Gonzalo Manzano Paule

Thermodynamics and Synchronization in Open Quantum Systems

Springer

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series "Springer Theses" brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student's supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today's younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

Gonzalo Manzano Paule

Thermodynamics and Synchronization in Open Quantum Systems

Springer

Author
Dr. Gonzalo Manzano Paule
Scuola Normale Superiore
Pisa, Italy

and

International Center for Theoretical
    Physics
Trieste, Italy

Supervisors
Prof. Juan M. R. Parrondo
Universidad Complutense de Madrid
Madrid, Spain

Prof. Roberta Zambrini
Universitat de les Illes Balears—CSIC
Palma de Mallorca, Spain

Supervisors' Foreword

Even a century after its birth, we are still challenged by fundamental questions posed by quantum mechanics and learning how to use its striking features for practical applications. The field of quantum information explores the computational power of quantum systems, which can greatly outperform classical computers; entanglement can be used to secure communications; the high sensitivity of quantum superpositions to external parameters is being used to design new sensors. Quantum computation, quantum communication, quantum sensing, and metrology are examples of the new technologies that make use of genuine quantum effects, like coherence and entanglement.

In recent years, a new field has been added to these attempts to exploiting quantum effects: *quantum thermodynamics*. Furthermore, the progress toward systems composed of several elementary units with increasing complexity requires the study of emergent phenomena, such as *quantum synchronization*. These timely topics are treated in the thesis of Gonzalo Manzano within the common theoretical framework of open quantum systems. Manzano's original contributions lead to a better understanding of a number of basic phenomena: synchronization, decoherence, thermalization, and irreversibility in open systems, whose control is crucial to implement the aforementioned quantum technologies. The thesis also includes the design and analysis of quantum thermal machines that can achieve higher efficiencies than classical engines and refrigerators.

As known, isolated systems are a useful idealization to start with, but only a more realistic approach considering interactions with the environment can explain most physical phenomena, taking into account the effects of exchanges of energy, matter, and information. In the classical regime, the interaction with the environment is necessary for basic tasks that require friction, such as walking, as well as to relax toward equilibrium, like when ice melts in our drink, and plays a prominent role in emergent phenomena and dissipative structures, ranging from synchronization of heart pacemaker cells to cyclones. Therefore, the study of open systems is a well-established topic intersecting with most research fields including, but not limited to, thermodynamics.

Still, it is in the quantum regime where the study of open systems becomes even more relevant and powerful, since open quantum systems play a fundamental role in establishing the conditions for the emergence of a classical world out of fundamental quantum laws valid in the microscopic regime. Superposition of states is at the heart of quantum physics, and the process of decoherence provides a mechanism for the transition to classical mixed states, with prominent experimental demonstrations in atomic systems known from the 1990s.

This thesis explores the behavior of open quantum systems in a variety of contexts. Its first part is a very valuable, self-contained, and exhaustive introduction (Part I) that covers the main aspects of (a) basic quantum theory, including several quantities to assess the correlation between quantum systems, (b) the theory of quantum open systems, including the formalism of quantum maps and stochastic trajectories, and (c) the more recent framework of stochastic thermodynamics and quantum thermodynamics.

The rest of the Gonzalo Manzano's thesis is devoted to his original contributions to these fields. Part II focuses on synchronization of quantum oscillators. Among complex phenomena, mutual synchronization is a paradigmatic one, reported in physical, biological, chemical, and social contexts, allowing for the adjustments of the rhythms of different systems. A natural question addressed in recent years is about the persistence of this phenomenon in the quantum regime, as well as its connection with quantum correlations. The thesis contains the first study in which mutual synchronization is actually found to witness the presence of quantum discord and entanglement, in a fundamental model of coupled oscillators (Chap. 4). Furthermore, it addresses the intriguing possibility that synchronization not only persists in the presence of quantum noise, but is also induced by dissipation into the environment. Quantum synchronization is discussed in bosonic models allowing for more complex forms of interaction with the environment, acting not only independently and identically on different system components, but also collectively or locally (Chaps. 4 and 5). Spontaneous synchronization can arise either during a pre-thermalization transient or also in the stationary state, when more than two detuned oscillators are considered. The last case is studied in connection with persistent decoherence-free subspaces (Chap. 5).

Can mesoscopic systems like quantum complex networks synchronize? In Chap. 6, it is shown that bosonic networks not only can display mutual synchronization induced by dissipation, but also have the possibility to be tuned locally (only at one node) to make the whole network synchronous, and therefore also strongly quantum correlated, or to select synchronous clusters. Furthermore, the conditions to synchronize and entangle two nodes through a network are also established. These results provide a comprehensive description of quantum synchronization in the framework of bosonic networks.

Part III is devoted to quantum fluctuation theorems (QFTs) that characterize the fluctuations of work, heat, and other quantities related to entropy production, along arbitrary nonequilibrium processes. Chapter 7 introduces a QFT for quantum maps and operations, a generic formalism that describes the evolution of open systems. The novelty of this QFT is that it is independent of the details of the environment

and can be applied when the physical mechanism behind a phenomenon is not fully understood, such as decoherence and the collapse of the wave function. Another general QFT, in this case for bipartite systems, is derived in Chap. 8. This theorem helps to clarify some aspects of the previous QFT for maps and also allows one to split the entropy production along nonequilibrium processes into two terms that obey respective "second laws": the adiabatic entropy production, which quantifies the entropy production due to nonequilibrium constraints, such as temperature gradients, and the nonadiabatic entropy production, which accounts for the local irreversible relaxation due to driving. All those results are illustrated in a number of relevant physical examples.

The last part of the thesis (Part IV) focuses on quantum thermal machines, that is, quantum systems that are in contact with thermal baths at different temperatures and are able to perform different tasks, like converting heat into work (motors) or pumping heat from cold to hot reservoirs (refrigerators). Over the last decade, a vast literature has developed on these machines, which is reviewed in the introduction, whereas Part IV of the thesis contains the original contributions to the field. Chapter 11 analyzes how the efficiency of these machines depends on the dimension of the Hilbert space. Another interesting aspect is the consideration of nonequilibrium reservoirs. In quantum mechanics, one can modify the state of an equilibrium thermal bath, by squeezing or adding coherences, to obtain a nonequilibrium reservoir. Then, we can imagine a thermal machine working with those reservoirs. In fact, there are already experimental realizations of thermal motors working with squeezed baths. Chapter 10 analyzes in detail several thermodynamic cycles between squeezed thermal baths using QFTs and shows that one can have motors and refrigerators that greatly outperform cycles with equilibrium reservoirs.

Summarizing, here you will find a number of relevant and original contributions that help to better understand the collective and thermodynamic properties of open quantum systems. Gonzalo Manzano has also included an exhaustive and self-contained introduction that makes the thesis an excellent resource for learning more about all these new developments, which are crucial for understanding both the fundamental aspects of quantum mechanics and the possibilities and limitations of quantum technologies.

Madrid, Spain   Prof. Juan M. R. Parrondo
Palma de Mallorca, Spain   Prof. Roberta Zambrini
April 2018

Abstract

Dissipation effects have profound consequences in the behavior and properties of quantum systems. The unavoidable interaction with the surrounding environment, with whom systems continuously exchange information, energy, angular momentum, or matter, is ultimately responsible for decoherence phenomena and the emergence of classical behavior. However, there exists a wide intermediate regime in which the interplay between dissipative and quantum effects gives rise to a plethora of rich and striking phenomena that has only started to be understood. In addition, the recent breakthrough techniques in controlling and manipulating quantum systems in the laboratory have made this phenomenology accessible in experiments and potentially applicable. In this thesis, we aim to explore from a theoretical point of view some of the connections between dissipative and quantum effects regarding two main aspects: the thermodynamical behavior of quantum systems and the relation between dynamical and quantum correlations shared between them.

Quantum correlations are one of the most surprising characteristics of nature, attracting a long-standing interest from the formulation of quantum theory. The understanding of the mechanisms creating, preserving, or destroying quantum correlations becomes of major importance when exploring the quantum-to-classical boundary, while being essential to designing schemes in which decoherence phenomena can be avoided in practical applications. An important type of dynamical correlations with a more classical flavor is synchronization phenomena, which have been studied in a broad range of physical, chemical, and biological systems. Synchronization may arise as a spontaneous cooperative behavior of different oscillatory units that, when coupled, adapt their rhythms to a common frequency. This *mutual synchronization* phenomenon has been recently considered in the quantum regime, mostly from a classical point of view, while genuine quantum traits of synchronization are now starting to be investigated.

A first main objective of this thesis is to determine the possible connections between mutual synchronization and quantum correlations, as measured by entanglement or quantum discord. In order to investigate this connection, we use the machinery of open quantum systems theory. More precisely, we consider

many-body systems consisting of interacting quantum harmonic oscillators coupled to the environment. The environment will be modelled in two main different ways, which will be compared. In the first case, all the units in the many-body system feel the same dissipation modelled as a common heat bath. In the second case, each unit is assumed to feel an independent dissipation modelled by separate thermal baths. We start with the simplest case of two quantum harmonic oscillators in Chap. 4 which allows us to identify the basic mechanisms leading to transient synchronization and its relation with the slow decay of quantum correlations. We find that both phenomena are produced due to the presence of collective dissipation. We then consider the case of three oscillators in Chap. 5, in which a richer phenomenology appears while still allowing an analytical treatment in several cases of interest. Finally, we scale the system up to complex harmonic networks in Chap. 6, where a broader class of local/global dissipation can be addressed, and our previous findings let us engineer the normal modes of the network. We can then obtain synchronization and protection of quantum correlations in the whole network or in a selected cluster, by simply tuning one or few parameters, such as one frequency or certain coupling strengths. The importance of the results presented in this part of the thesis relies on the fact that they show for the first time that synchronization is related to genuine quantum features and that it may emerge, even in linear systems, due to the presence of dissipation.

The remaining parts of the thesis are dedicated to explore the thermodynamic features of open quantum systems. In particular, we explore the quantum versions of *fluctuation theorems*. These theorems are universal relations which introduce constraints in the statistics followed by quantities such as work, or entropy, defined as stochastic fluctuating variables in processes occurring arbitrarily far from equilibrium. They can be understood as a refined version of the second law of thermodynamics for small systems dominated by fluctuations where the laws of thermodynamics are only expected to be fulfilled on average.

Work fluctuation theorems have been extensively investigated in the quantum regime under an inclusive Hamiltonian approach. Also, fluctuation theorems for the exchange of heat and particles in transient and steady-state regimes have been established, as well as entropy production fluctuation theorems. Other approaches considered specific open-system dynamics, including unital measurements, quantum trajectories, or Lindblad master equations. However, the different attempts to generalize those results to general completely positive and trace-preserving (CPTP) maps are limited by the presence of an efficacy (correction) term. Furthermore, the characterization of entropy production in situations going beyond the assumption of ideal equilibrium reservoirs constitutes an open challenge.

The second main objective we pursue in this thesis is the development of fluctuation theorems valid for quantum CPTP maps, together with the interpretation of the quantities fulfilling them. This theoretical development may then be applied to gain insight into the characterization of entropy production in general quantum evolution and the thermodynamic description of specific configurations. We define thermodynamic protocols generating trajectories by means of quantum measurements and the occurrence of the quantum operations which compose the CPTP

maps. The probabilities of such trajectories then must be compared with those of their time-reversed twins, defined in a suitable way. The application to specific situations will require as well an adequate modelling of the dynamical evolution. In Chap. 7, we develop a general fluctuation theorem for a large class of quantum CPTP maps. The theorem is based on the properties of the invariant states of the dynamics. We discuss the meaning of the quantity fulfilling the theorem in many situations of physical interest as different versions of the entropy production. This interpretation is then clarified in Chap. 8, where we characterize entropy production from first principles and explore the conditions under which it splits into adiabatic and nonadiabatic contributions, each of them fulfilling an independent fluctuation theorem. In Chap. 9, we illustrate our findings with some particular models of interest in quantum thermodynamics and discuss their implications.

Thermodynamic theory was developed from the analysis of real heat engines, such as the steam engine along the nineteenth century. Those macroscopic engines have quantum analogues, whose analysis constitutes an important branch of quantum thermodynamics. A quantum thermal machine is intended as a small quantum system operating between different thermal reservoirs (or more general reservoirs) and possibly subjected to external driving. The machine performs a thermodynamic task such as work extraction, refrigeration, heat pumping, or information erasure. Quantum thermal machines provide simple setups in which quantum thermodynamics can be studied at the fundamental level, but also tested experimentally.

Clarifying the impact of quantumness in the operation and properties of the machines represents a major challenge. Quantum effects may be incorporated, e.g., by means of nonequilibrium reservoirs. There have been different works in the literature pointing that nonequilibrium quantum reservoirs may be used to increase both power and efficiency. Nevertheless, a solid understanding of this enhancement and their optimization has remained elusive, as it requires a precise formulation of the second law of thermodynamics in such nonequilibrium situations. Furthermore, the sole fact that energy levels are discretized may also introduce limitations when trying to improve the performance of machines by means of increasing the number of levels. Indeed, the scaling properties of small thermal machines have not been yet established.

A final general objective of this thesis is to provide insight into the role played by quantumness in the performance and operation of quantum thermal machines. We perform a thermodynamic analysis of the quantum Otto cycle for a single bosonic mode in the presence of a nonequilibrium squeezed thermal reservoir. Equipped with the findings about entropy production in quantum processes and the generalized formulation of the second law previously developed, we will perform an entropic analysis of this setup in Chap. 10. We identify nonequilibrium features introduced by the squeezed thermal reservoir in the operation of the engine, optimize it, and discuss its many striking consequences such as the appearance of multitask regimes in which the heat engine may extract work and refrigerate a cold reservoir at the same time. Finally, we study the performance of multi-level autonomous thermal machines in terms of the number of levels in Chap. 11. We

first identify the primitive operation of autonomous machines and then characterize the different elements determining their performance. This allows us to compare different ways of scaling the system by adding extra levels. Fundamental limitations to improve the performance of the machine then naturally arise, leading to a novel statement about the third law of thermodynamics in terms of the Hilbert space dimension of the machine.

Acknowledgements

This work would not have been possible without the invaluable help of many people, who directly or indirectly contributed to push forward this thesis. It is my intention to dedicate here some words of gratitude to all of them.

In the first place, I want to acknowledge the advice and dedication of my supervisors, Juan M. R. Parrondo and Roberta Zambrini. At this point in time, I can say that I have learned quite much from them during these years. They have generously shared with me their wide knowledge of quantum theory and nonequilibrium thermodynamics and taught me how to make difficult problems understandable in rather simpler terms and how to solve them by making use of a broad range of techniques. I also learned from them to immerse myself in the literature to catch the state of the art of some topic and to communicate my research results in worthy scientific English. They have always helped me when I needed in both scientific and administrative areas, and given to me the opportunity to interact with other distinguished physicists of different institutions.

Next, it is a pleasure for me to acknowledge the helpful comments and advices I received from all the people of my group at Universidad Complutense de Madrid, the *Group of Statistical Mechanics.*[1] I am especially grateful to Luis Dinis for their vigorous support, including their recommendations when I was collaborating with him in teaching *Laboratorio de Física para Biólogos*, to Léo Granger for his inspiration and the very interesting conversations about thermodynamics we frequently maintained during his postdoc in Madrid, and to Jordan M. Horowitz for his precious help and splendid work during our collaboration. I would like also to show my gratitude to the whole GISC group[2] for giving me the opportunity to participate in their annual workshops.

Thanks to the members of the *Institute For Cross-Disciplinary Physics and Complex Systems* (IFISC) in Mallorca, who welcomed me during my many visits and provided for me all the comforts to carry out my work there. At IFISC, I have

---

[1] Web site: http://seneca.fis.ucm.es.

[2] Grupo de Física Interdisciplinar y Sistemas Complejos.

had the opportunity to interact with many people working on different fields, attend to outstanding seminars on a variety of topics, and to present some of the results of my research. It has been a pleasure to collaborate with Fernando Galve during these years, who shared interesting perspectives with me and always offered his crucial help. Thanks also to Gian-Luca Giorgi for his help with master equations and the rest of my collaborators in the synchronization part of this thesis, and Pere Colet and Emilio Hernández-García, for their respective contributions.

During my two stays in the *H. H. Wills Physics Laboratory* at the University of Bristol, Prof. Sandu Popescu took care of me and integrated me as a full member of his group. I am very grateful to him for his kind hospitality, the very interesting conversations he is capable of provoking, and his inspirational suggestions that opened my mind in a number of ways. I also acknowledge the rest of the people of the *Quantum Information and Foundations Group* for hosting me. In particular, I would like to thank my collaborators Ralph Silva and Paul Skrzypczyk for sharing their excellent work and interesting viewpoints, and Tony Short for helping me with the crazy stuff of the stay certificate. Thanks also to Nicolas Brunner from Université de Genève for his contribution to our work on autonomous multi-level quantum thermal machines.

I must also recall the importance of the professors who awake my interest in physics when I still was an undergraduate student at the Universidad Complutense de Madrid trying to understand something. I have been actually lucky, because one of them has been indeed my supervisor during my Ph.D. research, Prof. Juan M. R. Parrondo. I also acknowledge the insightful lessons on classical mechanics of Prof. Enrique Maciá Barber, from which I could catch his passion for understanding the underlying "melody of the universe." Thanks also to Alvaro de la Cruz-Dombriz for his instructive teaching of space–time structure and cosmology matters, to Prof. Ricardo Brito, who introduced me for the first time to out-of-equilibrium processes, and to the exemplary teacher Prof. Joaquín Retamosa, who is resting in peace now. Furthermore, during my master's degree in fundamental physics I had the opportunity to meet other great scientists whose teaching I really appreciated. In particular, I want to thank Isabel Gonzalo Fonrodona and David Gómez-Ullate Otzeida.

Finalmente quisiera dar las gracias a toda la gente que me ha apoyado en el plano personal y animado durante estos años. Estoy seguro de que sin este entorno vital y social no hubiera llevado esta tesis a cabo. Es por tanto que se podría decir que su contribución ha sido la más importante e imprescindible. Gracias a mi madre Esther por su cariño y cuidado incondicionales. A mis abuelos Concesa y Victoriano, a Honorio, a mi tía Mariángeles y al resto de mi familia por su ayuda y su consejo. Mi último agradecimiento va dedicado a todos mis amigos y amigas con los cuales he podido compartir momentos importantes y forjar unos lazos sólidos a través del tiempo. Como saben, son y han sido siempre un gran apoyo para mi.

Contents

Acronyms

CB	Common bath
COP	Coefficient of performance
CP	Completely positive
CPTP	Completely positive and trace-preserving
DFS	Decoherence-free subspace/subsystem
ETH	Eigenstate thermalization hypothesis
FT	Fluctuation theorem
GGE	Generalized Gibbs ensemble
LB	Local bath
LOCC	Local operations and classical communication
NS	Noiseless subsystem
NEMS	Nanoelectromechanical structures
NMR	Nuclear magnetic resonance
NSD	No sudden death
TMP	Two-measurement protocol
POVM	Positive-operator-valued measure
PPT	Positive partial transpose (criterion)
QND	Quantum nondemolition (measurement)
RWA	Rotating wave approximation
SB	Separate baths
SD	Sudden death
SDR	Sudden death and revivals
SME	Stochastic master equation
SSE	Stochastic Schrödinger equation

Fundamental Constants

ℏ   Planck constant ($6.62607004 \times 10^{-34}$ m^2 kg s^{-1})
k_B Boltzmann constant ($1.38064852 \times 10^{-23}$ m^2 kg s^{-2} K^{-1})

Part I
Introduction to Open Quantum Systems and Quantum Thermodynamics

Chapter 1
Basic Concepts

Any realistic quantum system cannot be completely isolated. In general, it is unavoidably coupled to a larger environment and thus, even if this interaction is weak, needs to be regarded as an open system, just like happens when one considers small classical particles. The environment, which is frequently (but not only) regarded as a thermal *reservoir* or *bath*, influences the quantum system under consideration in a non-negligible way, which must be taken into account when describing its dynamical evolution and properties. System and environment are continuously sharing information, which is manifested in the building up of correlations between them. This information is no longer available in general, as it involves a huge number of uncontrollable degrees of freedom. Indeed, obtaining a complete microscopic description of the whole ensemble involved in the problem is both intractable and generally not needed from a practical point of view, but a rather simpler probabilistic approach is highly desirable. The theory of open quantum systems provides such an effective description, allowing the treatment of complex systems by means of a small number of relevant variables. The irrelevant degrees of freedom are instead described only approximately, which results in the appearance of dissipative and stochastic terms in the final form of the effective equations of motion, a characteristic feature of an irreversible evolution [1, 2].

Open quantum systems theory has been widely studied and applied by many scientists from different communities in the last half-century. Nowadays it constitutes an everyday tool in modern quantum optics, atomic physics, condensed matter, chemical physics, quantum information science or the novel field of quantum thermodynamics. A more rigorous treatment of open quantum systems from a mathematical point of view complements this heterogeneity and provides consistency to the theory (see e.g. [3] and references therein).

The study of open quantum systems is also of special importance for fundamental questions about the quantum description of nature. One example is quantum measurement theory, as long as any measurement requires a description in terms of the

interaction of the system to be measured with an apparatus (a second quantum system), which records the result and leads to fundamental back-action on the former. Another example comes from the fact that the interaction of a quantum system with its environment leads to the well-known phenomenon of *decoherence*, through which superpositions of quantum states are irreversibly lost producing the emergence of classical behavior [4]. It is thus clear that the detailed study of open quantum systems constitutes a key point if one wants to benefit from quantum phenomena in practical applications, as become patent in modern quantum computation, quantum metrology or quantum cryptography [5, 6].

This chapter aims to provide an introduction to some of the most important concepts employed when dealing with open quantum systems. In particular, we review and illustrate the essential concepts and methods which are going to be used in this thesis, while skipping rigorous demonstrations and referring to more specific books or reviews on this topic. We organized the chapter as follows. In Sect. 1.1 we start by reviewing the necessary elements of quantum theory needed for the description of open quantum systems, the dynamical evolution of closed (completely isolated) quantum systems, and its relation with the open system dynamics experienced by one of its constituents in the case of many-body systems. Next, in Sect. 1.2, we focus on the case of qubits and harmonic oscillators, as they are two prototypical systems where the basic elements of the theory can be well illustrated. In Sect. 1.3 we review the basics of quantum measurement theory, its general mathematical formulation in terms of operations and effects, and introduce the most important classes of measurements. Finally, in Sect. 1.4, we define classical and quantum correlations, introducing different quantifiers such as entanglement, mutual information, and discord, discussing their main physical interpretations.

1.1 Quantum Mechanics

In the general framework of quantum mechanics, each state of an isolated quantum system can be represented by a normalized state vector $|\psi\rangle$ in an associated Hilbert vectorial space $\mathcal{H}$. Any measurable quantity on this system is represented by an hermitian (or self-adjoint) operator, $\hat{\mathcal{O}} = \hat{\mathcal{O}}^\dagger$, in the same space, whose eigenvalues represent possible results (or outcomes) of a quantum measurement, as we will see in more detail in Sect. 1.3. Quantum theory is intrinsically random and the *pure* state $|\psi\rangle$ contains all the information one can know about the probability of obtaining different outcomes for all different observables of the system. To illustrate this point let us decompose the operator $\hat{\mathcal{O}} = \sum_n o_n |o_n\rangle\langle o_n|$ where $\{|o_n\rangle\}$ is the set of eigenvectors (or eigenstates) of $\hat{\mathcal{O}}$ providing a basis of $\mathcal{H}$, and o_n its corresponding (non-degenerate) eigenvalues. The probability of obtaining the result o_n in a measurement of the observable $\hat{\mathcal{O}}$ is the scalar product $0 \leqslant |\langle\psi|o_n\rangle|^2 \leqslant 1$, as given by Born rule [7]. Moreover the mean value of some observable in the state $|\psi\rangle$ is given by the quantum mechanical expectation value $\langle\hat{\mathcal{O}}\rangle = \langle\psi|\hat{\mathcal{O}}|\psi\rangle$, representing

the mean of different results when the observable is measured, weighted with their different probabilities to occur. In the same manner the variance of $\hat{O}$ on $|\psi\rangle$ reads $\sigma^2(\hat{O}) = \langle \hat{O}^2 \rangle - \langle \hat{O} \rangle^2$. The latter is zero if and only if the state $|\psi\rangle$ is an eigenstate of the operator, that is, when $\hat{O}|\psi\rangle = \alpha|\psi\rangle$, being α a real number (then $|\psi\rangle = |o_n\rangle$ and $\alpha = o_n$ for some n). At difference from classical physics, $\sigma(\hat{O})$ cannot be simultaneously zero for all observables $\hat{O}$, as the Heisenberg uncertainty principle asserts [8]. Indeed for any quantum system, non-commuting observables such as position and momentum, $[\hat{x}, \hat{p}] \equiv \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar\mathbb{1}$ being $\mathbb{1}$ the identity operator, cannot share any common eigenstate. A general form of the Heisenberg uncertainty principle for arbitrary observables $\hat{O}$ and $\hat{O}'$ is the Robertson uncertainty relation [9] Robertson uncertainty relation.

$$\sigma(\hat{O})\sigma(\hat{O}') \geqslant \frac{1}{2}|\langle\psi|[\hat{O}, \hat{O}']|\psi\rangle|, \tag{1.1}$$

which unravels the connection between the commutativity of observables and the complementarity of their uncertainties [10].

1.1.1 The Density Operator

When considering open quantum systems we need to incorporate in the description new sources of randomness other than the intrinsic uncertainty of quantum states, coming e.g. from our lack of knowledge about the specific state of the environment, the preparation procedure, or the correlations built up in the interaction between system and surroundings. In this case we represent the state of our open system by a density operator (or density matrix) ρ,[1] firstly introduced by von Neumann [11] and Landau [12] in 1927. It characterizes our state of knowledge about the system and represents the quantum analogue to the phase-space probability distribution of classical statistical mechanics. The use of the density operator allows us to work with statistical mixtures of state vectors:

$$\rho = \sum_k p_k|\psi_k\rangle\langle\psi_k|, \qquad \text{with } k = 1, 2, \ldots, N, \tag{1.2}$$

where p_k are the probabilities $\left(0 \leqslant p_k \leqslant 1, \ \sum_k p_k = 1\right)$ of being our microscopic system in each of the N pure states $|\psi_k\rangle$, and the operators $|\psi_k\rangle\langle\psi_k|$ are *projectors* onto the state $|\psi_k\rangle$. The density operator is self-adjoint ($\rho = \rho^\dagger$), positive-semidefinite ($\rho \geqslant 0$), and has unit trace (Tr$[\rho] = 1$).

In principle any *mixed* state ρ can be decomposed into a mixture of pure states in an infinite number of ways,[2] but there is only one in which the states $|\psi_k\rangle$ in

---

[1] We omit the hat symbol ˆ used to distinguish between operators and scalars for the density operator.

[2] All of them related by a unitary transformation. Furthermore the same density operator can be also decomposed in a mixture of *mixed* states in an infinite number of ways.

the decomposition are mutually orthogonal between them, i. e. for which they verify $\langle \psi_k | \psi_l \rangle = \delta_{k,l}$. This is guaranteed by the spectral theory of density operators, as long as ρ has only a countable set of strictly positive eigenvalues [1]. In such case, we may call Eq. (1.2) the spectral decomposition of ρ, the probabilities p_k and the states $|\psi_k\rangle$ being respectively the eigenvalues and eigenstates of the ρ, and N the dimension of the Hilbert space $\mathcal{H}$ (which may be infinite). Given a density operator, ρ, the most likely pure state the system is in, is given by the eigenstate $|\psi_k\rangle$ corresponding to the largest eigenvalue p_k [13].

It is worth mentioning that the density operator ρ is sufficient to describe all the possible results of measurements on the system for any observable. Indeed the expression for the mean value introduced earlier, can be now rewritten for the case of a mixed state as

$$\langle \hat{O} \rangle = \mathrm{Tr}[\hat{O}\rho] = \sum_k p_k \langle \psi_k | \hat{O} | \psi_k \rangle, \tag{1.3}$$

In a similar way we may use the trace to rewrite the expression for the variance $\sigma^2(\hat{O})$ in terms of ρ, or the general uncertainty relation in Eq. (1.1).

Another important property of the density operator is that it always verify $\mathrm{Tr}[\rho^2] \leqslant \mathrm{Tr}[\rho] = 1$, where the equality is only reached in the case of a pure state $\rho = |\psi\rangle\langle\psi|$, when the information about the state of the microscopic system is complete. On the opposite side, the maximally mixed state reads $\rho = \mathbb{1}/N$, where N again denotes the dimension of the system Hilbert space $\mathcal{H}$. This corresponds to the case in which all the possible physical pure states of the microscopic system are equally probable. Hence we may define the quantity $\mathcal{P}(\rho) \equiv \mathrm{Tr}[\rho^2]$, called the *purity* of a state, in order to quantify its degree of mixedness. This quantity takes values in the range $1/N^2 \leqslant \mathcal{P}(\rho) \leqslant 1$, with the upper bound reached for pure states and the lower bound reached for maximally mixed states.

It is however important to distinguish a mixture of pure states, as given in Eq. (1.2), from a *superposition* of the form

$$|\psi\rangle = \sum_k c_k |\psi_k\rangle, \qquad \text{with } k = 1, 2, \ldots, N, \tag{1.4}$$

where $c_k = \langle \psi_k | \psi \rangle$ are a set of complex numbers such that $\sum_k |c_k|^2 = 1$. The existence of such states, as motivated by the superposition principle, lies at the heart of quantum theory. The differences between mixture and superposition states are fundamental. While the former simply describes our lack of knowledge in the specific pure state the system is in, the latter corresponds to a single pure state. Hence we can no longer interpret the system being in different states $|\psi_k\rangle$ with certain probability, but we have to really consider that the system is in all those states at once. Let us assume the set of states $\{|\psi_k\rangle\}$ to form a basis of the Hilbert space of the system with dimension N, and compare the density operator $\rho = |\psi\rangle\langle\psi|$ for the superposition state (1.4) with the one of the mixed state in Eq. (1.2). The state (1.2) has only diagonal elements (using the basis $\{|\psi_k\rangle\}$) given by the probabilities
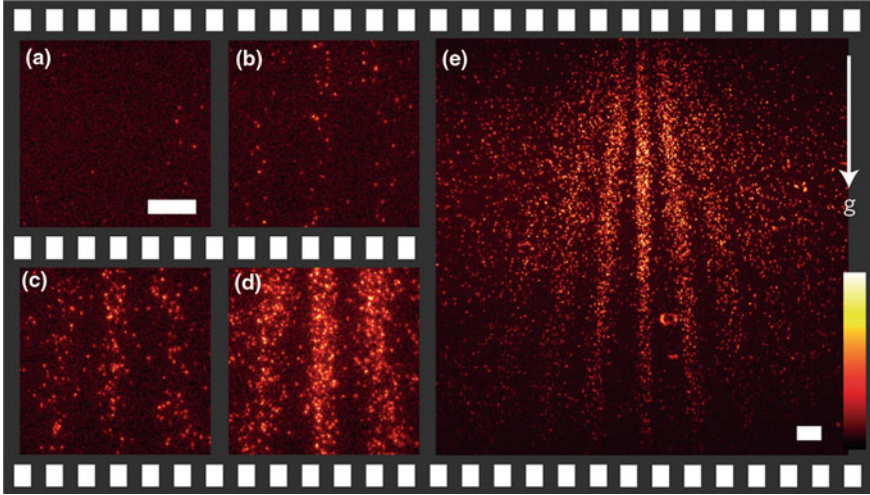
Fig. 1.1 Interference pattern for stochastically arriving single PcH$_2$ molecules in a modern double-slit experiment. The images correspond to selected frames from a false-color movie recorded with an EMCCD camera. Obtained from Ref. [15]

p_k, while the state (1.4) gets diagonal elements $\rho_{kk} = \langle \psi_k | \rho | \psi_k \rangle = |c_k|^2$, but also off-diagonal ones $\rho_{kl} = \langle \psi_k | \rho | \psi_l \rangle = c_k^* c_l$ for $k \neq l$. Off-diagonal terms are called *coherences* between the states $\{|\psi_k\rangle\}$, and are responsible of the interference effects due to the wave-particle complementarity of quantized matter, just as in Young's famous double-slit experiment [14]. Modern *which-path* experiments within different setups have considerably evolved from the 90s [2], being nowadays able to test some of the most famous thought-experiments formulated from the very beginning of the quantum theory for larger and larger systems (electrons, atoms, molecules), testing in the laboratory the connections between complementarity and decoherence (see Fig. 1.1).

1.1.2 Liouville–von Neumann Equation

The time evolution of a (non-relativistic) isolated quantum system in terms of its density operator, ρ, is given by the Liouville–von Neumann equation

$$i\hbar \frac{d}{dt} \rho(t) = [\hat{H}(t), \rho(t)], \tag{1.5}$$

being $\hat{H}(t)$ the Hamilton operator representing the energy of the system. Notice that we have included the possibility of time-dependent Hamilton operators, allowing for the description of external driving. The Liouville–von Neumann equation

describes the reversible evolution of the quantum system and when ρ is a pure state it is equivalent to the usual Scrödinger equation, first introduced in 1926 [16]. The formal solution of Eq. (1.5), given the initial state $\rho(t_0)$ at time t_0, reads $\rho(t) = \hat{U}(t, t_0)\rho(t_0)\hat{U}(t, t_0)^\dagger$, with

$$\hat{U}(t, t_0) \equiv \hat{T}_+ \exp\left(-\frac{i}{\hbar} \int_{t_0}^t ds\, H(s)\right), \tag{1.6}$$

the unitary evolution operator, $\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \mathbb{1}$, fulfilling

$$i\hbar\frac{d}{dt}\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0), \tag{1.7}$$

and with initial condition $\hat{U}(t_0, t_0) = \mathbb{1}$. It fulfills the chain rule $\hat{U}(t, t_0) = \hat{U}(t, t_1)$ $\hat{U}(t_1, t_0)$ for $t \leqslant t_1 \leqslant t_0$. Due to the fact that the Hamilton operator may not commute with itself at different times, we introduced in the integral above the time-ordering operator, $\hat{T}_+$, implying that in general the unitary evolution operator can be only calculated from an infinite series in the form

$$\hat{U}(t, t_0) = \mathbb{1} + \sum_{n=1}^\infty \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t ds_n \hat{H}(s_n) \int_{t_0}^{s_n} ds_{n-1}\hat{H}(s_{n-1})\, \ldots$$
$$\ldots \int_{t_0}^{s_3} ds_2\hat{H}(s_2) \int_{t_0}^{s_2} ds_1\hat{H}(s_1), \tag{1.8}$$

where time ordering implies $t > s_n > s_{n-1} > \cdots > s_2 > s_1$, an expression known as the Dyson series. When the Hamilton operator in Eq. (1.6) is independent of time the unitary evolution operator reduces to

$$\hat{U}(t, t_0) = \hat{U}(t - t_0) = \exp\left(-\frac{i}{\hbar}\hat{H}(t - t_0)\right), \tag{1.9}$$

and then $\hat{U}^\dagger(t - t_0) = \hat{U}(t_0 - t)$, corresponding to the evolution operator when time is reversed.

1.1.3 Heisenberg and Interaction Pictures

The above Eq. (1.5) gives us the evolution of the density operator $\rho(t)$ in the *Schrödinger picture*. An equivalent formulation, the so-called *Heisenberg picture*, is obtained by assuming the state of the system fixed and letting the observables evolve in time. Then the equation of motion for an arbitrary observable $\hat{O}(t)$, can be written as

$$\frac{d}{dt}\hat{\mathcal{O}}(t) = \frac{i}{\hbar}[\hat{H}(t), \hat{\mathcal{O}}(t)] + \left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)_H, \tag{1.10}$$

whose solution is given by $\hat{\mathcal{O}}(t) = \hat{U}^\dagger(t, t_0)\, \hat{\mathcal{O}}\, \hat{U}(t, t_0)$, $\hat{\mathcal{O}}$ being the initial (Schrödinger picture) observable and $\hat{U}$ given by Eq. (1.6). Here we denote $\left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)_H =$ $\hat{U}^\dagger(t, t_0)\left(\frac{\partial\hat{\mathcal{O}}}{\partial t}\right)\hat{U}(t, t_0)$. It's straightforward to check that both pictures produce identical expectation values for all observables.

A third frame, the *interaction picture*, can be also introduced by splitting the Hamiltonian into time-independent and time-dependent parts, which we denote as $\hat{H} = \hat{H}_0 + \hat{V}(t)$. Typically $\hat{H}_0$ is easy to deal with, and represents the Hamilton operator of two or more non-interacting systems, while $\hat{V}(t)$ usually represents a time-dependent interaction term. In this case we split the evolution operator into a product of two unitary operators

$$\hat{U}(t, t_0) = \hat{U}_0(t - t_0) \times \hat{U}_I(t, t_0), \tag{1.11}$$

where $\hat{U}_0(t - t_0) \equiv \exp\left(-\frac{i}{\hbar}\hat{H}_0(t - t_0)\right)$ is generated by the time-independent part of the Hamiltonian, and $\hat{U}_I(t, t_0)$ is given by Eq. (1.6) replacing $\hat{H}(t)$ by $\hat{U}_0^\dagger \hat{V}(t)\hat{U}_0$. Hence the operator $\hat{U}_0$ governs the evolution of observables, while the density operator evolves accordingly with $\hat{U}_I$. By redefining the density operator and observables, we have the following time-evolution equations:

$$\begin{aligned}
\rho_I(t) &= \hat{U}_I\, \rho(0)\, \hat{U}_I^\dagger, &\quad \text{with} \quad \rho_I(t) &\equiv \hat{U}_0^\dagger\, \rho(t)\, \hat{U}_0, \\
\hat{\mathcal{O}}_I(t) &= \hat{U}_0^\dagger\, \hat{\mathcal{O}}\, \hat{U}_0, &\quad \text{with} \quad \hat{\mathcal{O}}_I(t) &\equiv \hat{U}_I\, \hat{\mathcal{O}}(t)\, \hat{U}_I^\dagger,
\end{aligned} \tag{1.12}$$

where we call $\rho_I(t)$ and $\hat{\mathcal{O}}_I(t)$ the *interaction frame* density operator and observables respectively. The *interaction picture* has proven very useful in deriving and solving the dynamics for open quantum systems, as we will see in the next sections. It allows to split the effects of the interaction between a system and its surroundings from the (isolated) free-evolution, simplifying considerably the mathematical treatment.

1.1.4   The Microreversibility Principle

The microreversibility principle is a crucial symmetry of time evolution in isolated quantum systems. It relates the unitary evolution operator of a non-autonomous quantum system, as introduced in Eq. (1.6), with the one describing the time-reversed evolution [17, 18]. Let us assume a quantum system evolving from time $t = 0$ to time τ under the action of some Hamiltonian $\hat{H}(\lambda(t))$, whose time-dependence arises from external manipulation through a control parameter $\lambda(t)$. Consider that this parameter vary in time according to some prescribed protocol $\Lambda = \{\lambda(t) \text{ for } 0 \leqslant t \leqslant \tau\}$. The

unitary time evolution operator for the system, $\hat{U}(t,0)[\Lambda]$, obeys

$$i\hbar\frac{d}{dt}\hat{U}(t,0)[\Lambda] = \hat{H}(\lambda(t))\hat{U}(t,0)[\Lambda], \tag{1.13}$$

in the interval $t \in [0,\tau]$ where the protocol Λ is defined.

Now we compare this evolution with the one generated by the *time-reversed* protocol $\tilde{\Lambda} = \{\tilde{\lambda}(t) \text{ for } 0 \leqslant t \leqslant \tau\}$, where $\tilde{\lambda}(t) = \lambda(\tau - t)$, i.e. the control parameter takes on exactly the inverse sequence of values. The corresponding time-evolution operator $\hat{U}(t,0)[\tilde{\Lambda}]$ generated by the Hamiltonian $\hat{H}(\tilde{\lambda}(t))$ now reads:

$$i\hbar\frac{d}{dt}\hat{U}(t,0)[\tilde{\Lambda}] = \hat{H}(\tilde{\lambda}(t))\hat{U}(t,0)[\tilde{\Lambda}] \tag{1.14}$$

where again $t \in [0,\tau]$. The microreversibility principle ensures the following relation between *forward* and *backward* evolutions [18]:

$$\hat{U}^{\dagger}(\tau,t)[\Lambda] = \hat{\Theta}^{\dagger}\,\hat{U}(\tau - t,0)[\tilde{\Lambda}]\,\hat{\Theta}, \tag{1.15}$$

where $\hat{\Theta}$ is the anti-unitary time-reversal operator in quantum mechanics, $\Theta\Theta^{\dagger} = \Theta^{\dagger}\Theta = \mathbb{1}$ and $\hat{\Theta}(a|\psi\rangle + b|\phi\rangle) = a^{*}\hat{\Theta}|\psi\rangle + b^{*}\hat{\Theta}|\phi\rangle$.[3] It is responsible of sign inversion of odd variables under time-reversal such as linear and angular momenta, spin or magnetic field, while leaving even variables, such as position, unaltered [19]. The microreversibility principle in Eq. (1.15) is always fulfilled provided the Hamilton operator is invariant under time-reversal, $\hat{\Theta}^{\dagger}\hat{H}(\lambda(t))\hat{\Theta} = \hat{H}(\lambda(t))$ (for a proof see [18]). Otherwise the Hamiltonian governing the time-reversed evolution can be set as

$$\hat{H}_{R}(\tilde{\lambda}(t)) \equiv \hat{\Theta}\hat{H}(\tilde{\lambda}(t))\hat{\Theta}^{\dagger}, \tag{1.16}$$

in Eq. (1.14) [instead of $\hat{H}(\tilde{\lambda}(t))$]. The latter implies the change in sign of the odd variables appearing in $\hat{H}$, such as external magnetic fields [17]. We provide a proof of this claim in Appendix.

The microreversibility principle relates the evolution from some arbitrary initial state $\rho(0)$ to $\rho(\tau) = \hat{U}(t,0)[\Lambda]\,\rho(0)\,\hat{U}^{\dagger}(t,0)[\Lambda]$, to the evolution from the time-reversed final state $\tilde{\rho}(0) = \hat{\Theta}\,\rho(\tau)\,\hat{\Theta}^{\dagger}$ to the time reversed initial state $\tilde{\rho}(\tau) = \hat{\Theta}\,\rho(0)\,\hat{\Theta}^{\dagger}$ as:

$$\tilde{\rho}(\tau) = \hat{U}(\tau,0)[\tilde{\Lambda}]\,\tilde{\rho}(0)\,\hat{U}^{\dagger}(\tau,0)[\tilde{\Lambda}], \tag{1.17}$$

as is illustrated in Fig. 1.2. It is worth noticing that the notion of time-reversal here corresponds to an *operational* point of view, as it is defined via the time-reversed protocol for the external drive controlling the parameter $\lambda(t)$. We finally stress that

---

[3]This antilinearity property is what differentiates anti-unitary from unitary operators. Unitary operators fulfills linearity, while anti-unitary ones fulfills anti-linearity, and for both of them $\hat{\Theta}\hat{\Theta}^{\dagger} = \hat{\Theta}^{\dagger}\hat{\Theta} = \mathbb{1}$.