in this case the variances

$\sigma^2_{s's,t't}$ which appears in eq. (8.2.2) are to be intended as the variance of the element of the Reduced Density Matrix $\mu(t)$.

8.3 EQUILIBRIUM DYNAMICS OF AN ISOLATED QUANTUM SYSTEM

First let us see what can be stated about the equilibrium fluctuations of the whole, isolated, system described by a Pure State which belong to the RPS Ensemble characterized by well defined typical value of thermodynamic functions, as the energy per component ε. From the analysis of the time evolution conducted in Chapter 2, we know that the diagonal elements of the density matrix (in the energy representation) are the populations which are conserved quantities which do not fluctuate at all in the time. On the contrary, off diagonal elements of the density matrix are periodic functions of time

$$\rho_{nm}(t) = \sqrt{P_n P_m}\exp[-i\alpha_{n,m}(t)] \tag{8.3.1}$$

and thus each of them oscillates with an amplitude determined by the populations. As a consequence the variance of such elements during the evolution is

$$\sigma^2_{n'n,m'm} = \begin{cases} P_n P_m & \text{if} \qquad m' = n \quad n' = m \neq n \\ 0 & \qquad\qquad \text{otherwise} \end{cases} \tag{8.3.2}$$

It should be noted that the variance of a single density matrix element always depends on the details of the considered pure state. It does not assume a typical value in the Ensemble of Pure States, however we can say that *on average* it is of the order of N_ε^{-2}. On the other hand the variance which characterized a generic operator A eq. (8.2.2), with many non zero off diagonal elements in the energy representation, has a typical value in the RPSE given by

$$\sigma_A^2 \approx \frac{1}{N_\varepsilon^2}\sum_n \sum_{n'\neq n} A_{nn'} A^*_{nn'} \tag{8.3.3}$$

Since also the number of terms in the summation is of the order of N_ε^2, in principle the standard deviation σ_A of an observable can be of the order of its typical average

$$\overline{a(t)} = \frac{1}{N_\varepsilon}\sum_n A_{nn} \tag{8.3.4}$$

The actual value of the variance depends on the structure of the representation of the observable in the eigen energy basis of the total Hamiltonian. Some results about this point are available for a class of operators which has a well defined classical limit, [Feingol, (1986)]. However an estimate of (8.3.3) on these basis is dependent on certain hypotheses about the chaoticity of the model in the classical limit [Peres, (1984); Srednicki, (1996)].

As we have already noted in Section 2.4, a quantum sub-system described by a pure state should be considered the exception rather then the rule. Thus, let us analyse the fluctuations of the RDM of a subsystem S which is part of an isolated system $S+E$. The whole system is described by a pure state $\psi(t)$. Let us first consider the case of no interaction between the two subsystems S and E, in this case the total Hamiltonian can be expressed as the sum of the Hamiltonians of the system and of the environment

$$H = H_S + H_E \tag{8.3.5}$$

In this ideal system the RDM evolves in time according to its Liouville Equation, eq. (2.4.11). Thus, in the eigen energy basis of the system Hamiltonian $\left\{ |s\rangle, s = 1 ... N_S \right\}$, the elements of the reduced density matrix read

$$\mu_{ss'}(t) = e^{i\omega_{ss'}t} \mu_{ss'}(0) \tag{8.3.6}$$

Where the RDM at the instant $t=0$ is determined by tracing out the degrees of freedom of the environment from the whole pure state density matrix, $\omega_{ss'} = (E_s - E_{s'})$ being the eigenvalues of the system Liouville operator in frequency units (that is, $\hbar = 1$). Since the subsystem is assumed to be isolated the diagonal elements of the RDM are conserved during the evolution and are determined from the global populations

$$\mu_{ss}(t) = \mu_{ss}(0) = \sum_b P_{sb} := P_s \tag{8.3.7}$$

We shall call the diagonal elements of the RDM the “reduced populations”, P_s, of the subsystem. However it is necessary to stress that the reduced populations have very different properties with respect to the global populations whose statistics we have studied up to now. First it has been shown in the previous chapters that they assume a typical value on Ensembles. In particular they are very likely to be of the standard canonical form if we consider a pure state which belongs to the RPSE. Second, we stress that, contrary to the global populations P_n, the reduced populations are not necessary constant during the time evolution of the system. They are conserved only in the absence of energy exchange between system and the environment. The dynamical aspects of the equilibrium state of the subsystem in the presence of the interactions with the surrounding will be the central issue of the following Sections.

The off-diagonal elements of the RDM are instead oscillatory functions of time and they are given explicitly by

$$\mu_{ss'}(t) = \exp[-i\omega_{ss'}]\sum_{b}^{N_E}\sqrt{P_{sb}P_{s'b}}\exp\left[i\left(\alpha_{sb}-\alpha_{s'b}\right)\right] \tag{8.3.8}$$

with $s' \neq s$. Their variance along a trajectory is easily obtained under the assumption of no frequency degeneracy in the spectrum of the system, eq. (2.3.16), and reads

$$\sigma^2_{ss',s's} = \sum_{bb'}^{N_E^2}\sqrt{P_{sb}P_{s'b}P_{sb'}P_{s'b'}}\exp\left[i\left(\alpha_{sb}-\alpha_{s'b}+\alpha_{s'b'}-\alpha_{sb'}\right)\right] \tag{8.3.9}$$

Notice that if the subsystem is in a pure state, then the global populations are factorized, while the initial phases are the sum of the initial phases of the wavefunction of the system $\psi_S(0)$ and that of the environment $\psi_E(0)$, that is

$$P_{sb} = P_s P_b \tag{8.3.10}$$

$$\alpha_{sb} = \alpha_s + \alpha_b \tag{8.3.11}$$

If this is the case, one sees that the elements of the RDM, eq. (8.3.7) and eq. (8.3.8), does not depend on the environment and the variance eq. (8.3.9) assumes its maximum value

$$\max\left[\sigma^2_{ss',s's}\right] = P_s P_{s'} \tag{8.3.12}$$

As we have already noted also the extent to which the system is entangled with its environment cannot change in the absence of interactions. The purity $\mathcal{P}$, defined in eq. (2.4.7), and which is a measure of this property, is conserved during the motion and can be related to the variance, eq. (8.3.9), as follows

$$\mathcal{P}(t) = \mathcal{P}(0) = \sum_s P_s^2 + \sum_s\sum_{s'\neq s}\sigma^2_{ss',s's} \tag{8.3.13}$$

If the subsystem is in a pure state then the variance is given by eq. (8.3.12), and the unity value $\mathcal{P} = 1$ is recovered. Notice that, even if the purity of the system is bounded from below by $1/N_S$ in the general case, the minimum value of the purity compatible with a given set of populations P_S is

$$\mathcal{P}_{min} = \sum_{s}^{N_S} P_s^2 \tag{8.3.14}$$

which corresponds to the case of a completely mixed initial state.

To illustrate this result let us consider a total system composed of $n = 8$ spins $1/2$ and look at the time evolution of one of them. The system Hamiltonian is

$$H_S = \omega_0 S_Z \tag{8.3.15}$$

In the upper panel of Figure 8-1 the time oscillation of the real part of the off diagonal elements of the single spin RDM, $\mu_{\alpha\beta}(t)$ are shown for different values of the initial bipartite entanglement given by the purity. In the lower panel the corresponding probability distributions obtained by sampling the trajectory of $\mu_{\alpha\beta}(t)$ are reported. Notice the common shape of these distributions which represent a coherent oscillation; in this special case the variance $\sigma^2_{\alpha\beta,\beta\alpha}$ provides information about the amplitude of such an oscillation. In the reported case the global population are equal to the average populations of the RPSE which correspond to an average energy per spin equal to $\varepsilon = 0.45$. The corresponding inverse temperature calculated on the basis of the subsystem populations according to eq. (5.4.20) is $\beta \approx 0.2$. It is interesting to note that the RPSE global population cannot be in general factorized as in eq. (8.3.10), so that the maximum purity which can be obtained for the subsystem with this global population is $\mathcal{P} = 0.9133$ (green line). On the contrary a pure state for the subsystem is obtain by using canonical global populations (red line) which, in the absence of interactions are naturally factorized. For both the set of populations the minimum purity, eq. (8.3.14), is $\mathcal{P} = 0.5046$ and corresponds to an exactly diagonal density matrix.

These considerations can be directly employed to derive a lower and an upper bound to the equilibrium fluctuations of any observable. Let us define the following

$$\begin{aligned} \max_{ss'} \langle s | A | s' \rangle &= a_{\max} \\ \min_{ss'} \langle s | A | s' \rangle &= a_{\min} \end{aligned} \tag{8.3.16}$$

that is, the maximum and the minimum value of the considered operator in the energy representation. Then, from eqs. (8.2.2), (8.3.13) and (8.3.14), it follows that the variance of the observable $a(t)$ at the equilibrium is bounded between

$$a_{\min}^2\left(\mathcal{P}-\mathcal{P}_{min}\right)\le\sigma_A^2\le a_{\max}^2\left(\mathcal{P}-\mathcal{P}_{min}\right) \tag{8.3.17}$$

This result relates the amplitude of the equilibrium fluctuations to the measure of the entanglement between the system and its environment. If a subsystem is isolated from its environment at a certain time $t=0$, but remains nearly maximally entangled with it, then large deviation of its properties from the equilibrium average value will be extremely rare. A similar result is used in [Reimann, (2008)] to justify the validity of equilibrium statistical mechanics under “experimentally realistic conditions”, i.e. for macroscopic system.

On the other hand, eq. (8.3.17), also means that the dynamical fluctuations for observables with $a_{\min}\neq 0$ are never absent unless we start with a perfectly mixed state.

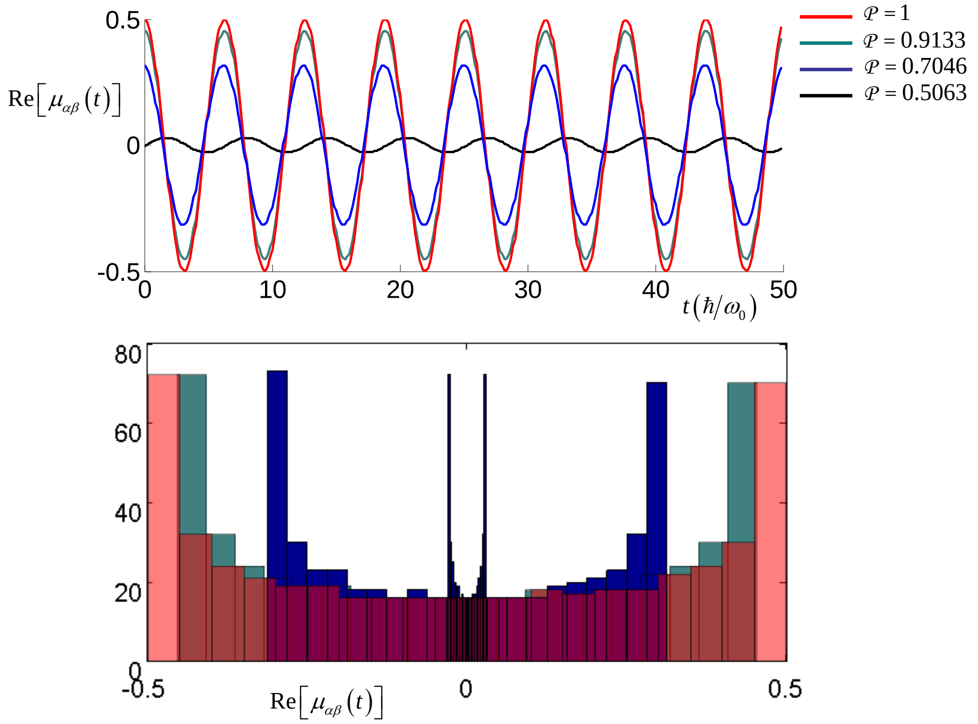


Figure 8- 1: Time evolution of the off diagonal element of one spin which is entangled with an environment of other 7 spins. The different evolutions refer to different values of the purity of the subsystem. In the lower panel we show the corresponding probability distributions, obtained from the sampling of the trajectory.

Having established this connection, one can now use the results about the Ensemble Distribution of the purity of bipartite quantum system. It is well known that typical large bipartite state are highly entangled. However the reduced state resulting from a generic bipartition of a random pure state is, on average, *not maximally* entangled as noted for example in ref. [Facchi, (2006), (2008)]. The average has to be taken over the set of all pure state in $\mathcal{H}$ according to the unitarily invariant Haar measure. The first moment of the purity distribution is calculated in [Lubkin, (1978); Page, (1993)] and reads

$$\langle \mathcal{P} \rangle = \frac{N_S + N_E}{1 + N_S N_E} \approx \frac{1}{N_S} + \frac{1}{N_E} \tag{8.3.18}$$

where the last term is a good approximation when $N = N_S N_E >> 1$.

In [Scott, (2003); Giraud (2007)] also the higher order moments has been exactly calculated, with the following result for the variance

$$\langle \mathcal{P}^2 \rangle - \langle \mathcal{P} \rangle^2 = \frac{2\left(N_S^2 - 1\right)\left(N_E^2 - 1\right)}{\left(1 + N_S N_E\right)^2 \left(2 + N_S N_E\right)\left(3 + N_S N_E\right)} \approx \frac{1}{N^2 + N}\left(2 - \frac{1}{N_S^2} - \frac{1}{N_E^2}\right) \tag{8.3.19}$$

It should be noted that the above results eq. (8.3.18) and eq. (8.3.19) corresponds to the typical value for RPSE in the limit of infinite temperature. But in our framework we have seen that the typical subsystem populations, eq. (8.3.7), are canonical at a temperature determined by the typical energy per component of the system. Thus, it becomes clear that the minimum purity of the system, eq. (8.3.14) as well as the typical purity on the ensemble, eq. (8.3.13), can be related to the typical energy of the wavefunctions which belong to the ensemble. In Figure 8-2 the ensemble distributions of the purity of a spin $1/2$ in a global system of $n = 8$ similar spins is shown for different values of the typical energy per spin.

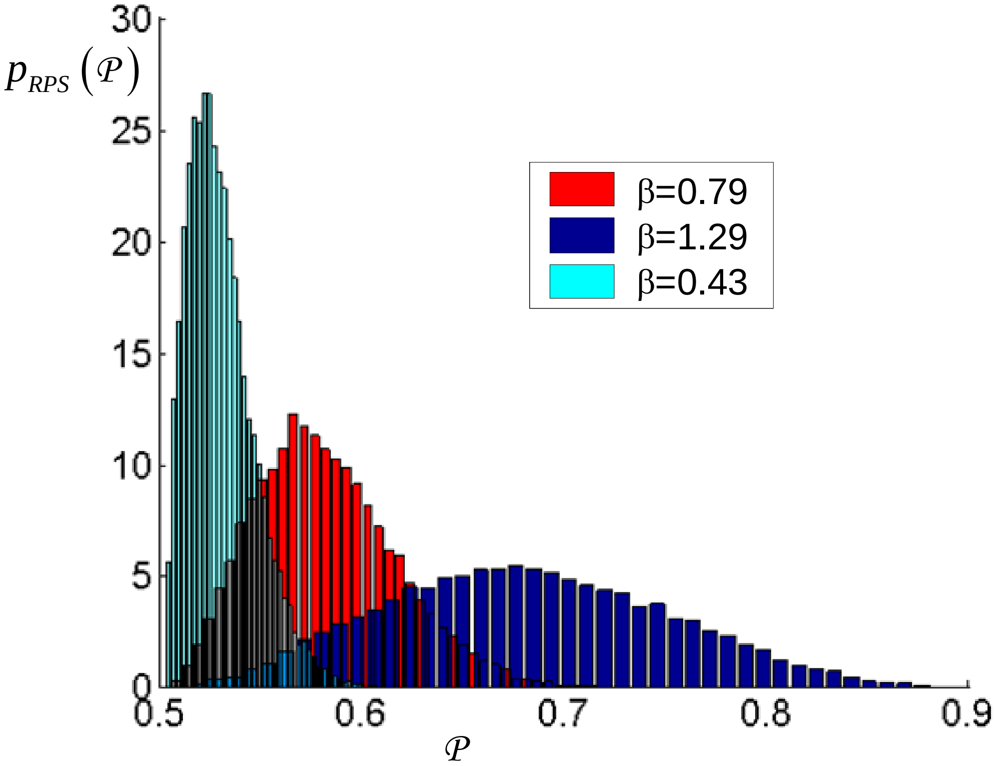


Figure 8- 2: Random Pure State Ensemble Distribution of the purity of a single spin $1/2$ in a system composed of $n=8$ spins, the (normalized) histograms refers to different typical energy per spin. The corresponding inverse temperature are reported in the inset.

To formalize this observation, let us derive the RPSE average purity of a bipartition of the total system by using the ensemble distributions obtained for the global population. First let us recall the result obtained for the ensemble average of the subsystem populations, given in eq. (5.5.26): in order to compute $\langle P_s \rangle$ we have to sum the average global population of the energy levels $E_n = E_s + E_b \leq E_{\max}$. The number of terms which contribute to this sum obviously depends on the specific subsystem population we are considering and it is denoted by N_b^s. If the spectrum of the environment is characterized by a smoothed density of states $g(E_b)$ this reads

$$N_b^s = \int_{E_s}^{E_{\max}-E_s} g(E_b)\, dE_b \tag{8.3.20}$$

Then the average subsystem population can be expressed as

$$\langle P_s \rangle = \frac{N_b^s}{N_\varepsilon} \tag{8.3.21}$$

where $N_\varepsilon = \sum_s N_b^s$ denotes as usual the total number of states which one has to consider in order to obtain a typical energy per component equal to ε. The ensemble average minimum purity is then given as

$$\langle \mathcal{P}_{min} \rangle = \sum_s^{N_S} \langle P_s^2 \rangle = \sum_s^{N_S} \sum_b^{N_{sb}} \sum_{b'}^{N_{sb}} \langle P_{sb} P_{sb'} \rangle = \sum_s^{N_S} \langle P_s \rangle^2 + \sum_s^{N_S} \frac{\langle P_s \rangle}{N_\varepsilon} \tag{8.3.22}$$

Where we have used the definition of the reduced population eq. (8.3.21). If the total number of states is large then the second term can be neglected and one obtains an ensemble average minimum purity as a function of the typical subsystem populations which we know to be canonical. Notice that in the limit of infinite temperature, $\beta \to 0$, $\langle \mathcal{P}_{min} \rangle \approx 1/N_s$ which is the usual lower bound. For the average purity one finds

$$\langle \mathcal{P} \rangle = \langle \mathcal{P}_{min} \rangle + \sum_s^{N_S} \sum_{s' \neq s}^{N_S - 1} \sum_b^{N_{sb}} \langle P_{sb} P_{s'b} \rangle = \langle \mathcal{P}_{min} \rangle + \sum_s^{N_S} \sum_{s' \neq s}^{N_S - 1} \frac{N_b^{\max(s,s')}}{N_\varepsilon^2} \tag{8.3.23}$$

Where in the last term $N_b^{\max(s,s')}$ is the number of states associated with the highest energy between E_s and $E_{s'}$. In the $\beta \to 0$ limit one exactly recovers eq. (8.3.18), since $N_{sb} = N_E$. The above result also contains the Random Pure State Ensemble typical value of the variance of the off diagonal elements of the RDM. For a spin $1/2$, one has

$$\langle \sigma^2_{\alpha\beta,\beta\alpha} \rangle = \frac{\langle P_\alpha \rangle}{N_\varepsilon} \tag{8.3.24}$$

The whole Random Pure State Ensemble distributions of the variance of the off diagonal elements of the RDM of a single spin which belong to a total system composed of $n = 8$ spins are depicted in Figure 8-3 for three different values of the temperature.

At this stage the typical amplitude of the fluctuations, eq. (8.3.24), as well as the typical value of the purity of the subsystems, eq. (8.3.23), still refers to the great majority of the wavefunctions which belong to the considered RPSE. However it remains a “geometric” result. If, for any reason, one starts with a wavefunction which is not typical in this sense, the actual value of the purity of the subsystems and thus of the fluctuation amplitude does not change during the time evolution. This because we are considering the ideal case of no interaction between the two subsystems $S+E$. In the next Sections we shall consider the effects of the presence of interactions. The interaction between the system and its environment is necessary in order to approach the equilibrium state from a “non typical” initial value. Indeed, if we follow the time evolution ideally for infinite time we obtained the Pure State Distribution, however if we start from a particular state and consider only a finite time window we can eventually observe *relaxation* toward the equilibrium average.

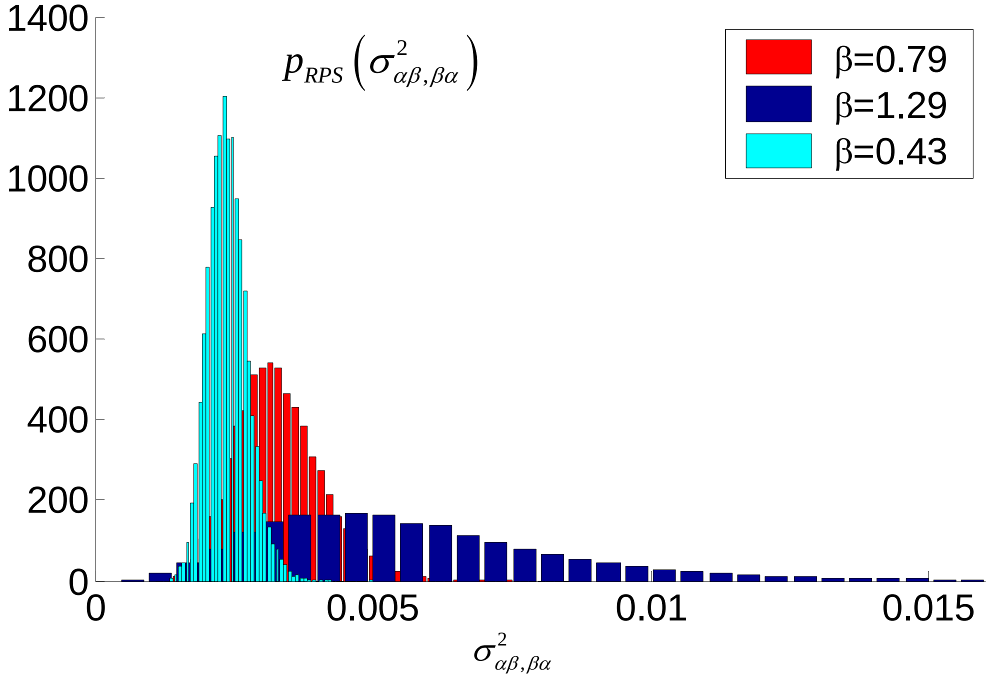


Figure 8- 3: Random Pure State Ensemble Distribution of the variance of the off diagonal elements of the RDM of a single spin $1/2$ in a system composed of $n=8$ spins, the (normalized) histograms refers to different typical energy per spin. The corresponding inverse temperature are reported in the inset.

8.4 EQUILIBRIUM DYNAMICS IN OPEN SYSTEMS

We now consider the equilibrium dynamics of the system of interest S, which is part of a composed system $S+E$ described by a pure state $\psi(t)$, and which interacts with its environment E. In all generality the total Hamiltonian which determines the time evolution of the whole system can be specified as

$$H = H_S + H_E + H_{SE} \qquad (8.4.1)$$

where H_S is the Hamiltonian of the subsystem of interest, H_B is the Hamiltonian of the rest of the overall system, i.e. the environment, and H_{SB} is the interaction Hamiltonian. The presence of the interaction has deep consequences on the dynamics of the subsystem: the first point to stress is that the subsystem cannot, in principle, be described by a pure state. Even if one assume that at some time $t=0$ the global state is factorized, $\psi(0)=\psi_S(0)\psi_E(0)$, this is not true for any successive time, [Gemmer, (2001), (2002)]. One necessarily has to describe the subsystem by means of its Reduced Density Matrix $\mu(t)$.

The second main point to stress is that, if the system is not isolated, an autonomous equation for the time evolution of the RDM can not be exactly formulated. It is well know that the dynamics of an open system has to account for relaxation. Several approaches has been developed and successfully used to describe the non equilibrium dynamics of an open quantum system, as the introduction of master equations for the statistical density matrix of the open system. Here we shall focus on another very general approach to this problem that does not need the assumptions about the non correlation between the system and its environment discussed in Chapter 1. The main idea is that to treat the system and its environment as a whole, by solving the Schrödinger equation for the global pure state. We will see that the time evolution of the subsystem can be quasi-irreversible even when the subsystem interacts with a relatively small environment. Still we shall investigate the relation between the dynamics of the equilibrium fluctuations and the relaxation dynamics.

By considering the presence of a generic interaction Hamiltonian between the system and the environment, we have to deal in general with two different basis set: the eigenfunctions of the total Hamiltonian (8.4.1)

$$H|n\rangle = E_n|n\rangle \qquad (8.4.2)$$

and the product basis $\left\{ |sb\rangle = |s\rangle |b\rangle, s = 1,...N_S, b = 1,...N_E \right\}$ which diagonalizes the Hamiltonian in the absence of the interaction term, i.e. if $H_{SE} = 0$. Indeed the first basis is convenient in order to evaluate the time evolution, while only with the product basis we can perform the partial trace over the to determine the reduced density matrix. In such a basis the instantaneous RDM is given explicitly by

$$\mu(t) = \sum_{ss'} \sum_{b} \sum_{n} \sum_{n'} e^{-i(E_n - E_{n'})t} e^{i(\alpha_n - \alpha_{n'})} \sqrt{P_n P_{n'}} \langle sb|n\rangle \langle n'|s'b\rangle |s\rangle \langle s'| \tag{8.4.3}$$

It can be divided into a constant part, for $n = n'$, and a fluctuating part

$$\mu_{ss'}(t) = \overline{\mu_{ss'}} + \delta\mu_{ss'}(t)$$

where

$$\overline{\mu_{ss'}} = \sum_{b} \sum_{n} \langle sb|n\rangle \langle n|s'b\rangle P_n \tag{8.4.4}$$

$$\delta\mu_{ss'}(t) = \sum_{b} \sum_{n} \sum_{n'\neq n} \langle sb|n\rangle \langle n'|s'b\rangle \sqrt{P_n P_{n'}} e^{-i(E_n - E_{n'})t} e^{i(\alpha_n - \alpha_{n'})} \tag{8.4.5}$$

with $\overline{\delta\mu_{ss'}(t)} = 0$.

The variance of the equilibrium distribution of any observable can be obtained from eq. (8.2.2) where now the variances of the RDM elements are explicitly given by

$$\sigma^2_{s's,t't} = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} dt \delta\mu_{ss'}(t) \delta\mu_{tt'}(t) = \sum_{bb'} \sum_{n} \sum_{n'\neq n} \langle sb|n\rangle \langle n'|s'b\rangle \langle tb'|n'\rangle \langle n|t'b'\rangle P_{n'} P_n \tag{8.4.6}$$

Of course the variance of the equilibrium distribution does not contains all the information required to characterize the equilibrium state. Indeed we are also interested to study the whole equilibrium distribution and the time scale of the fluctuations. In particular the correlation function, eq. (8.2.4), of the equilibrium fluctuations of the expectation values of an observable for the subsystem is given as

$$C_A(\tau) = \sum_{ss'} \sum_{tt'} A_{ss'} A_{tt'} \sum_{bb'} \sum_{n} \sum_{n'\neq n} \langle sb|n\rangle \langle n'|s'b\rangle \langle tb'|n'\rangle \langle n|t'b'\rangle P_{n'} P_n \exp\left[-i\omega_{nn'} t\right] \tag{8.4.7}$$

A general approach requires the analysis of the exact time evolution of the whole system $S+E$, for which the Schrödinger equation is well defined. Accordingly the time evolution of the Density Matrix $\rho(t)$ is determined by the Liouville-Von Neumann equations (2.2.7) with the total Hamiltonian eq. (8.4.1). At any time t, the total density matrix is given as

$$\rho(t)=e^{-\frac{i}{\hbar}Ht}\rho(0)e^{\frac{i}{\hbar}Ht} \tag{8.4.8}$$

Now, if $\rho(t)$ is traced out over the environment E for a given set of points of the time axis, one gets the reduced density matrix of S at these times. Then one can study the distribution of the reduced density matrix elements $\mu(t)$ from the resulting time series. A pictorial representation of these procedure is given in Figure 8-4. For previous works with a similar approach but different intents see refs. [Nag, (2005); Lahiri, (2003); Miller (1999), Borowski, (2003)].

It is worthy to mention that assumptions on phenomenological, random, time dependent interactions are sometimes made in studies about the reduced dynamic, e.g. in the Stochastic Theory of Lineshape by Kubo and Anderson, [Kubo, (1954), (1963); Anderson (1954); Faid (1986)]. In the present approach these assumptions are not needed, because we work with the full, time independent Hamiltonian, and any time dependence should come out as a consequence of the model.

As we have already noted the presence of the interaction produce entanglement between the subsystem and the environment. Consequently the purity of the bipartition is not conserved during the evolution, and its explicit general expression is

$$\begin{aligned}\mathcal{P}(t)&=\sum_{ss'}\mu_{ss'}(t)\mu_{s's}(t)\\&=\sum_{ss'}\sum_{bb'}\sum_{rr'}\sum_{tt'}\langle sb|r\rangle\langle r'|s'b\rangle\langle s'b'|t\rangle\langle t'|sb'\rangle\sqrt{P_rP_{r'}P_tP_{t'}}\,e^{-i(E_r-E_{r'}+E_t-E_{t'})t}e^{i(\alpha_r-\alpha_{r'}+\alpha_t-\alpha_{t'})}\end{aligned} \tag{8.4.9}$$

A relation like eq. (8.3.13) between this measure of the entanglement and the equilibrium fluctuation amplitude is recovered by considering the equilibrium average, i.e. the asymptotic time average, of the purity

$$\overline{\mathcal{P}(t)}=\sum_{ss'}\overline{\mu_{ss'}}\,\overline{\mu_{s's}}+\sum_{ss'}^{N_S(N_S-1)}\overline{\delta\mu_{ss'}\delta\mu_{s's}}=\mathcal{P}_{min}+\sum_{ss'}^{N_S(N_S-1)}\sigma^2_{ss',s's} \tag{8.4.10}$$

It is clear that the time evolution of all the quantities of interest critically depends on the form of the interaction between the two subsystems S and E. It is possible to recognize two main class of such interactions:

1. Pure dephasing interaction: this is achieved when the Hamiltonian of the system H_S commutes with the interaction term of the Hamiltonian,

   $$\left[H_S, H_{SE}\right] = 0 \tag{8.4.11}$$

   In this case no energy exchange occurs between the two subsystems. For this type of interaction the population of the system, i.e. the diagonal elements of the reduced density matrix, does not evolve during the motion. As will be illustrated in detail in Section 8.5 the main effects of the interaction is to induce *Decoherence* in the system.

2. Non adiabatic interaction: in this case the interaction Hamiltonian is not diagonal in the eigenenergy basis of the system and the energy exchange between the system and the environment is allowed. Thus the system energy usually dissipates into the environment irreversibly and we name this effect quantum dissipation, [Leggett (1987), Weiss (1992)]. In this case the interaction affects either the eigenenergies and the eigenstates of the total Hamiltonian.

One can further distinguish between the absence of self-interaction between the environmental degrees of freedom and the case of a self-interacting environment. Of course the first assumption is an idealization largely used in the literature because of the great simplification of the algebra which entails. However it was point out in ref. [Tessieri, (2003)] that the intrabath coupling have interesting effects on the decoherence dynamic of the system. This observation has stimulated a great amount of studies in this direction, see e.g. [Dawson (2005), Rossini (2007), Cormick (2008), Yuan (2008)]. It appears clearly that both the fluctuation amplitudes, eq. (8.4.6), and the equilibrium correlation function of a subsystem observable, eq. (8.4.7), does not depend on the specific spectrum of the environment in the absence of an interaction which couples different states, b and b', of the environment. We will consider in the next Chapter the equilibrium dynamic of a model system which account for the presence of an intrabath interaction.

In the following Sections and in the next Chapter we shall consider the equilibrium dynamics of two model systems taken as paradigms of the two kinds of interactions introduced above. The system of interest S will be always a two level system for which the usual notation used for the description of a spin $1/2$ will be employed.

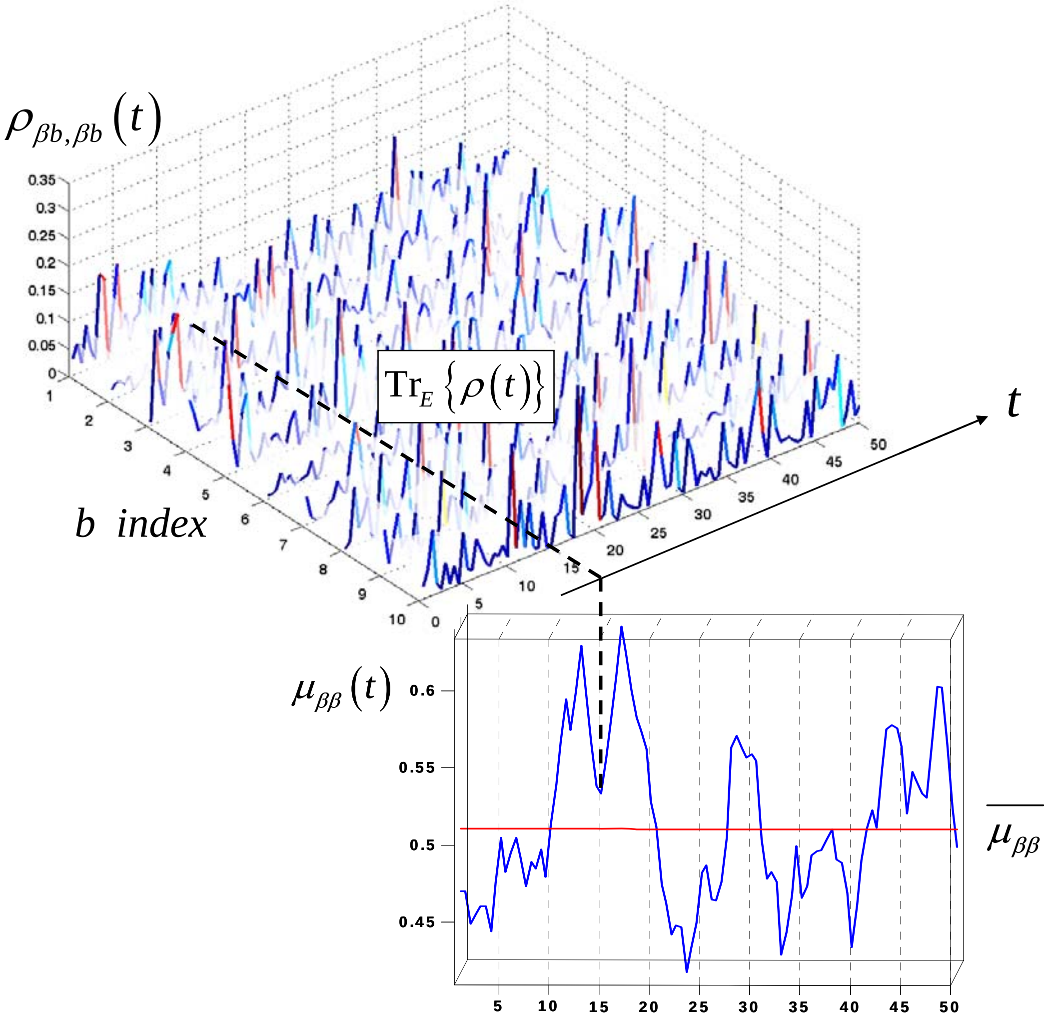


Figure 8- 4: Representation of the procedure used for obtaining the exact time evolution of the Reduced Density Matrix of a subsystem.

8.5: TWO LEVEL SYSTEM IN A SPIN ENVIRONMENT: EQUILIBRIUM DYNAMICS AND DECOHERENCE

The first model we shall analyze is a central spin $1/2$ in an environment of n similar spins $1/2$. The Zeeman frequency of the central spin will be taken as the reference energy unit. Thus the system and the environment Hamiltonian are specified as

$$H_S = S_z^0 \tag{8.4.12}$$

$$H_E = \sum_{k=1}^{n} H_E^{(k)} = \sum_{k=1}^{n} \omega_k S_Z^{(k)} \tag{8.4.13}$$

Which are diagonal in the product basis $\{|n\rangle = |s\rangle|M\rangle\}$

$$H_S|s\rangle = m_s|s\rangle \qquad |s\rangle = \{|\alpha\rangle,|\beta\rangle\} \qquad m_s = \pm\frac{1}{2} \tag{8.4.14}$$

$$H_E|M\rangle = \omega_M|M\rangle \qquad |M\rangle = \{|m_1...,m_n\rangle\} \quad \omega_M = \sum_{k=1}^{n} m_k\omega_k \quad m_k = \pm\frac{1}{2} \tag{8.4.15}$$

We will first consider a pure dephasing interaction

$$H_{SE} = S_z^0\sum_{k=1}^{n} g_k S_Z^{(k)} \tag{8.4.16}$$

This is equivalent to the model introduced by Zurek some time ago, [Zurek, (1982)], as the simplest solvable model to study the *decoherence* process. The special feature of this Hamiltonian is that it is diagonal in the product basis $\{|sM\rangle\}$

$$H_{SE}|sM\rangle = m_s\lambda_M|sM\rangle$$

Where

$$\lambda_M = \sum_{k=1}^{n} g_k m_k \tag{8.4.17}$$

We can consider the set of indices $\{m_k, k = 1...,n\}$ as a set of independent random variables which take the values $\pm 1/2$ with probability $1/2$. Thus both the parameters ω_M, eq. (8.4.15) and λ_M, eq. (8.4.17) are sum of random variables. By virtue of the Central Limit Theorem, and under mild assumptions about the distribution of the single spin parameters g_k and ω_k, [Cucchietti, (2005)], they will be distributed according to a Gaussian smoothed density of states, that is

$$\begin{aligned} g(\omega_M) &= G(\mu_\omega,\sigma_\omega) \qquad \mu_\omega = 0 \quad \sigma_\omega^2 = \frac{1}{4}\sum_{k}^{n}\omega_k^2 \\ g(\lambda_M) &= G(\mu_\lambda,\sigma_\lambda) \qquad \mu_\lambda = 0 \quad \sigma_\lambda^2 = \frac{1}{4}\sum_{k}^{n} g_k^2 \end{aligned} \tag{8.4.18}$$

It was shown in ref. [Zurek, (1982)] that the Reduced Density Matrix of the system S which is initially in a pure state represented by a coherent superposition of eigenstates $\{|s\rangle\}$ undergoes a rapid decoherence process, which results in a RDM which is approximately diagonal in the pointer basis. In the case of the Hamiltonian eq. (8.4.16) the pointer basis coincides with the eigenstates of the system Hamiltonian. As we have already noted the diagonal elements of the RDM do not evolve and they are given by eq. (8.3.7), while according to eq. (8.4.3) the off diagonal elements are specified as

$$\mu_{\alpha\beta}(t) = \delta\mu_{\alpha\beta}(t) = \sum_{M}^{N\alpha b} \sqrt{P_{\alpha M} P_{\beta M}}\, e^{i(\alpha_{\alpha M} - \alpha_{\beta M})} \exp\left[-i(1+\lambda_M)t\right] \tag{8.4.19}$$

If the system is initially descried by an autonomous wavefunction, then conditions (8.3.10) and (8.3.11) are satisfied and eq. (8.4.19) can be rewritten as

$$\mu_{\alpha\beta}(t) = \sqrt{P_\alpha P_\beta}\, e^{i(\alpha_\alpha - \alpha_\beta)} z(t) \tag{8.4.20}$$

where $z(t) = \sum_{M}^{N\alpha b} P_M \exp\left[-i\lambda_M t\right]$ is the *decoherence factor*. Notice that $z(0)=1$ for the system initially in a pure state. It was shown by Zurek, [Zurek, (1982)], that the variance of such a quantity around its zero asymptotic time average is of the order of $(N_E)^{-1}$ with N_E being the number of the active environmental state. He also argued that the distribution of the decoherence factor sampled from a time trajectory should be normal by virtue of the Central Limit theorem. Here, we recover the results of the analysis of Zurek. Indeed, the variance of the off diagonal elements of the RDM reads, according to eq. (8.4.6)

$$\sigma^2_{\alpha\beta,\beta\alpha} = \sum_{M=1}^{N_{\alpha M}} P_{\alpha M} P_{\beta M} \tag{8.4.21}$$

which scales with the number of energy levels that contribute to the overall wavefunction in the case of pure states of the RPSE. Moreover, as it is shown in Figure 8-5, the distribution obtained from the sampling of the time evolution of $\mu_{\alpha\beta}(t)$ is Gaussian, in contrast to the distribution which characterized an isolated system reported in Figure 8-1.

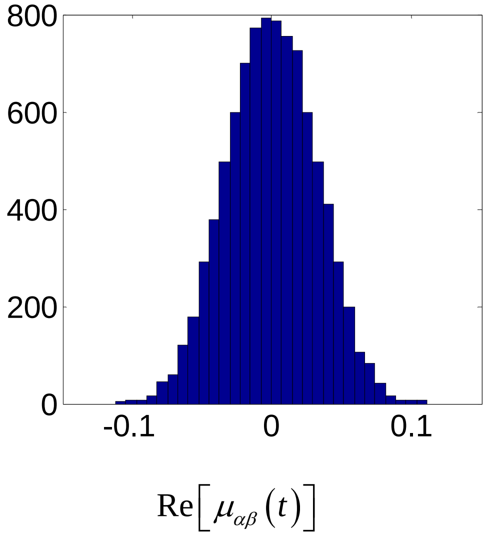


Figure 8- 5: Distribution of the off-diagonal element of the reduced density matrix of a single spin which interacts with an environment composed of 7 spins trough a pure dephasing interaction.

The decoherence process is associated with an increase of the extent to which the subsystem is entangled with its environment. Thus , the purity of the subsystem (and that of the environment), eq. (8.4.9), evolves in time. For this model one explicitly obtains

$$\begin{aligned}\mathcal{P}(t) &= P_{\alpha}^{2}+P_{\beta}^{2}+2\mu_{\alpha\beta}(t)\,\mu_{\beta\alpha}(t)\\ &= \mathcal{P}_{min}+\frac{2N_{\alpha M}}{N_{\varepsilon}}+\frac{4}{N_{\varepsilon}^{2}}\sum_{MM'\neq M}^{N_{\alpha M}}\cos\left[\left(\lambda_{M}-\lambda_{M'}\right)t+\left(\alpha_{\alpha M}-\alpha_{\alpha M'}\right)\right]\end{aligned} \tag{8.4.22}$$

where $\mathcal{P}_{min}$ is the minimum purity compatible with the actual set of system populations, eq. (8.3.14). It is well know that almost periodic functions, such as eqs. (8.4.19) and (8.4.22) return arbitrarily close to any value within their range infinitely many times in the course of their evolution, [Percival, (1961)]. However, when a moderately large number of the energy states results populated, it can be shown that the time required for these recurrences is so huge that is physically uninteresting. Thus, we can effectively define a characteristic time scale in which this functions *decay* to its average value and fluctuates around it. For a more quantitative analysis of the recurrence phenomenon we refer to [Zurek, (1982); Peres, (1982); Kolovsky, (1994)]. In order to see such a relaxation one has to start with a state which is *far* from the equilibrium average. From eq. (8.4.22) it is clear that the equilibrium average purity is near to the minimum one, if we choose an initial state characterized by a high purity for the subsystem, for example an initially factorized state, we expect to see relaxation. This point has been analyzed also in the framework of quantum thermodynamics based on the Hilbert space average method developed by Gemmer et al. [Gemmer, (2004)]. Within this framework one first selects the region of the phase space which a quantum system composed of two subsystems interacting only through a pure decoherence interaction can explore during its motion. Then one can show that the large majority of those state are characterized by purity which is close to the minimum one $\mathcal{P}_{min}$. This implies that the Von Neumann entropy of the subsystems is close to its maximum value, and this evidence has been proposed as the quantum origin of the second low of thermodynamics, [Gemmer, (2001)]. Here we shall not give any thermodynamical role to the purity, rather we are interesting to its dynamics in order to establish a connection between its evolution from a non typical initial state and its equilibrium dynamics.

First let us consider the time evolution of the purity of a central spin which interacts through the decoherence Hamiltonian, eq. (8.4.16), whit other 5 spins representing the environment. The strength of the interaction Hamiltonian is modulated by a parameter x_λ defined with respect to the central spin Zeeman energy, that is

$$\left\langle sM \middle| H_{SE} \middle| sM \right\rangle = s x_\lambda \lambda_M$$

while the coefficients λ_M are drawn from a Gaussian distribution of unit variance. The populations of the total wavefunction are chosen in correspondence of the average population of the RPSE for an inverse temperature of $\beta \approx 0.5$. We start with an initial state in which the system is characterized by a purity much greater then the minimum one, actually the maximum value compatible with the chosen population. The results are shown in Figure 8-6. In the central panels the short time behaviour of the purity is depicted: we observe a decay of the purity, with a characteristic time determined by the strength of the interaction. Moreover, according to the analysis in ref. [Cucchietti, (2005)], it is evident that the relaxation is not exponential, but rather the purity follows a Gaussian decay. After the short time behaviour we recover the equilibrium dynamics, that is, the value of the purity fluctuates around its equilibrium average, eq. (8.4.10), which is represented by the black continuous line in the left panels. The average amplitude of these fluctuations depends on the number of spins which form the whole system. Indeed, Figure 8-7 refers to a central spin which interacts with other 7 spins, and it is evident that in this case the variance of the purity is smaller. However, an interesting feature arises if we look at the time autocorrelation function of the equilibrium fluctuations of the purity. This is defined in analogy with the correlation function of an observable, eq. (8.2.4), as

$$C_{\mathcal{P}}\left(\tau\right)=\frac{\overline{\delta\mathcal{P}\left(t\right)\delta\mathcal{P}\left(t+\tau\right)}}{\sigma_{\mathcal{P}}^{2}}=\frac{1}{\sigma_{\mathcal{P}}^{2}}\lim_{t\to\infty}\frac{1}{T}\int_{0}^{T}\delta\mathcal{P}\left(t\right)\delta\mathcal{P}\left(t+\tau\right)dt \qquad (8.4.23)$$

The time correlation functions of the equilibrium fluctuations of the purity are shown in the right panels: interestingly the correlation functions decay with the time constant of the relaxation from the non typical initial state.

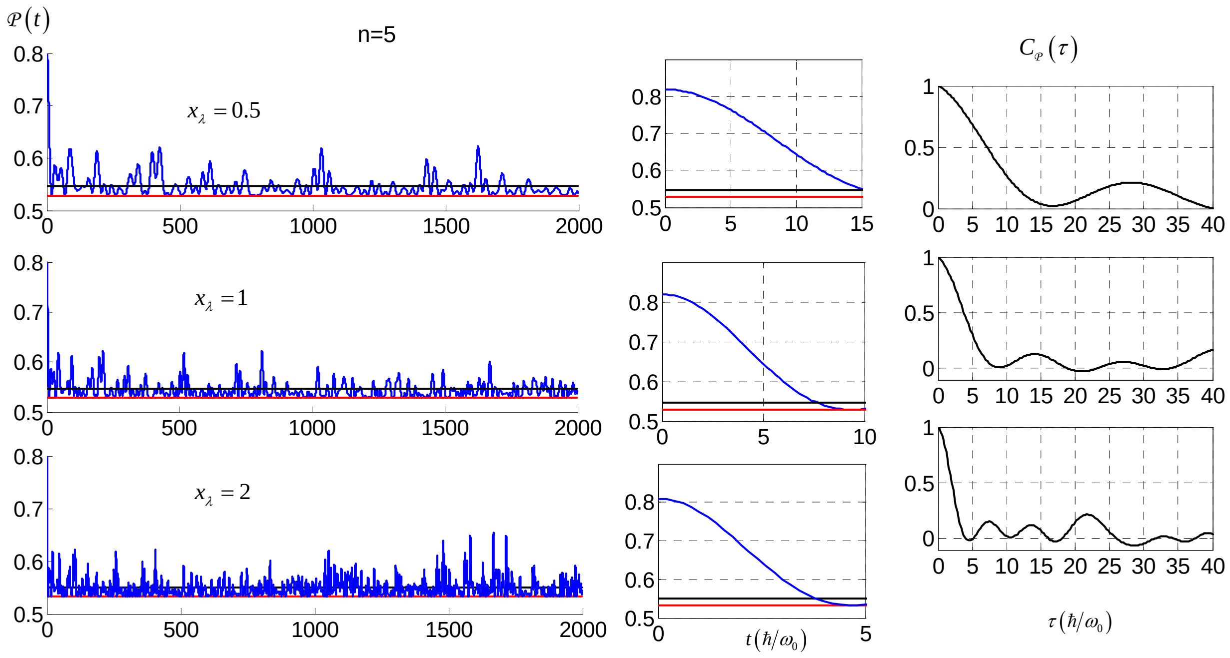


Figure 8- 6: Evolution of the purity of one spins interacting through a pure decoherence Hamiltonian with an environment composed of 5 spins. The left panels depict the entire evolution for three different values of the interaction strength. The central panels show the initial decay of the purity from a non typical initial value. The right panels shows the correlation function of the purity fluctuations at the equilibrium.

In figure 8-7 the purity evolution of the central spin which interacts con 7 spins of the environment is depicted for three different values of the interaction strength. On the right panels the corresponding time correlation function of the purity fluctuations at the equilibrium is reported. The decay of the correlations clearly reflects the decay of the initial purity toward its equilibrium average. The red lines refers to the infinite temperature limit, where all the energy levels is populated and the average RPSE population can be factorized in the product of system and environment populations, eq. (8.3.10), i.e. the total wavefunction can be written as the product of two autonomous wavefunctions. The black trace refers to different temperatures, as specified in the figure caption. While the equilibrium average value of the purity depends on the subsystem populations, eq. (8.3.7), and thus on the temperature of the system, the relaxation and the fluctuation dynamics are the same for the two different temperatures and it is dominated by the interaction strength.

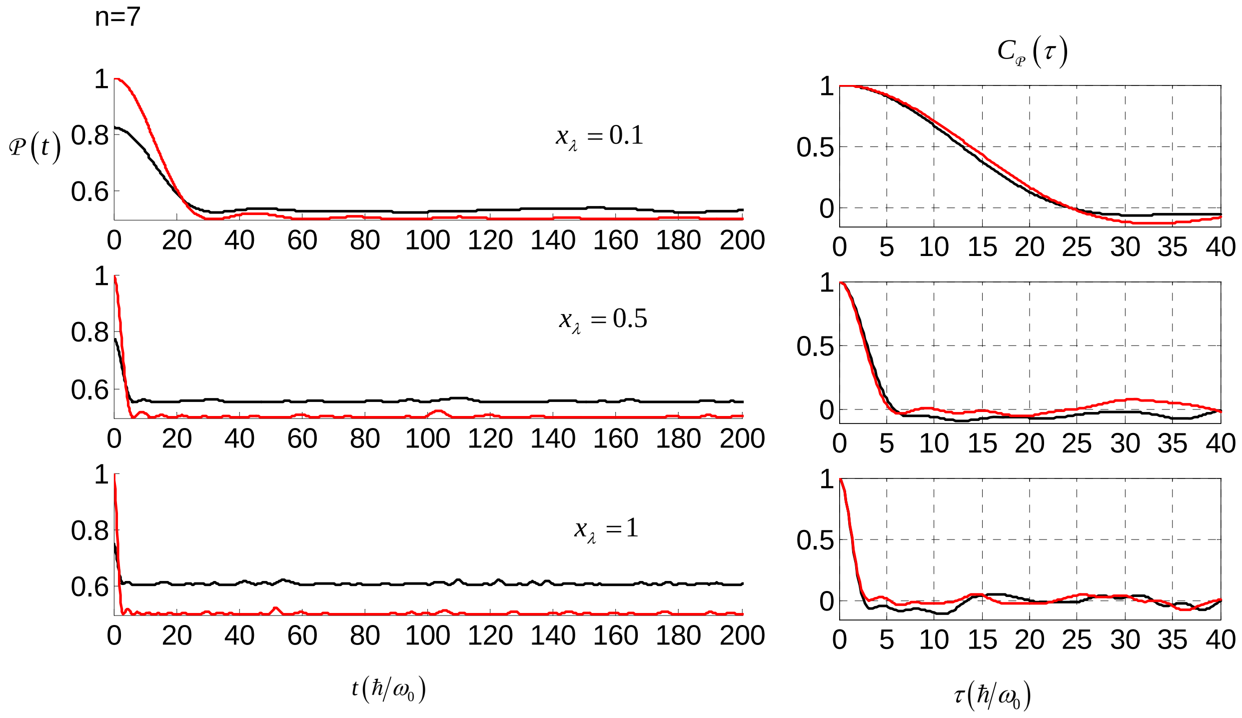


Figure 8- 7: Evolution of the purity of one spins interacting through a pure decoherence Hamiltonian with an environment composed of 7 spins. The left panels depict the evolution for three different values of the interaction strength, while the right panels shows the correlation function of the purity fluctuations at the equilibrium. The red lines correspond to the infinite temperature limit, while the black lines refer to the following temperatures: $\beta = 0.462$ for $x_\lambda = 0.1$, $\beta = 0.68$ for $x_\lambda = 0.5$, $\beta = 0.99$ for $x_\lambda = 0.1$.

While the time evolution of the purity of the system, eq. (8.4.22), depends only on the differences between the eigenenergy of the interaction Hamiltonian, the evolution of the off diagonal terms of the Reduced density matrix depends also on the Zeeman frequency of the observed spins, which we have taken as the unit measure of the frequency, i.e. $\omega_0 = 1$. Let us consider for simplicity the x component of the polarization vector of the central spin

$$p_x(t) = \mathrm{Tr}\left(S_x \mu(t)\right) = 2\,\mathrm{Re}\,\mu_{\alpha\beta}(t) = 2\sqrt{P_\alpha P_\beta}\sum_{M}^{N_{ab}} \cos\left(\alpha_{\alpha M} - \alpha_{\beta M}\right)\cos\left[\left(1+\lambda_M\right)t\right] \tag{8.4.24}$$

Clearly its equilibrium average is zero and the equilibrium fluctuation amplitude are given in eq. (8.4.21). However if we start from an initial state characterized by high purity also the initial value $p_x(0)$ is rather far from its asymptotic time average. In figure 8-8 the time evolution of such an observable is depicted for the system composed of the central spin and other 7 spins as environment. Also this observable shows a decay toward its equilibrium average value, and then fluctuations around it with a typical amplitude (left panels). However the dynamics of the short time relaxation, shown in the right panels, is completely different from that we have seen for the purity and presents characteristic oscillations. Also in this case we find that the correlation function of the equilibrium fluctuations of the observable, depicted in Figure 8-9, reproduces exactly the initial relaxation from the non typical state.

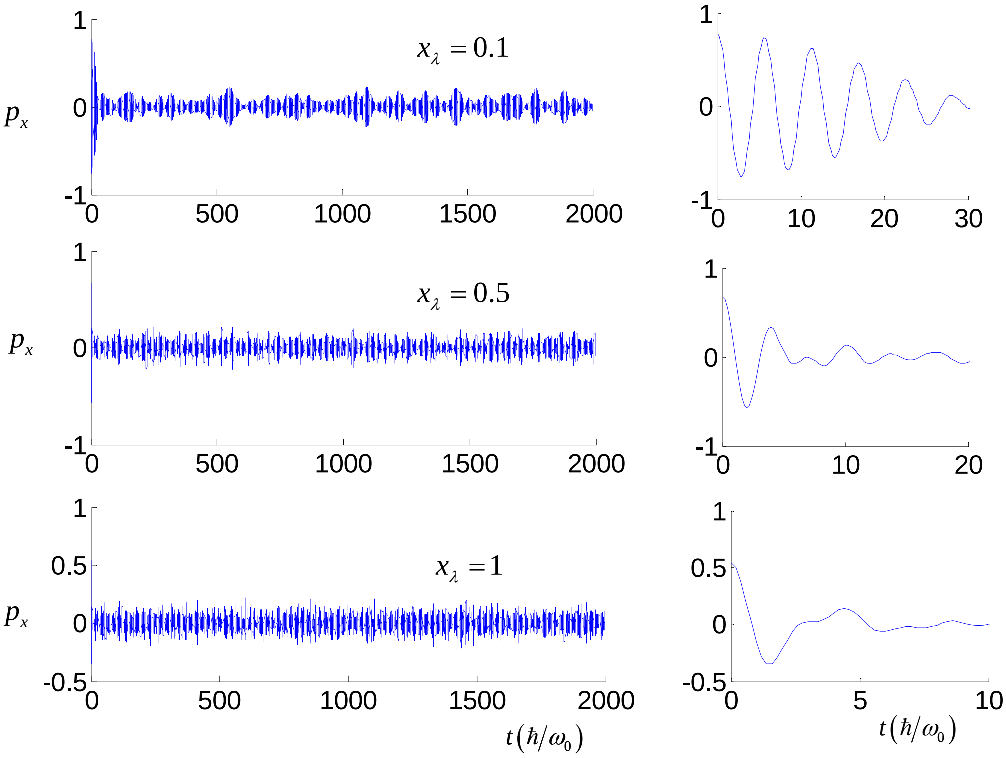


Figure 8- 8: Evolution of the x component of the polarization vector of one spins interacting through a pure decoherence Hamiltonian with an environment composed of 7 spins. The left panels depict the equilibrium evolution for three different values of the interaction strength, the right panel depicts the initial dynamic on a much shorter time scale.

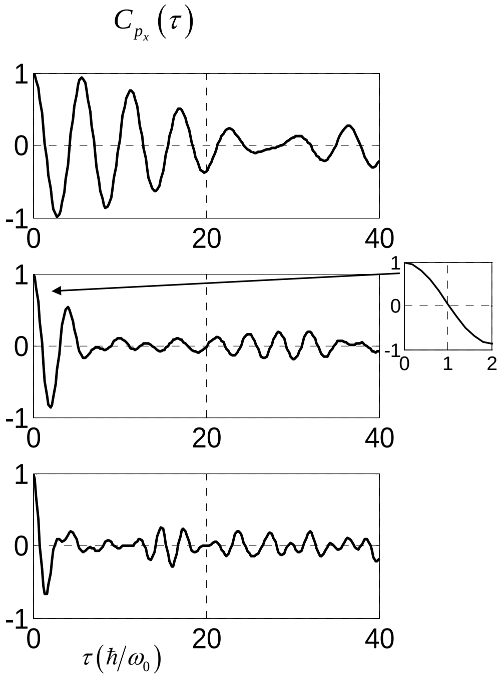


Figure 8- 9: correlation function of the equilibrium fluctuations of the x component of the polarization vector for the same system as in figure 8-8.

In this Section we have considered the simplest model Hamiltonian which produces the decoherence of an initial state characterized by high purity with respect to the equilibrium average purity. The initial state is set “by hand” as a state characterized by a non typical value of such a quantity. In the next chapter we shall consider a more general Hamiltonian with a non adiabatic interactions: in this case also the population of the subsystem fluctuates as a consequence of the interaction with the surrounding. Moreover, as already noted, the equilibrium dynamics does not depend on the environment energy spectrum as long as an “ideal bath” without self interaction is assumed. In the next model we consider an interaction Hamiltonian containing also intra bath interactions terms, and we will see that in this case the equilibrium fluctuations display an interesting dependence on the energy spectrum of the bath.

CAPITOLO 9

A RANDOM MATRIX MODEL FOR THE RELAXATION

9.1 INTRODUCTION

In the framework of “system plus bath” models, the system undergoes relaxation and fluctuations due to the interactions with the bath. These processes are frequently found to be insensitive to the details of the interactions, only a few “gross properties”, such as the diffusion coefficient in the Brownian motion problem, being relevant for their description. In this last Chapter we will consider a model system proposed in [Esposito, (2003)] and named spin-GORM model. This model provides a very general form of the environment and the interaction Hamiltonian which are modeled as Gaussian Orthogonal Random Matrices. Wigner in 1960 [Wigner, (1967)] was the first to develop random matrix theory for modeling spectra of complex quantum system containing many states. This tool has now become very common in many fields [Guhr, (1998)] from nuclear physics to quantum chaos [Casati, (1996)]. One might picture the complex environment whose Hamiltonian is taken to be a random matrix as a “black box” in which a large number of particles are interacting according to unknown laws. The system of interest will be always a two level system described as a spin $1/2$. We emphasize two important aspects of the model Hamiltonian considered in the following sections: first the coupling between the central spin and the environment is taken proportional to the S_x spin operator, thus the interaction is non adiabatic and imply an energy exchange between the system and the environment. This implies that also the diagonal elements of the Reduced Density Matrix, i.e. the reduced populations, evolves in time and fluctuates around its equilibrium average. This can be seen from equation (8.4.5) since now the eigenvector of the total Hamiltonian, $\left|n\right\rangle$, does not coincide with the product basis, $\left|sb\right\rangle$. Moreover the presence of a coupling between the degrees of freedom of the environment has important consequence on the equilibrium dynamics of the system. Again this is due to the structure of the eigenstates of the total Hamiltonian, which are linear combinations of product basis states which correspond to different states of the bath, that is, $\left\langle n\middle|sb\right\rangle \neq 0$ and $\left\langle n\middle|s'b'\right\rangle \neq 0$ also for $b \neq b'$. Under these conditions, both the amplitude and the dynamics of the equilibrium fluctuations depend on the spectrum of the environment. We will recognize different regimes for such dependence on the basis of the system-environment interaction strength.

Finally a numerical experiment is considered in order to explore the relation between the equilibrium dynamics and the relaxation from a non equilibrium state. While in the previous Chapter we have studied the decoherence process of the central spin initialized “by hand” in a non typical state characterized by high purity, here we will start with a typical state of the Random Pure State Ensemble. Thus, the subsystem is in a high entangled state from the beginning. Thus, the non equilibrium initial state will be “created” through an interaction with an external field.

9.2 THE MODEL

The model we shall consider is a spin $1/2$ coupled to a complex environment described by random matrix of dimension n. The Hamiltonian of the composite system is therefore a $2n \times 2n$ matrix of the form

$$\tilde{H} = \tilde{\Delta}_S S_Z \otimes \mathbf{1}_n + \mathbf{1}_2 \otimes \tilde{H}_B + \tilde{\lambda} S_X \otimes \tilde{V} \tag{9.2.1}$$

where $\mathbf{1}_m \left(m = 2, n\right)$ is the $m \times m$ unit matrix, S_X and S_Z are the spin $1/2$ operators

$$S_Z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \qquad S_X = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \tag{9.2.2}$$

$\tilde{\Delta}_S$ and $\tilde{\lambda}$ are positive constants which represent the energy spacing between the two states of the system and the strength of the system-environment coupling, respectively.

The representations of the environmental operators of the Hamiltonian (9.2.1) are

$$\tilde{H}_B = \frac{\tilde{\sigma}_{bath}}{\sqrt{2}} W_1 \tag{9.2.3}$$

$$\tilde{V} = \frac{\tilde{\sigma}_{int}}{\sqrt{2}} W_2 \tag{9.2.4}$$

where W_i, $i=1,2$, are Gaussian orthogonal random matrices with zero mean and unitary variance for the diagonal elements. W_1 and W_2 are different realization of the same random matrix ensemble and have therefore the same statistical properties. The definition of the random matrix ensembles and the description of some of their salient feature are briefly illustrated in Appendix 9.1. The parameters $\tilde{\sigma}_{bath}$ and $\tilde{\sigma}_{int}$ are the standard deviation of the diagonal elements of $\tilde{H}_B$ and $\tilde{V}$, respectively. We define the variances which characterize the bath and the interaction terms in the Hamiltonian as follows

$$\tilde{\sigma}_{bath}^2 = \frac{\tilde{\Delta}_B^2}{8n} \qquad\qquad \tilde{\sigma}_{int}^2 = \frac{1}{8n} \tag{9.2.5}$$

where $\tilde{\Delta}_B$ is the width of the spectrum of the environment Hamiltonian. With this choice of $n-$dependent total variance for the bath Hamiltonian, the density of the states increases with n without changing its width, and the average smoothed density of states of the environment reads:

$$d(\tilde{E}) = \begin{cases} \dfrac{8n}{\pi\tilde{\Delta}_B^2}\sqrt{\dfrac{\tilde{\Delta}_B^2}{4} - \tilde{E}^2} & if \ \left|\tilde{E}\right| < \dfrac{\tilde{\Delta}_B}{2} \\ 0 & if \ \left|\tilde{E}\right| \geq \dfrac{\tilde{\Delta}_B}{2} \end{cases} \tag{9.2.6}$$

Similarly the interaction spectrum is bounded between $\pm\lambda/2$ and its density linearly increases with n. For an immediate comparison between the different energy scales involved in the model we shall express all the energies in units of the system energy gap $\tilde{\Delta}_S$. The Hamiltonian (9.2.1) thus becomes

$$H = S_Z + \frac{\Delta_B}{4\sqrt{n}} W_1 + \frac{\lambda}{4\sqrt{n}} S_X W_2 = S_Z + H_B + \lambda S_X V \tag{9.2.7}$$

The model is therefore defined by the following parameters:

$$\Delta_B = \frac{\tilde{\Delta}_B}{\tilde{\Delta}_S}, \quad \lambda = \frac{\tilde{\lambda}}{\tilde{\Delta}_S}, \quad n \tag{9.2.8}$$

In the following we will set $\Delta_B = 10$ and $n = 100$, and we shall study the equilibrium dynamics of the subsystem reduced density matrix for different values of the interaction strength λ. Notice that, due to the scaling of the random matrix variance, eq. (9.2.5), the elements of the interaction matrix V are on average of the order of $O\left(10^{-2}\right)$. The maximum value of λ which will be considered is around $\lambda \approx 100$, and in this limit the elements of the interaction matrix are of the same order of the system Zeeman energy. The representation of the total Hamiltonian has the following structure with respect to the basis of the spin system

$$\begin{bmatrix} H_{\alpha\alpha} & H_{\alpha\beta} \\ H_{\beta\alpha} & H_{\beta\beta} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2}+H_B & \lambda V \\ \lambda V & \frac{1}{2}+H_B \end{bmatrix} \tag{9.2.9}$$

Each block is a matrix in an arbitrary basis for the Hilbert space of the environment. We will denote the basis set which diagonalizes the bath Hamiltonian, eq. (9.2.3), as $\left|b\right\rangle$, while the different basis set in which the interaction operator, eq. (9.2.4), is diagonal will be denoted as $\left|\eta\right\rangle$. Notice that the reduced density matrix can be obtained equivalently by performing the partial trace operation in the product basis $\left|sb\right\rangle$ or $\left|s\eta\right\rangle$.

9.3 FLUCTUATIONS AT THE EQUILIBRIUM: THE PERTURBATIVE TREATMENT

Let us consider the variance of the equilibrium distribution of the diagonal elements of the reduced density matrix for different values of the interaction strength. According to eq. (8.4.6), the variance of the reduced population reads

$$\sigma^2_{\beta\beta,\beta\beta} = \sum_{bb'}\sum_{n}\sum_{n'\neq n} \left\langle \beta b \middle| n \right\rangle \left\langle n' \middle| \beta b \right\rangle \left\langle \beta b' \middle| n' \right\rangle \left\langle n \middle| \beta b' \right\rangle P_{n'} P_n \tag{9.3.1}$$

In Figure 9-1 we shows the variance of the reduced population $\mu_{\beta\beta}\left(t\right)$ calculated for different value of the parameter λ. For the global populations P we use the RPSE average populations corresponding to a high temperature case, $\beta \approx 0.01$. The different sets of data refer to different realizations of the random matrices W_1, W_2. Thus, the equilibrium fluctuations amplitude of the reduced population depends on the fine detail of the energy spectrum, i.e. from the particular realization of the random matrices, for a range of values of λ, and then tends to converge to common values for stronger interactions, $\lambda > 10^{-1}$. An insight into the nature of this dependence can be obtained by means of a perturbation treatment: this permits to evaluate the correction to the eigenstate of a zero order Hamiltonian due to the presence of a weak perturbation.

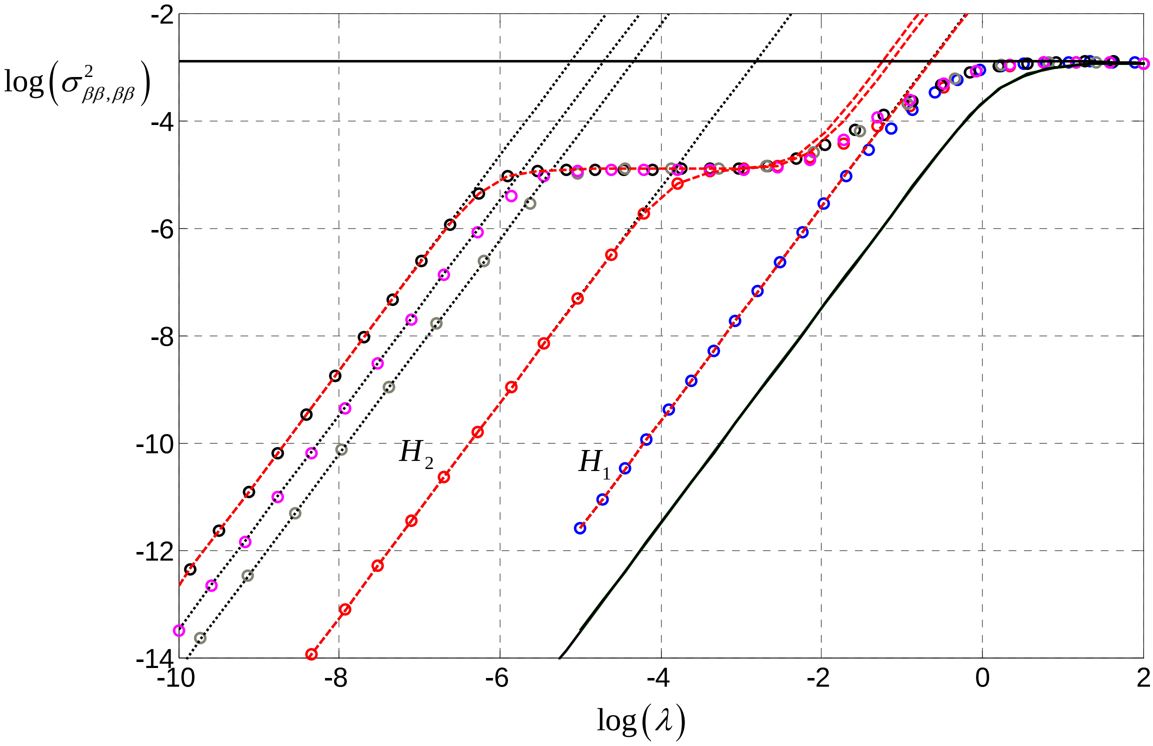


Figure 9- 1: Variance of the equilibrium distribution of the reduced population $\mu_{\beta\beta}$ as a function of the interaction strength, for the spin- GORM model. The different sets of data refers to different realizations of the random matrices which define the Hamiltonian of the model, eq. (9.2.7). The lines depict the trends predicted from different perturbative treatments as described in the text.

In the case under study the system and the environment Hamiltonians are of order 1 and $\Delta_B = 10$, respectively, while the coupling term is of order λ. Therefore we can examine two different extreme cases that can be treated perturbatively: the weak and the strong coupling regimes. Notice that, by virtue of the random nature of the interaction and the environment Hamiltonian, the total Hamiltonian is never strictly degenerate.

<u>The weak coupling regime:</u> $\lambda << \Delta_B$

For small value of the parameter λ we can treat the interaction as a perturbation. In this case the zero-th order description is defined as

$$H_0\left|sb\right\rangle = \frac{s}{2} + E_b\left|sb\right\rangle \qquad s = \mp 1 \tag{9.3.2}$$

where $\left\{E_b\right\}$ is the energy spectrum of H_B and $\left|b\right\rangle$ its eigenvectors. We take into account the effects of the perturbation H_{SB} by a power series expansion on the interaction parameter λ. Since we have assumed a pure non adiabatic coupling with the environment the first correction to the energy is of order λ^2

$$E_{n(sb)} = E_{sb}^{(0)} + E_{sb}^{(1)} + E_{sb}^{(2)} = \frac{s}{2} + E_b + \lambda^2 \sum_{s'b' \neq sb} \frac{\left\langle s'b'\right|V\left|sb\right\rangle}{E_{sb}^{(0)} - E_{s'b'}^{(0)}} \tag{9.3.3}$$

However the first order correction exists for the eigenvectors, and reads

$$\left|n\right\rangle = \left|sb\right\rangle + \lambda\left|\phi_{sb}^{(1)}\right\rangle \tag{9.3.4}$$

with the correction given explicitly by

$$\left|\phi_{sb}^{(1)}\right\rangle = \sum_{b'}^{n}\left|s'b'\right\rangle \frac{\left\langle b'\right|H_{SB}\left|b\right\rangle}{s + E_b - E_{b'}} \qquad for \;\; s' \neq s \tag{9.3.5}$$

We can use this result in order to evaluate the variance of the reduced population given in eq. (9.3.1). After some algebra one obtains the average reduced population $\overline{\mu}_{\beta\beta}$ and its variance as explicit functions of the interaction strength λ

$$\overline{\mu}_{\beta\beta} = \sum_b P_{\beta b} - \lambda^2 \sum_{b,b'} \frac{\left|\left\langle b'\right|V\left|b\right\rangle\right|^2}{\left(1 + E_{b'} - E_b\right)^2} P_{\beta b'} \tag{9.3.6}$$

$$\sigma^2\left(\mu_{\beta\beta}\right) = 2\lambda^2 \sum_{b,b'} \frac{\left|\left\langle b'\right|V\left|b\right\rangle\right|^2}{\left(1 + E_{b'} - E_b\right)^2} P_{\beta b} P_{\alpha b'} \tag{9.3.7}$$

In Figure 9-1 the perturbative approximation for the variance, eq. (9.3.7), is represented by a dotted black line. From this explicit expression it is clear that in the perturbative regime the fluctuation amplitude of the reduced population are controlled by the quantity $m = \inf\left[E_{\alpha b'} - E_{\beta b}\right] = \inf\left[1 + E_{b'} - E_b\right]$. That is, if there exists a frequency of the environment which is very close to the system frequency, then the corresponding term dominate the sum in equation (9.3.7) and thus determines the fluctuation amplitude. Of course, the perturbative treatment is valid only when the interaction is smaller than the parameter m

$$\lambda <\approx \inf\left[1 + E_{b'} - E_b\right] \tag{9.3.8}$$

Notice that the Hamiltonians corresponding to the sets of data represented in Figure 9-1 by the red, black, gray and magenta circles have been obtained by selecting some realizations of the random matrices with a particular low value of the parameter m among hundreds of thousands of realizations. Indeed a “typical” realization of the Hamiltonian produces a trend of the variance of the reduced population which is similar to the set represented in the Figure by the blue circles. It is interesting to look at the entire distribution of the reduced population obtained by sampling the time evolution of the system: this is shown in Figure 9-2 for the Hamiltonians corresponding to the red sets of Figure 9-1, for which $m \approx 10^{-5}$, and for the Hamiltonian corresponding to the blue sets, for which $m \approx 10^{-3}$. We will name the first Hamiltonian H_1 and the second H_2, as reported in the Figure. The distributions refers to a common value of the interaction strength $\log\lambda = -4.6$, which is in the perturbative regime. It turns out that the equilibrium distribution $p\left(\mu_{\beta\beta}\right)$ is Gaussian for H_1, while for H_2 we recover a distribution which resemble that of a classical oscillator. Again, this can be understood on the basis of the structure of the perturbed eigenstates. Indeed, according to eq (8.4.5) and by using the result from perturbation theory, eqs. (9.3.4) (9.3.5), one obtains the following explicit form (at the first order in λ) for the time dependent part of the reduced population

$$\delta\mu_{\beta\beta}(t) = 2\lambda \sum_b \sum_{b'} \frac{\langle b'|V|b\rangle}{\left(-1 + E_b - E_{b'}\right)} \sqrt{P_{\beta b} P_{\alpha b'}} \cos\left(\alpha_{\beta b} - \alpha_{\alpha b'}\right) \cos\left(E_b - E_{b'} - 1\right) \tag{9.3.9}$$

Thus if a single oscillating term has much higher weight in the summation, the time evolution is dominated by the corresponding frequency. Consequently the probability distribution characteristic of a pure oscillatory function arises. On the contrary, if many terms of about the same magnitude contributes to the summation, a Gaussian distribution results.

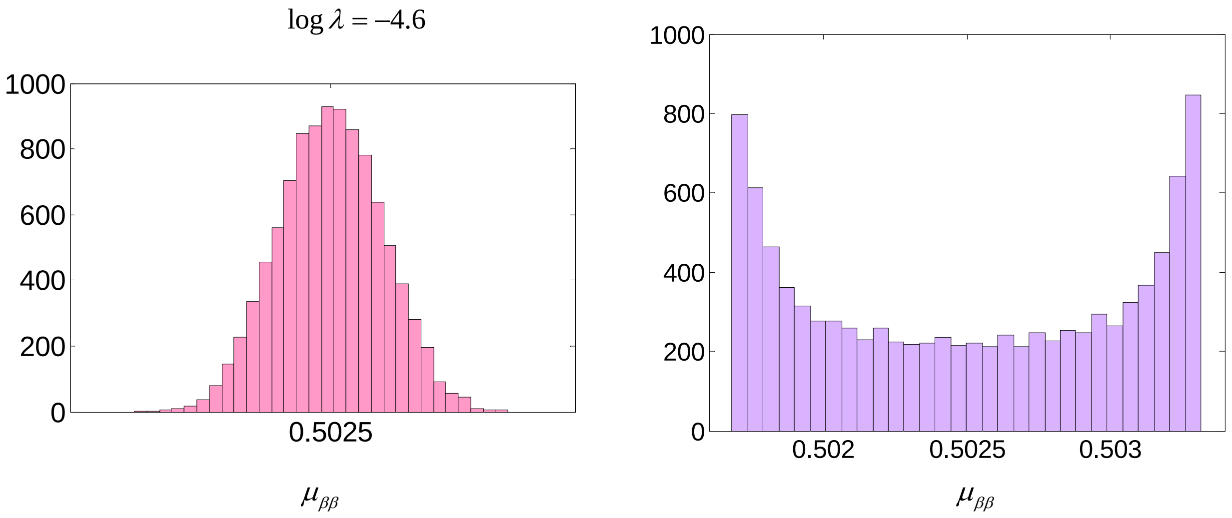


Figure 9- 2: Equilibrium probability distribution function of the reduced population $\mu_{\beta\beta}$ for two different realizations of the random matrix terms in the Hamiltonian. On the right we have shown the distribution corresponding to H_1, while on the left the distributions refers to the Hamiltonian H_2.

<u>*Perturbation for nearly degenerate state*</u>

Notice that when the weak coupling condition, eq. (9.3.8), is not satisfied the validity of the perturbative approximation for the variance, eq. (9.3.7), breaks down and a common plateaux around the value $\log\sigma^2\left(\mu_{\beta\beta}\right)\approx -5$ emerges. One can think that, when the interaction becomes larger than the m parameter then the two states corresponding to $inf\left[E_{s'b'} - E_{sb}\right]$ are seen as degenerate. In order to include this idea in the perturbative treatment we have to identify the degenerate subspace and thus removing the degeneration by the diagonalization of the corresponding subspace. This procedure is described in the following.

Let $\left|\alpha d\right\rangle$ and $\left|\beta d'\right\rangle$ be the pair of nearly degenerate state and λw the element of the interaction Hamiltonian which connects such states, i.e. $\lambda w = \lambda\left\langle d\right|V\left|d'\right\rangle$. By means of the diagonalization of this two dimensional subspace one obtains the following eigenvalues

$$E_{kD} = \frac{1}{2}\left\{\left(E_d + E_{d'}\right) + k\sqrt{4\lambda^2 w^2 + m^2}\right\} \qquad k = \mp 1 \tag{9.3.10}$$

where E_d are the eigenvalues of the environment Hamiltonian, $H_B\left|d\right\rangle = E_d\left|d\right\rangle$, and $m = E_{\alpha d} - E_{\beta d'}$. The eigenvalues are modulated by the ratio $\frac{m}{2\lambda w}$, indeed

$$
\begin{aligned}
&E_{kD} \xrightarrow{\frac{m}{2\lambda w} \gg 1} E_{sB}^{(0)} \\
&E_{kD} \xrightarrow{\frac{m}{2\lambda w} \ll 1} \frac{1}{2}\left(E_d + E_{d'} + k2\lambda w\right)
\end{aligned}
$$

The corresponding eigenvector can be written as

$$
\begin{aligned}
\left|k^+D\right\rangle &= c_\alpha^+\left|\alpha d\right\rangle + c_\beta^+\left|\beta d'\right\rangle \\
\left|k^-D\right\rangle &= c_\alpha^-\left|\alpha d\right\rangle + c_\beta^-\left|\beta d'\right\rangle
\end{aligned}
\tag{9.3.11}
$$

where the coefficients are given by

$$
\begin{aligned}
c_\alpha^+ &= \frac{1}{N_+}\left(E_{d'} - \frac{1}{2} - E_{k^+D}\right) & \qquad c_\beta^+ &= \frac{-\lambda w}{N_+} \\
c_\alpha^- &= \frac{-\lambda w}{N_-} & \qquad c_\beta^- &= \frac{1}{N_-}\left(E_d + \frac{1}{2} - E_{k^-D}\right)
\end{aligned}
\tag{9.3.12}
$$

with normalization factors

$$
\begin{aligned}
N_+ &= \left[\left(E_{d'} - \frac{1}{2} - E_{k^+D}\right)^2 + \lambda^2 w^2\right]^{1/2} \\
N_- &= \left[\left(E_d + \frac{1}{2} - E_{k^-D}\right)^2 + \lambda^2 w^2\right]^{1/2}
\end{aligned}
\tag{9.3.13}
$$

One can now use the eigenvectors (9.3.11) as the new zero-th order component of the basis instead of $\left|sd\right\rangle$, so removing the degeneracy. In order to evaluate explicitly the variance $\sigma^2\left(\mu_{\beta\beta}\right)$ one has to take into account that the overlap integrals will be different for the pair of nearly degenerate state. In particular the perturbed states $\left|n\right\rangle$ at the first order in λ are of four different kinds. Explicitly

$$
\left|\phi_{\alpha B}\right\rangle_{B\neq d} = \left|\alpha B\right\rangle + \lambda \sum_{B'\neq d'} \frac{V_{B'B}}{1 + E_B - E_{B'}}\left|\beta B'\right\rangle - \frac{\left(c_\alpha^- V_{dB} + c_\beta^- V_{d'B}\right)}{E_{k^-D} - E_{\alpha B}}\left(c_\alpha^-\left|\alpha d\right\rangle + c_\beta^-\left|\beta d'\right\rangle\right)
$$

$$\left|\phi_{\beta B}\right\rangle_{B\neq d'} = \left|\beta B\right\rangle + \lambda \sum_{B'\neq d} \frac{V_{B'B}}{-1+E_B-E_{B'}}\left|\alpha B'\right\rangle - \frac{\left(c_\alpha^+ V_{dB} + c_\beta^+ V_{d'B}\right)}{E_{k^+D}-E_{\beta B}}\left(c_\alpha^+\left|\alpha d\right\rangle + c_\beta^+\left|\beta d'\right\rangle\right)$$

$$\left|\phi_{k^+D}\right\rangle = c_\alpha^+\left|\alpha d\right\rangle + c_\beta^+\left|\beta d'\right\rangle - \sum_{B\neq d'} \frac{\left(c_\alpha^+ V_{dB} + c_\beta^+ V_{d'B}\right)}{E_{\beta B}-E_{k^+D}}\left|\beta B\right\rangle$$

$$\left|\phi_{k^-D}\right\rangle = c_\alpha^-\left|\alpha d\right\rangle + c_\beta^-\left|\beta d'\right\rangle - \sum_{B\neq d} \frac{\left(c_\alpha^- V_{dB} + c_\beta^- V_{d'B}\right)}{E_{\alpha B}-E_{k^-D}}\left|\alpha B\right\rangle$$

With a, as lengthy as straightforward, evaluation of the non vanishing contributions in eq. (9.3.1) and by retaining only the second order terms, we obtain the following explicit expression for the variance of the reduced population

$$\begin{aligned}\sigma^2\left(\mu_{\beta\beta}\right) = {} & 2\sum_{B\neq d'}^{n-1}\sum_{B'\neq d'}^{n-1} \frac{V_{BB'}^2}{\left(1+E_{B'}-E_B\right)^2} P_{\beta B}P_{\alpha B'} + 2\sum_{B\neq d'}^{n-1} \frac{\left(c_\alpha^+ V_{dB} + c_\beta^+ V_{d'B}\right)^2}{\left(E_{\beta B}-E_{k^+D}\right)^2} P_{k^+D}P_{\beta B} + \\ & + 2\sum_{B\neq d}^{N} \frac{\left(c_\alpha^- V_{dB} + c_\beta^- V_{d'B}\right)^2}{\left(E_{k^-D}-E_{\alpha B}\right)^2}\left(c_\beta^-\right)^2 P_{k^-D}P_{\alpha B} + 2\left(c_\beta^-\right)^2\left(c_\beta^+\right)^2 P_{k^-D}P_{k^+D}\end{aligned} \tag{9.3.14}$$

This result is represented by the red dotted lines in Figure 9-1. Thus, this approximation is valid for a larger range of λ in comparison with the previous perturbative result, eq. (9.3.7). However the regime between the first and the second plateaux in the values of the variance, i.e. from about $\lambda = 10^{-2}$ to $\lambda = 1$, is not described by any of our perturbative treatments. It is reasonable to think that, as λ increases, increases also the number of states that should be considered as degenerate. When this is the case, the perturbation theory is no longer a convenient tool in order to describe the trend of the variance. Nonetheless we can still consider the opposite limit of strong interaction.

The strong coupling regime: $\lambda > \Delta_B$

In this case the zero-th order Hamiltonian is defined as the Hamiltonian of the system and the interaction term, while the Hamiltonian of the environment is treated as the perturbation, that is

$$H_0 = H_S + \lambda\sigma_X V \tag{9.3.15}$$

By representing the environment operator in the basis which diagonalize the interaction matrix

$$V\left|\eta\right\rangle = E_\eta \left|\eta\right\rangle \tag{9.3.16}$$

the Hamiltonian (9.3.15) has a 2×2 block diagonal form in the basis $\left|s\eta\right\rangle$ as depicted in figure 9-3.

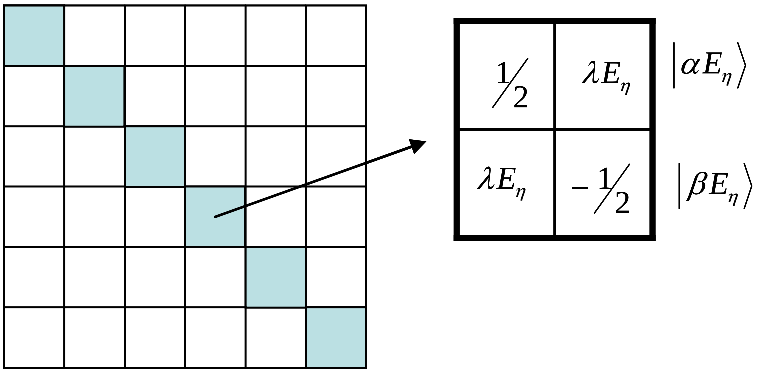


Figure 9- 3: Block structure of the zero-th order Hamiltonian in the strong coupling limit

By the diagonalization of the spin subspace we define the following eigen-energies and the corresponding eigenstates which depend on the parameter $x_\eta = 4\lambda^2 E_\eta^2$ as

$$E_{k\eta} = \frac{k}{2}\sqrt{1+x_\eta} \qquad k = \mp 1 \tag{9.3.17}$$

$$\left|k\eta\right\rangle = c_\alpha^k \left|\alpha\eta\right\rangle + c_\beta^k \left|\beta\eta\right\rangle \tag{9.3.18}$$

where

$$\begin{aligned} c_\alpha^+ &= -c_\beta^- = -\frac{1}{N\left(x_\eta\right)}\left(1+\sqrt{1+x_\eta}\right) \\ c_\beta^+ &= c_\alpha^- = -\frac{1}{N\left(x_\eta\right)}\left(\sqrt{x_\eta}\,\mathrm{sgn}\left(E_\eta\right)\right) \end{aligned} \tag{9.3.19}$$

with the normalization factor

$$N\left(x_\eta\right)=\left[2+2x_\eta+2\left(1+x_\eta\right)^{1/2}\right]^{1/2} \tag{9.3.20}$$

The first order correction due to the presence of the bath Hamiltonian to the zero-th order energies, eq. (9.3.17), is thus

$$E_{k\eta}^{(1)}=\left\langle\eta\right|H_B\left|\eta\right\rangle \tag{9.3.21}$$

while for the eigenvectors one obtains

$$\left|n\right\rangle=\left|k\eta\right\rangle+\left|\phi_{k\eta}^{(1)}\right\rangle \tag{9.3.22}$$

$$\left|\phi_{k\eta}^{(1)}\right\rangle=-\sum_{\eta'\neq\eta}\left|k\eta'\right\rangle\frac{\left\langle\eta'\right|H_B\left|\eta\right\rangle}{\frac{k}{2}\left[\left(1+x_{\eta'}\right)^{1/2}-\left(1+x_\eta\right)^{1/2}\right]} \tag{9.3.23}$$

However this correction does not contribute to the definition of the reduced density matrix, eq. (8.4.3), because

$$\left\langle s\eta\middle|n\right\rangle=\left\langle s\eta\middle|k\eta\right\rangle-\sum_{\eta'\neq\eta}\left\langle s\eta\middle|k\eta'\right\rangle..... \tag{9.3.24}$$

but $\left\langle s\eta\middle|k\eta'\right\rangle=0$ due to the orthogonality of the basis vector. We thus obtain for the mean value of the subsystem population and its variance the following equations

$$\overline{\mu_{\beta\beta}}=\sum_\eta^n\left\{\left(c_\beta^+\right)^2P_{k^+\eta}+\left(c_\beta^-\right)^2P_{k^-\eta}\right\} \tag{9.3.25}$$

$$\sigma^2\left(\mu_{\beta\beta}\right)=2\sum_\eta^n\left\{\left(c_\beta^+\right)^2\left(c_\beta^-\right)^2P_{k^-\eta}P_{k^+\eta}\right\} \tag{9.3.26}$$

Equation (9.3.26) is represented by the black continuous line in Figure 9-1. It is the same for all the realization of the Hamiltonian; indeed it does not depend on the specific Hamiltonian of the environment.

Notice the following asymptotic limits of the square of the overlap integral $\left|\left\langle k^-\eta\middle|\beta\eta\right\rangle\right|^2=\left(c_\beta^-\right)^2$

$$\begin{aligned} x_\eta &\to 0 & \left(c_\beta^-\right)^2 &\to 1 \\ x_\eta &\to \infty & \left(c_\beta^-\right)^2 &\to 1/2 \end{aligned} \qquad (9.3.27)$$

Thus, by not considering the Hamiltonian environment at all, the eigenstates of the system smoothly change from the S_Z eigenbasis to the S_X eigenbasis due to the influence of the interaction term. This is related to the change of the pointer basis dynamically selected from the environment, see [Cucchietti, (2005), Paz (1999)]. Indeed, the self Hamiltonian of the system competes with the interaction for establishing the direction in which the decoherence process is effective, that is, the basis in which the reduced density matrix of the system is approximately diagonal. This change in the direction of the pointer states also affects the fluctuation amplitude of the Reduced Density Matrix written in the S_Z eigenbasis representation.

The asymptotic value of the variance of the reduced population can be calculated for the limit $x_\eta \to \infty$ and reads

$$\sigma^2_{x_\eta \to \infty}\left(\rho_{\beta\beta}\right) = \frac{1}{2}\sum_\eta P_{k^-\eta} P_{k^+\eta} \qquad (9.3.28)$$

This limiting value is represented in figure 9-1 as the horizontal black line which matches the common asymptotic limit of the population variance. Such a value is mostly controlled in this model by the dimension of the active environment subspace.

9.4 APPROACHING THE EQUILIBRIUM: SIMULATION OF THE FREE INDUCTION DECAY EXPERIMENT

In the previous section we have characterized statistically the equilibrium distribution of the reduced population of the spin. We shall now consider the route toward the equilibrium from a non equilibrium initial state. The first problem to face is: what is a "non equilibrium" initial state? We have established that, by considering a generic random pure state which belongs to the RPSE, the *equilibrium average* of the reduced population of a subsystem is very likely represented by a canonical distribution at a given temperature. Thus, we have to look for an initial state for which the reduced populations are "far" from this value. This can be done with the aid of an external field.

The basic idea which has motivated the experiment described in this Section is the following: the equilibrium state of a subsystem, which is part of an isolated quantum system which evolves in time according to its Hamiltonian, is characterized by dynamical fluctuations of the subsystem properties around the corresponding equilibrium average value. The average amplitude, i.e. the square root of the variance, of such fluctuations scales with the dimension of the whole system thus, even if we look at the properties of one small subsystem, the probability of observing a fluctuation of large amplitude, as compared to the average amplitude, is very low. However if one acts with an external perturbation on the system and then follows the time evolution, one expects to see it to relax toward its equilibrium state. This intuition suggests that the non equilibrium initial state induced by an external field can be interpreted as a state corresponding to a very improbable equilibrium fluctuation, and thus it evolves as a fluctuation would relax. In the following we will investigate the foundation of this conjecture through a numerical experiment.

The set up of the experiment is the following:

First we choose a wavefunction from the RPSE. We recall here that the equilibrium average of the RDM has a typical value in the ensemble. Since the Ensemble Distribution is Gaussian, the typical value can be identified with the value obtained from the average global populations. For this reason we choose an initial wavefunction $\psi\left(t_0^-\right)$ defined by the set of average populations $P=1/N_\varepsilon$ and a set of phases each drawn from a uniform distribution between $\left(0,2\pi\right]$. We emphasize that the wavefunction is defined for the whole system, no factorization is assumed. Indeed the subsystem results highly entangled with its surrounding from the beginning, because this is the typical condition for a subsystem of a random quantum state. The total density matrix at the time t_0^- is thus defined as $\rho\left(t_0^-\right)=\left|\psi\left(t_0^-\right)\right\rangle\left\langle\psi\left(t_0^-\right)\right|$

At the instant $t = t_0$ we simulate the application of a magnetic pulse acting on the spin. The effect of a magnetic pulse of frequency ω_1 which acts on the spin system for a time t, can be described by means of a rotation operator

$$R = \begin{bmatrix} \cos\frac{\omega_1 t}{2} & i\sin\frac{\omega_1 t}{2} \\ i\sin\frac{\omega_1 t}{2} & \cos\frac{\omega_1 t}{2} \end{bmatrix} \otimes \mathbf{1}_n \tag{9.4.1}$$

The total density matrix right after the application of the magnetic pulse is given by

$$\rho\left(t_0^+\right) = R^\dagger \rho\left(t_0^-\right) R \tag{9.4.2}$$

and we shall analyze the effect of a $\pi/2$ pulse.

After the pulse the time evolution is governed according to the model Hamiltonian, eq. (9.2.7). We shell follow the time evolution of the x and z component of the spin polarization vector

$$\begin{aligned} p_x(t) &= \mathrm{Tr}\left(\mu(t) S_X\right) = 2\,\mathrm{Re}\,\mu_{\alpha\beta}(t) \\ p_z(t) &= \mathrm{Tr}\left(\mu(t) S_Z\right) = \mu_{\alpha\alpha}(t) - \mu_{\beta\beta}(t) \end{aligned} \tag{9.4.3}$$

The usual picture of a magnetic resonance experiment of this kind is the following: the magnetization is initially aligned along the static field which defines the Z axis, then the $\pi/2$ pulse brings the magnetization in the X-Y plane where it starts its precession motion around the Z axis which induces the Free Induction Decay (FID) signal.

This simple experiment numerically performed on a single spin which interacts with the random matrix environment shows a variety of interesting aspects whose theoretical interpretations are not obvious. Here, we shall illustrate some results.

We use the Hamiltonian H_2 with $\lambda = 1$ which is in the regime where the fluctuation amplitude does not depend on the details of the bath (see Figure 9-1). The exact time evolution of the two observables, eqs. (9.4.3), depends from the details of the initial state. In Figure 9-4 the time evolution of the polarization $p_z(t)$ is represented. The blue and the red dotted lines represent the time evolution obtained for two different initial states, characterized by different sets of phases before the pulse. As already mentioned the populations are chosen as the average population of the RPSE at a certain temperature, and thus they are fixed. Figure 9-4 refers to a system for which the number of populated state is $N_\varepsilon = 85$, which correspond to a spin inverse temperature of about $\beta \approx 0.3$ before the pulse is applied, while in Figure 9-5 the same Hamiltonian is assumed but the number of populated states is $N_\varepsilon = 50$, which correspond to a lower temperature for the subsystem. We can now think to treat the initial time of the experiment $t = t_0$ as a uniformly distributed random variable and average the response with respect to it. This corresponds to average the density matrix just before the pulse application with respect to the corresponding Pure State Distribution. The time evolution of the PSD average density matrix is represented in the Figures by the bold black line, and of course this does not depend any more on the particular phases of the initial state. An important question arises about the equilibrium average, i.e. the asymptotic time average, of the single realizations after the application of the pulse:

is the equilibrium average independent on the initial state right after the pulse? If the answer is yes, does it coincide with the equilibrium average of the trajectory of the PSD average density matrix?

The numerical evidence shows that for the considered value of the interaction strength $\lambda = 1$ the answer is *approximately yes*, however larger deviations appear for smaller values of the interaction strength. To have an insight into the nature of this problem, one has to consider in detail what happens to the total density matrix during the experiment: before the application of the pulse our system is described, according to eq. (2.3.18), by

$$\rho\left(t_0^-\right) = \left|\psi\left(t_0^-\right)\right\rangle\left\langle\psi\left(t_0^-\right)\right| = \sum_{n,m} \sqrt{P_n P_m}\, \exp[-i\alpha_{n,m}(t_0^-)]\left|n\right\rangle\left\langle m\right| \tag{9.4.4}$$

where $\alpha_{n,m}(t_0^-) := \alpha_n - \alpha_m - \omega_{n,m} t_0^-$. After the application of the pulse each elements of the total density matrix is a linear combination of the elements of the density matrix before the pulse

$$\left[\rho\left(t_0^+\right)\right]_{ij} = \sum_{n,m} \left(R^\dagger\right)_{in} \rho_{n,m}\left(t_0^-\right) R_{mj} \tag{9.4.5}$$

where R_{kj} are the elements of the rotation operator, eq. (9.4.1), represented in the total eigenenergy basis. After the pulse the new initial density matrix, (9.4.5), evolves in time according to the Liouville Von-Neumann equation. Its asymptotic time average determines the equilibrium average of the subsystem, indeed $\overline{\mu} = \mathrm{Tr}_B\left\{\overline{\rho}\right\}$. As usual the asymptotic time average procedure washes out the oscillating off-diagonal elements of the total density matrix in the energy representation. As a consequence we can identify a new set of population $\tilde{P}$, i.e. the diagonal elements of $\rho\left(t_0^+\right)$, which will determine the equilibrium average of the subsystem observable for each particular trajectory, that is

$$\tilde{P}_k = \sum_{n,m} \left(R^\dagger\right)_{kn} \rho_{nm}\left(t_0^-\right) R_{mk} \tag{9.4.6}$$

$$\overline{\mu_{ss'}} = \sum_b \sum_k \langle sb|k\rangle\langle k|s'b\rangle \tilde{P}_k \tag{9.4.7}$$

Notice that the equilibrium average at which the subsystem state has to tend after the pulse, eq. (9.4.7), depends in general on the time t_0 at which the pulse is applied since the new population (9.4.6) are determined as combination from all the elements of the density matrix at $t = t_0^-$, eq. (9.4.4).

Let us now consider the asymptotic time average corresponding to the PSD average initial state. In this case the elements of the density matrix right after the pulse are combination only of the diagonal elements of the density matrix at t_0^-:

$$\left[\left\langle \rho\left(t_0^+\right)\right\rangle_{PSD}\right]_{ij} = \sum_{n,m} \left(R^\dagger\right)_{in} \left\langle \rho_{n,m}\left(t_0^-\right)\right\rangle_{PSD} R_{mj} = \sum_n \left(R^\dagger\right)_{in} P_n R_{nj} \tag{9.4.8}$$

Thus, in this case, the new populations which determines the equilibrium average are given as

$$\left\langle \tilde{P}_k \right\rangle_{PSD} = \sum_n \left(R^\dagger\right)_{kn} P_n R_{nk} \tag{9.4.9}$$

At this point we can ask: under which condition the equilibrium average state of each trajectory is likely to be close to that which characterizes the equilibrium of the density matrix averaged over the initial condition? Stated differently: when the equilibrium state does not depend on the initial state?

From eqs. (9.4.6) and (9.4.9) one has that

$$\tilde{P}_k = \left\langle \tilde{P}_k \right\rangle_{PSD} + \sum_n \sum_{m\neq n} R_{kn} \rho_{nm}\left(t_0^-\right) R_{mk} \tag{9.4.10}$$

thus, by using (9.4.7) and (9.4.4), one obtains

$$\overline{\mu_{ss'}} = \left\langle \overline{\mu_{ss'}} \right\rangle_{PSD} + \sum_{b} \sum_{k} \sum_{n} \sum_{m \neq n} \left\langle sb \middle| k \right\rangle \left\langle k \middle| s'b \right\rangle R_{kn} R_{mk} \sqrt{P_n P_m} \exp[-i\alpha_{n,m}(t_0^-)] \tag{9.4.11}$$

If the second term of the right hand side is exactly zero then all the possible initial states relax in the same manner and toward the same equilibrium value. The actual magnitude of the deviations depends from the interaction trough the overlap between the perturbed and the unperturbed eigenstate. However, since the angle variables in (9.4.11) are uniformly distributed, one should expect that, for large enough number of populated state, the relaxation does not depend on the initial phases. Moreover we have also seen in the first part of this thesis that the subsystem equilibrium average state tends to assume a typical value also in ensembles of pure states and thus for different set of the populations. In this case one should expect that also the global populations just after the pulse, eq. (9.4.9), assume a typical value in the RPSE, being a sum of the original populations which are exponentially distributed random variables in the ensemble. In other words, when large systems are considered, the great majority of the possible pure states not only gives the same canonical average RDM for the subsystem, but also relaxes with the same dynamics when perturbed from an external field.

Another interesting aspect arises from the comparison between the relaxation dynamics of the PSD average initial state and the time correlation function of the equilibrium fluctuations of the same operator in a single trajectory, which are shown in the right panels of Figure 9-4 and 9-5. The evidence that the correlation functions decay with about the same characteristic time of the relaxation, supports the idea that a non equilibrium initial state produced by an external force will dissipate in the same way as a random fluctuations. However this point requires further future investigation, for example in relation to the correlation function which appears in the linear response theory developed by Kubo, [Kubo, (1957)].

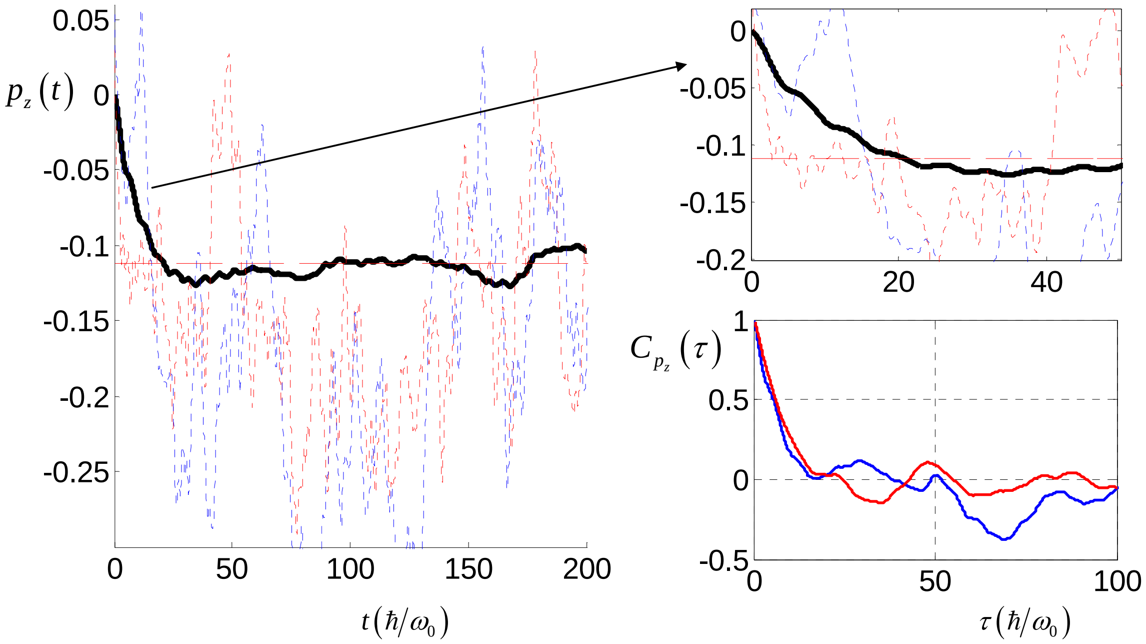


Figure 9- 4: Time evolution of the z component of the spin polarization vector, $p_z(t)$, after the application of the magnetic pulse. On the left panel the blue and red dotted lines refers to the evolution of two different initial states while the black line refers to the evolution of the PSD average initial density matrix. In the right upper panel a magnification of the initial relaxation is reported. The right lower panel shows the time correlation function of the equilibrium fluctuations of $p_z(t)$ calculated from the time evolution of the two different initial states.

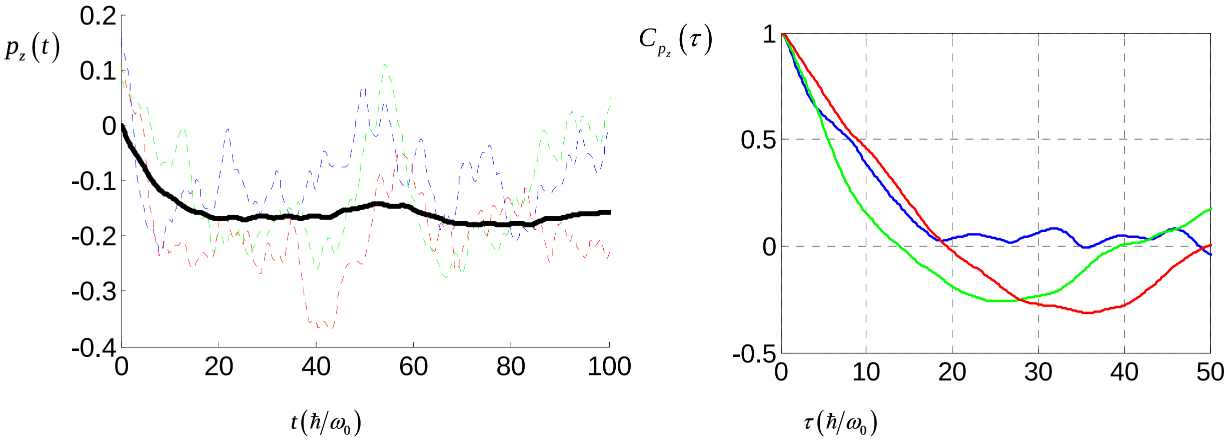


Figure 9- 5: As in Figure 9-5 but with different initial populations which correspond to a different temperature for the subsystem.

Figures 9-6 and 9-7 report the time evolution of the x component of the spin polarization vector for the system in the same conditions as before. The signal corresponding to the evolution of the density matrix averaged over the initial time (black line) resembles a real FID signal measured in a macroscopic sample. Again, the correlation functions of the p_x equilibrium fluctuations calculated from the single realizations show the same time dependence of the relaxation dynamic.

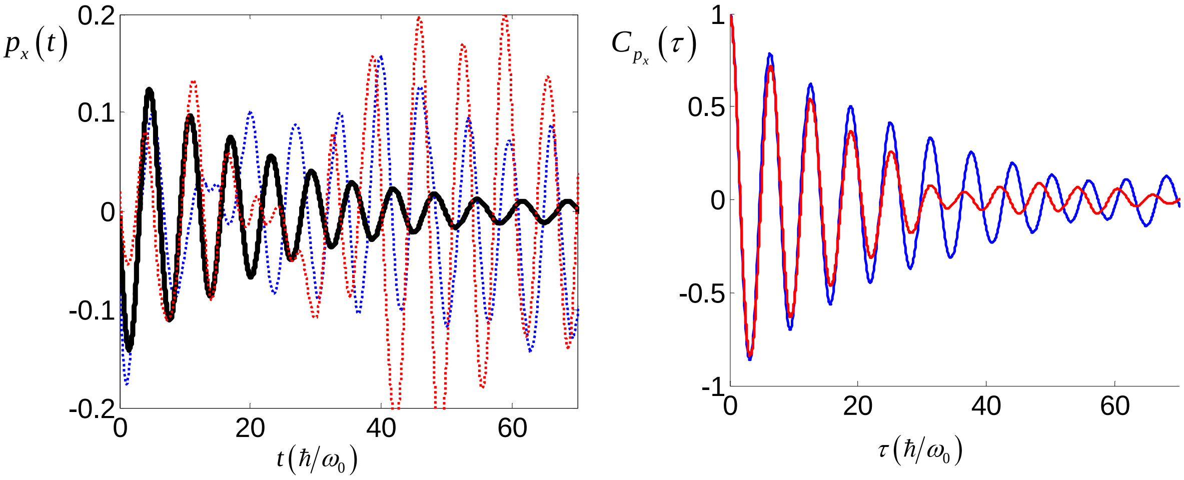


Figure 9- 6: Time evolution of the x component of the spin polarization vector, $p_x(t)$, after the application of the magnetic pulse. On the left panel the blue and red dotted lines refers to the evolution of two different initial states while the black line refers to the evolution of the PSD average initial density matrix. In the right panel we show the time correlation function of $p_x(t)$ calculated from the time evolution of the two different initial states.

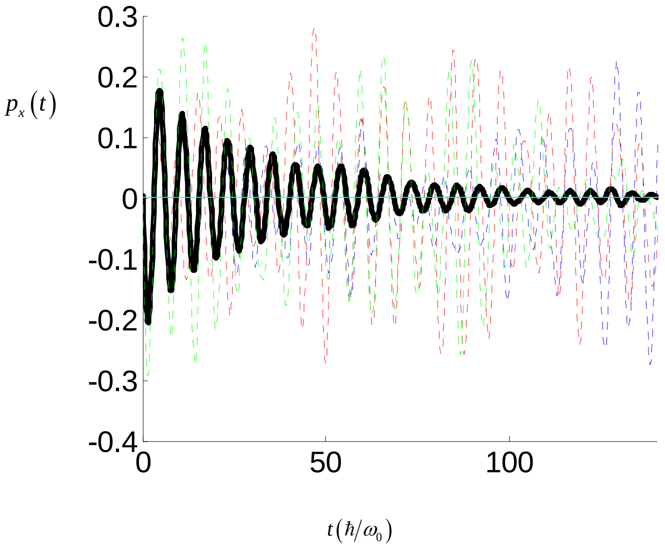


Figure 9- 7: As in Figure 9-6 but with different initial populations which correspond to a different temperature for the subsystem.

We emphasis that in this experiment, differently from the case presented in Figure 8-8, we are not observing a true decoherence dynamics of the spin. Indeed we have never assumed that the observed spin is described by an autonomous wavefunction. This can be understood by looking at the time evolution of the purity of the subsystem, shown in Figure 9-8 for three different realizations of the experiment. As it is evident no decay of the purity occurs, this is because the system is highly entangled with its surrounding from the beginning of the experiment. Thus, while we see the average polarization to relax toward its equilibrium value, the purity just fluctuates around its average value due to the continuous interactions with the environment.

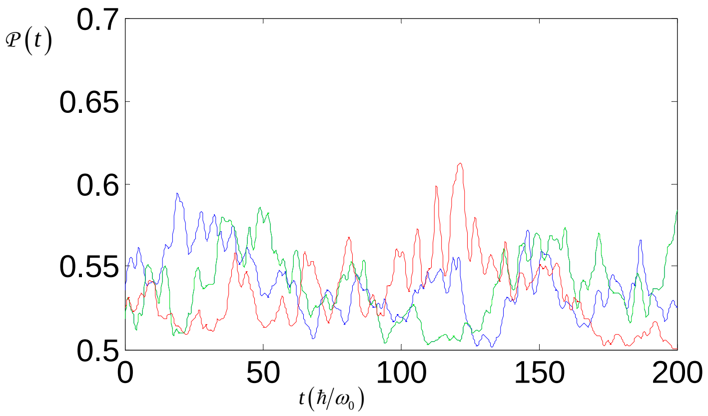


Figure 9- 8: Time evolution of the purity of the subsystem during three realizations of the FID experiment.

APPENDIX 9.1 : SOME PROPERTIES OF RANDOM MATRICES

There are three generic ensembles of random matrices, defined in terms of the symmetry properties of the Hamiltonian. For time-reversal invariant systems with rotational symmetry the Hamiltonian matrix can be chosen to be proportional to a real and symmetric random matrix

$$W_{ij} = W_{ji} = W_{ij}^{*} \tag{A9.1.12}$$

The requirement of invariance under orthogonal transformations and the assumption of statistical independence for the various elements $W_{ij,}\ i \leq j$, fix the functional form of the probability density which describes the Gaussian Orthogonal Ensemble (GOE):

$$P_n\left(W\right) = C\exp\left(-\frac{1}{2\sigma_W^2} Tr\left\{W^2\right\}\right) \tag{A9.1.13}$$

The probability of finding a particular matrix is thus given by the weight function $P_n\left(W\right)$ times the product of the differentials of all independent matrix elements. The ensemble is fully characterized by the parameters n and σ_W. The last one sets the scale of the eigenvalues and plays no role in the statistics of the energy spacing: a change in σ_W amounts to a multiplication of the matrix by a constant factor, which does not affect the eigenvectors.

The $\frac{n\left(n+1\right)}{2}$ independent elements are Gaussian random numbers with the following statistical properties

$$\left\langle W_{ij}\right\rangle_{GOE} = 0 \qquad \left\langle W_{ij}^2\right\rangle_{GOE} = \frac{\sigma_W^2}{2}\left(1+\delta_{ij}\right) \tag{A9.1.14}$$

where the average is respect to the distribution (A9.1.13). The averaged density of states in the limit of very large matrix dimension $n \to \infty$ obeys the Wigner semicircular law, (Figure 9-9), that in our notation is

$$\left\langle d(E)\right\rangle = \begin{cases} \frac{1}{\sigma_W^2 \pi}\sqrt{2\sigma_W^2 n - E^2} & if \;\; \left|E\right| < \sigma_W\sqrt{2n} \\ 0 & if \;\; \left|E\right| \geq \sigma_W\sqrt{2n} \end{cases} \tag{A9.1.15}$$

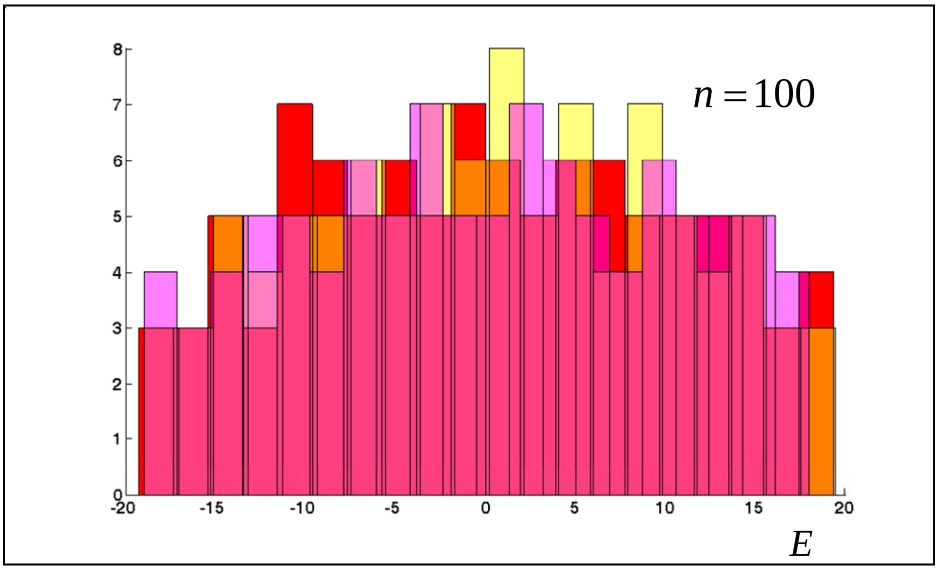


Figure 9- 9: Histograms of the spectrum of three different realizations of the Gaussian Orthogonal Ensemble.

If we assume the value of the total variance σ_W^2 to be independent on n then the width of the spectrum is $\Delta w = \sqrt{8n\sigma_W^2}$. We set $\sigma_W^2 = 2$ which implies that the range of energy where the eigenvalues are distributed scales with the matrix size as

$$\Delta w = 4\sqrt{n} \tag{A9.1.16}$$

An important feature of this family of matrices is the statistic of the eigenvalues level spacing s, which is characterized by a Wignerian distribution

$$P^W(s) = \frac{\pi}{2} s e^{-(\pi/4)s^2} \tag{A9.1.17}$$

This kind of distribution is typical for quantum systems that in the classical limit shows chaotic dynamic [Bohigas, (1984)]. On the other hand, the systems whose classical dynamics is completely integrable, are expected to be characterized by a Poisson-like level spacing distribution (Figure 9-10).

$$P^P(s) = e^{-s} \tag{A9.1.18}$$

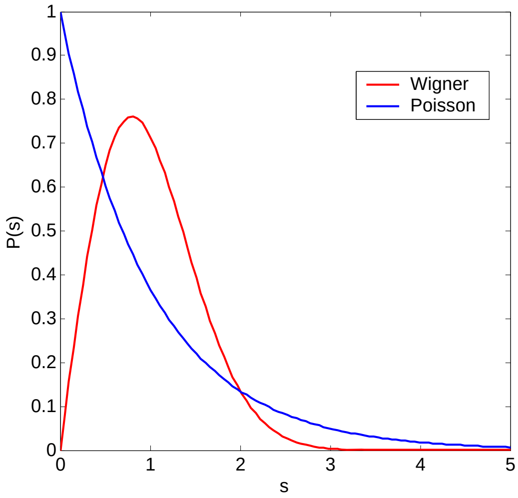


Figure 9- 10: Wigner and Poisson distributions.

With reference to the spectrum of a GORM (Gaussian Orthogonal Random Matrix), Figure 9-11, it is interesting to note that at least some properties as the density of states $d\left(E\right)$ or the nearest neighbors spacing s have the same distribution when taken *along an individual spectrum* a million levels above the ground state as when taken *across an ensemble* at the ground state itself. In other words in the limit of infinite size $n \to \infty$, the average over the spectrum of a GORM $\left(\langle \ldots \rangle_n\right)$ coincides with the average over the ensemble $\left(\langle \ldots \rangle_{GOE}\right)$.

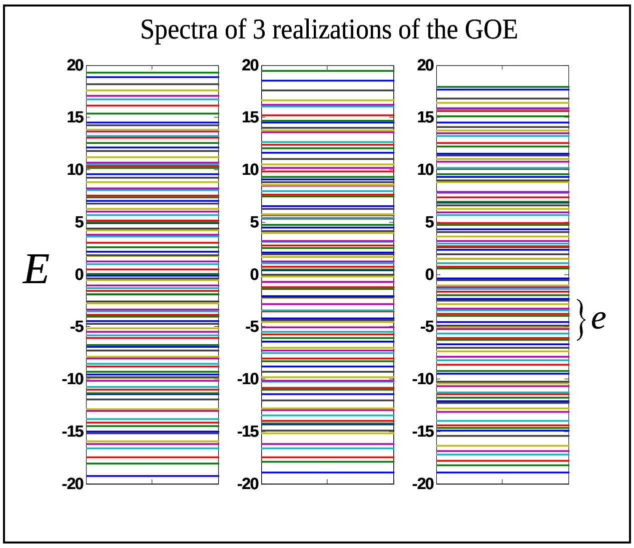


Figure 9- 11: Spectra of three different realizations of the Gaussian Orthogonal Ensemble.

CONCLUSION

Fundamental problems in quantum statistical mechanics are as intriguing as they are elusive. On the one hand standard statistical mechanics is very effective in accounting for many phenomena and experimental evidences, on the other hand when one try to re-conduce it to the underlying mechanical description one encounters all the interpretational and conceptual difficulties which characterized quantum theory. With this work we give our small contribution to this field: the intent has been that to develop a theoretical framework for the statistical description of quantum system which is coherent but at the same time as simple as possible. In this spirit we have often taken classical statistical mechanics as a conceptual benchmark.

One of the key ingredients of the developed framework is the separation between the Pure State Distribution, which is derived from the analysis of the time evolution of the quantum state, and the Ensemble Distributions which have instead a “geometrical” origin. The theoretical tools developed for the characterization of these distributions are very convenient in order to study the role and the importance of the typicality of the properties which characterized a given quantum system. The study conducted for the ensembles of spins, for example, shows how thermodynamic properties can emerge from the description of the whole system in term of a pure state.

Still, we think that the characterization of the quantum equilibrium state as a dynamical equilibrium, in which fluctuations play their role, is promising to give interesting insights into quantum dynamics.

REFERENCIES

Aharonov Y., J. Anandan, Meaning of the Density Matrix, Foundation of Physics Letters, 12, 571, (1999)

Alicki R., K. Lendi, Quantum Dynamical Semigroups and Applications, Springer, Berlin, (1987)

Anandan J., Reality and Geometry of States and Observables in Quantum Theory, Proceedings of the International Conference on Non Accelerator Particle, Physics, Jan. 2-9, 1994, R. Cowsik, World Scientific, (1995)

Anderson P. W., A Mathematical Model for the Narrowing of Spectral Lines by Exchange or Motion, J. Phys. Soc. Jpn. 9 , 316, (1954)

Bender C. M., D. C. Brody, D. W. Hook, Solvable Model of Quantum Microcanonical States, J. Phys. A: Math. Gen., 38, L607, (2005)

Berezovsky J., M. H. Mikkelsen, N. G. Stoltz, L. A. Coldren, D. D. Awschalom, Picosecond Coherent Optical Manipulation of a Single Electron Spin in a Quantum Dot, Science, 320, 349-352,(2008)

Bocchieri P., A. Loinger, Ergodic Theorem in Quantum Mechanics, Phys. Rev., 111, 668, (1958)

Bocchieri P., A. Loinger, Ergodic Foundation of Quantum Statistical Mechanics, Phys. Rev., 114, 948, (1959)

Bohigas O., M. J. Giannoni, C. Schmit, Characterization of Chaotic Quantum Spectra and Universality of Level Fluctuation Laws, Phys. Rev. Lett. 52, 1, (1984)

Borowski P., Gemmer J., G. Mahler, Relaxation into Equilibrium under Pure Schrödinger Dynamics, The European physical journal B, 35, 255, (2003)

Breuer H. P., F. Petruccione, The Theory of Open Quantum Systems, Oxford University Press, Oxford, (2002) Brody D. C., D. W. Hook , L. P. Hughston, Unitarity, Ergodicity and Quantum Thermodynamics, J. Phys. A: Math. Theor., 40, F503, (2007)

Brody D. C., D. W. Hook, L. P. Hughston, Microcanonical Distribution for Quantum System, Preprint quant-ph/05061632005, (2005)

Brody D. C., D. W. Hook, L. P. Hughston, Quantum Phase Transitions without Thermodynamic Limits, Proc. R. Soc. Lond. A, 463, 2021, (2007)

Brody D. C., L. P. Hughston, Geometric Quantum Mechanics, J.Geom.Phys., 38, 19, (2001)

Brukner C., V. Vedral, A. Zeilinger, Crucial Role of Quantum Entanglement in Bulk Properties of Solids, Phys. Rev. A, 73, 012110, (2006)

Casati, G., B.V. Chirikov, I. Guarneri, F.M. Izrailev, Quantum Ergodicity and Localization in Conservative System: the Wigner Band Random Matrix Model, Phys. Lett. A, 223, 430, (1996)

Casati, G. On the Foundation of Equilibrium Quantum-Statistical Mechanics, Il Nuovo Cimento B, 114, 11, (1999)

Chib S., E. Greenberg, Understanding the Metropolis - Hastings Algorithm, American Statistician, 49, 327, (1995)

Chruscinski D., Geometric Aspects of Quantum Mechanics and Quantum Entanglement, J. Phys.: Conf. Ser. 30, 9, (2006)

Cormick C., J. P. Paz, Decoherence Induced by a Dynamic Spin Environment: The Universal Regime, Phys. Rev. A, 77, 022317, (2008)

Cucchietti F. M., J. P. Paz, W. H. Zurek, Decoherence from Spin Environments, Phys. Rev. A, 72, 052113, (2005)

Davies E. B., Quantum Theory of Open Systems, Academic Press, London, (1976)

Dawson C. M., A. P. Hines, R. H. McKenzie, G. J. Milburn, Entanglement Sharing and Decoherence in the Spin-Bath, Phys. Rev. A, 71, 052321, (2005)

D'Espagnat B., Reply to Aharonov and Anandan's "Meaning of the Density Matrix", eprint arXiv:quant-ph/9804063, (1998)

D'Espagnat B., Towards a Separable “Empirical Reality”?, Found. Phys., 20, 1147, (1990) Deutsch J. M., Quantum Statistical Mechanics in a Closed System, Phys. Rev. A, 43, 2046, (1991)

Dieter Suter, T. S. Mahesh, Spins as Qubits: Quantum Information Processing by Nuclear Magnetic Resonance, J. Chem. Phys., 128, 052206, (2008)

Dubrovin B. A., A. T. Fomenko, S. P. Novikov, Modern Geometry - Methods and Applications, Part I, Berlin, Springer-Verlag, (1985)

Dwight H. B., Tables of Integrals and Other Mathematical Data, Macmillan Publishing Co., New York, (1961).

Esposito M., P. Gaspard, Spin Relaxation in a Complex Environment, Physical Review E, 68, 066113, (2003)

Facchi P., G. Florio, G. Parisi, S. Pascazio, Maximally Multipartite Entangled States, Phys. Rev. A, 77, 060304, (2008)

Facchi P., G. Florio, S. Pascazio, Probability-Density-Function Characterization of Multipartite Entanglement, Phys. Rev. A, 74, 042331, (2006)

Facchi P., G. Florio, U. Marzolino, G. Parisi, S. Pascazio, Statistical Mechanics of Multipartite Entanglement, arXiv:0803.4498 (2008)

Faid K., R. F. Fox , Stochastic Theory of Line Shape and Relaxation, 34, 4289, (1986)

Fano U., Description of States in Quantum Mechanics by Density Matrix and Operator Techniques, Rev. Mod. Phys., 29, 74, (1957)

Farquhar I. E., P. T. Landsberg, On the Quantum-Statistical Ergodic and H-Theorems, Proc. R. Soc. London, Ser. A, 239, 134, (1957)

Feingold M., A. Peres, Distribution of Matrix Elements of Chaotic Systems, Phys. Rev. A, 34, 591, (1986)

Gallavotti G., Fluctuation Theorem and Chaos, Europ. Phys. J. B., 64, 315, (2008)

Gardiner C. W., Quantum Noise and Quantum Langevin Equations, IBM J. Res. Develop., 32, 1, (1988)

Gemmer J., A. Otte, G. Mahler, Quantum Approach to a Derivation of the Second Law of Thermodynamics, Physical Review Letters, 86, 1927, (2001) Gemmer J., G. Mahler, Entanglement and the Factorization-Approximation, Eur. Phys. J. D, 17, 385, (2001)

Gemmer J., G. Mahler, Limits of Effective Potential Approach: Nucleus-Electron Entanglement in a Model of the -Ion, Europhys. Lett., 59, 159, (2002)

Gemmer J., M. Michel, G. Mahler, Typical Spectra of Large Systems, in Quantum Thermodynamics: Emergence of Thermodynamic Behavior Within Composite Quantum Systems, Edited by J. Gemmer, M. Michel, G. Mahler, Lecture Notes in Physics, Berlin Springer, 657, (2004)

Giraud O., Distribution of Bipartite Entanglement for Random Pure States, J. Phys. A, 40, 2793, (2007)

Goldstein S., J. L. Lebowitz, R. Tumulka, N. Zanghì, Canonical Typicality, Phys. Rev. Lett. 96, 050403, (2006)

Gorini V., A. Kossakowski, E. C. G. Sudarshan, Completely Positive Dynamical Semigroups of N-Level Systems, J. Math. Phys., 17, 821, (1976)

Guhr T., A. Muller–Groeling, H. A. Weidenmuller, Random Matrix Theories in Quantum Physics: Common Concepts, Phys. Rep., 299, 189, (1998)

Haar Ter D., Foundations of Statistical Mechanics, Rev. Mod. Phys, 27, 289, (1955)

Haario H., E. Saksman, J. Tamminen, Adaptive Proposal Distribution for Random Walk Metropolis Algorithm., Comput. Statist., 14, 375, (1999)

Hanson R., V. V. Dobrovitski, A. E. Feiguin, O. Gywat, D. D. Awschalom, Coherent Dynamics of a Single Spin Interacting with an Adjustable Spin Bath, Science, 320, 352, (2008)

Harville D. A., Matrix Algebra From a Statistician's Perspective, Springer-Verlag, (1997)

Hassani S., Mathematical Physics: A Modern Introduction to its Foundations, Springer-Verlag, New York, (1999)

Hastings W. K., Monte Carlo Sampling Methods Using Markov Chains and their Applications, Biometrika, 57, 97, (1970)

Hayden P., D. W. Leung, A. Winter, Aspects of Generic Entanglement, Commun. Math. Phys., 265, 95, (2006) Jaynes E. T., Information Theory and Statistical Mechanics, Phys. Rev., 106, 620, (1957)

Jensen R.V., R. Shankar, Statistical Behavior in Deterministic Quantum Systems with Few Degrees of Freedom, Phys. Rev. Lett., 54, 1879, (1985)

Kerson H., Statistical Mechanics, Wiley, 2nd edition, (1987)

Khinchin A. Y., Mathematical Foundations of Statistical Mechanics, New York, Ed. Dover, (1949)

Klein M. J., The Ergodic Theorem in Quantum Statistical Mechanics, Phys. Rev., 87, 111, (1952)

Kohen C., C. Marston, D. J. Tannor, Phase Space Approach to Theories of Quantum Dissipation, J. Chem. Phys. 107, 5236, (1997)

Kolovsky A. R., Number of Degree of Freedom for a Thermostat, Phys. Rev E, 50, 3569, (1994)

Kubo R., Note on the Stochastic Theory of Resonance Absorption, J. Phys. Soc. Jpn. 9, 935, (1954)

Kubo R., Stochastic Liouville Equations, J. Math. Phys., 4, 174, (1963)

Kubo R., Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems, J. Phys. Soc. Jpn. 12, 570, (1957)

Lahiri A., S. Nag, Dynamical Manifestation of Quantum Chaos: Density Matrix Fluctuations in Subsystems, Physics Letters A, 318, 6, (2003)

Lebowitz J. L., L. Pastur, A random matrix model of Relaxation, J. Phys. A: Math. Gen., 37, 1517, (2004)

Leggett A., S. Chakravarty, A. Dorsey, M. Fisher, A. Garg, W. Zwerger, Dynamics of the Dissipative Two-State System, Rev. Mod. Phys., 59, 1, (1987)

Lindblad G., On the Generators of Quantum Dynamical Semigroups, Commun. Math. Phys., 48, 119, (1976)

Long G., Zhou Yi-Fan, Jin Jia-Qi, Sun Yang, Lee Hai-Woong, Density Matrix in Quantum Mechanics and Distinctness of Ensembles Having the Same Compressed Density Matrix, Foundations of Physics, 36, 8, 1217, (2006) Lubkin E., Entropy of an N-System from its Correlation with a K-Reservoir, J. Math. Phys. 19, 1028, (1978)

Mahler G., Gemmer J., M. Michel, Emergence of Thermodynamic Behavior within Composite Quantum Systems, Physica E, 29, 53, (2005)

Mehta M. L., Random Matrices, 2nd edition, Academic Press, (1991)

Metropolis N., Rosenbluth A. W., Rosenbluth M. N., Teller A. H., Teller E., Equation of State Calculations by Fast Computing Machines, J. Chem. Phys., 21, 1087, (1953)

Miller Paul A., S. Sarkar, Signatures of Chaos in the Entanglement of Two Coupled Quantum Kicked Tops, Phys. Rev. E, 60, 1542, (1999)

Nag S., G. Ghosh, A. Lahiri, Quantum Chaos: Reduced Density Matrix Fluctuations in Coupled Systems, Physica D, 204, 110, (2005)

Naudts J., E. Van der Straeten, A Generalized Quantum Microcanonical Ensemble, J. Stat. Mech., P06015, (2006)

Neumann P., N. Mizuochi, F. Rempp, P. Hemmer, H. Watanabe, S. Yamasaki, V. Jacques, T. Gaebel, F. Jelezko, J. Wrachtrup, Multipartite Entanglement Among Single Spins in Diamond, Science, 320, 1326, (2008)

Nielsen M. A., I. L. Chuang, Quantum Computation and Quantum Information, Cambridge University, (2000)

Page Don N., Average Entropy of a Subsystem, Phys.Rev.Lett., 71, 1291, (1993)

Paz J. P., W. H. Zurek, Quantum Limit of Decoherence: Environment Induced Superselection of Energy Eigenstates, Phys. Rev. Lett., 82, 5181, (1999)

Pechukas P., Remarks on "Quantum Chaos", J. Phys. Chem., 88, 4823, (1984)

Percival I. C., Almost Periodicity and the Quantal H Theorem, J. Math. Phys., 2, 235, (1961)

Peres A., Ergodicity and Mixing in Quantum Theory, Phys. Rev. A, 30, 504, (1984)

Peres A., Recurrence Phenomena in Quantum Dynamics, Phys. Rev. Lett., 49, 1118, (1982)

Pereyra P., P. A. Mello, Marginal Distribution of the S-Matrix Elements for Dyson's Measure and some Applications, J. Phys. A: Math. Gen., 16, 237, (1983) Popescu S., A. J. Short, A. Winter, Entanglement and the foundations of Statistical Mechanics: Individual States vs Averages, Preprint at <http://arxiv.org/abs/quant-ph/0511225>, (2005)

Popescu S., A. J. Short, A.Winter, Entanglement and the Foundations of Statistical Mechanics, Nature, 2, 754, (2006)

Popescu S., D. Rohrlich, Thermodynamics and the Measure of Entanglement, Physical Review A, 56, R3319, (1997)

Reimann P., Typicality for Generalized Microcanonical Ensemble, Phys. Rev. Lett., 99, 160404, (2007)

Reimann P., Foundation of Statistical Mechanics under Experimentally Realistic Conditions, Physical Review Letters, 101, 190403, (2008)

Rigol M., V. Dunjko, M. Olshanii, Thermalization and its Mechanism for Generic Isolated Quantum Systems, Nature, 452, 854-858, (2008)

Rossini D., T. Calarco, V. Giovannetti, S. Montangero, R. Fazio, Decoherence Induced by Interacting Quantum Spin Baths, Phys. Rev. A, 75, 032333, (2007)

Schlosshauer M., Decoherence, the Measurement Problem, and Interpretations of Quantum Mechanics, Rev. Mod. Phys., 76, 1267, (2004)

Schrödinger E., An Undulatory Theory of the Mechanics of Atoms and Molecules, The Physical Review, 28, 1049, (1926)

Schrödinger E., Statistical Thermodynamics, Cambridge University Press, Cambridge, England, (1952)

Scott A. J., C. M. Caves, Entangling Power of the Quantum Baker's Map, J. Phys. A 36, 9553, (2003)

Shengjun Y., M. I. Katsnelson, H. De Raedt, Decoherence by a Spin Thermal Bath: Role of Spin-Spin Interactions and Initial State of the Bath, Phys. Rev. B, 77, 184301, (2008)

Srednicki M., Chaos and Quantum Thermalization, Phys. Rev. E, 50, 888-901, (1994)

Srednicki M., Does Quantum Chaos Explain Quantum Statistical Mechanics?, arXiv:cond-mat/9410046v2, (1995) Srednicki M., The Approach to Thermal Equilibrium in Quantized Chaotic Systems, J. Phys. A: Math. Gen., 32, 1163, (1999)

Srednicki M., Thermal Fluctuations in Quantized Chaotic Systems, J. Phys. A, 29, L75, (1996)

Strunz W.T., The Brownian Motion Stochastic Schrodinger Equation, Chemical Physics, 268, 237, (2001)

Sykora S., Quantum Theory and the Bayesian Inference Problems, Journal of Statistical Physics, 11, 17, (1974)

Tasaki H., From Quantum Dynamics to the Canonical Distribution: General Picture and a Rigorous Example, Phys. Rev. Lett., 80, 1373, (1998)

Tessieri L., J. Wilkie, Decoherence in a Spin–Spin-Bath Model with Environmental Self-Interaction, J. Phys. A, 36, 12305, (2003)

Tierney L., Markov Chains for Exploring Posterior Distributions (with Discussion), Annals of Statistics, 22, 1701, (1994)

Tolman Richard C., The Principles of Statistical Mechanics, Dover Publications, (1980)

Van Kampen N. G., How Good is Langevin, J. Phys. Chem. B, 109, 2193, (2005)

Van Kampen N. G., I. Oppenheim, Langevin and Master Equation in Quantum Mechanics, J. Stat. Phys., 87, 1325, (1996)

Vedral V., Quantifying Entanglement in Macroscopic Systems, Nature 453, 1004, (2008)

Von Neumann J., Mathematical Foundations of Quantum Mechanics, Princeton University Press, (1996)

Weiss U., Quantum Dissipative Systems, World Scientific, (1992)

Wigner E.P., Random Matrices in Physics, SIAM Rev. 9, 1, (1967)

Wilkie J., P. Brumer, Time - Dependent Manifestations of Quantum Chaos, Phys. Rev. Lett., 67, 1185, (1991)

Wootters W. K., Quantum Entanglement as a Quantifiable Resource, Philosophical Transactions of the Royal Society A, 356, 1717, (1998)

Wootters W. K., Random quantum states, Found. Phys., 20, 1365, (1990) Zurek W. H., Decoherence and the Transition from Quantum to Classical, Phys. Today, 44, 36, (1991)

Zurek W. H., Decoherence, Einselection, and the Quantum Origins of the Classical, Rev. Mod. Phys., 75, 715, (2003)

Zurek W. H., Environment-Induced Superselection Rules, Phys. Rev. D, 26, 1862, (1982)

Życzkowski K., M. Kus, Random Unitary Matrices, J. Phys. A: Math. Gen., 27, 4235, (1994).

Życzkowski K., Volume of the Set of Separable States, Phys. Rev. A, 60, 3496, (1999)

Życzkowski K., H. J. Sommers, Induced Measures in the Space of Mixed Quantum States, Journal of Physics A, 34, 7111, (2001)

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